

CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-3-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

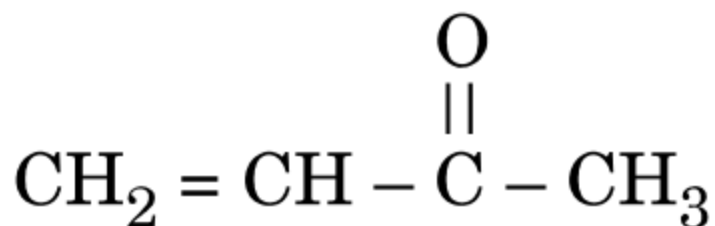
General Instructions

- (i) All questions are compulsory.
- (ii) Section A : Questions number **1 to 5** are very short answer questions and carry **1 mark** each.
- (iii) Section B : Questions number **6 to 12** are short answer questions and carry **2 marks** each.
- (iv) Section C : Questions number **13 to 24** are also short answer questions and carry **3 marks** each.
- (v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.
- (vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
- (vii) Use of log tables, if necessary. Use of calculators is **not** allowed.

Section A (5 marks)

1. Write the IUPAC name of the following compound:

[1 mark]



Solution:

Concept:

- The parent chain must contain the ketone carbonyl carbon and the carbon-carbon double bond.
- The ketone suffix has priority over an alkene bond when assigning the lowest locant.

Step 1: Select and number the parent chain The structure is $\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_3$. Its longest chain has four carbon atoms, so the parent is butane. Number from the methyl end: the carbonyl carbon is carbon 2, whereas numbering from the alkene end would place it at carbon 3. The lower carbonyl locant takes priority.

Step 2: Locate the double bond With this numbering, the double bond lies between carbon atoms 3 and 4, so its locant is 3. Combine the four-carbon root, the alkene infix and the ketone suffix, retaining both locants. The terminal e of the alkene name is omitted before the suffix one.

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

Quick Tip to Solve: Number from the methyl end to give the ketone carbonyl locant 2 before locating the double bond.

2. Arrange the following in increasing order of their acidic character:

Benzoic acid, Phenol, Cresol

[1 mark]

Solution:

Concept:

- Acid strength increases when the conjugate base formed after loss of H^+ is more stable.
- A methyl group donates electron density; a carboxylate ion delocalises negative charge over two oxygen atoms.

Step 1: Compare cresol with phenol Cresol is methyl-substituted phenol. Its methyl group has an electron-donating effect and makes formation of the negatively charged cresoxide ion less favourable than formation of phenoxide. Thus cresol is less acidic than phenol.

Step 2: Compare benzoic acid with phenol Benzoic acid forms benzoate, whose negative charge is delocalised over two electronegative oxygen atoms in equivalent resonance structures. Phenoxide also has resonance, but some contributing structures place charge on ring carbon atoms. Benzoate is

Quick Tip to Solve: First compare the two phenols using the methyl group, then place the carboxylic acid at the strongest end.

better stabilised, so benzoic acid is more acidic than phenol.

Step 3: Conclusion The increasing order is $\text{Cresol} < \text{Phenol} < \text{Benzoic acid}$.

Quick Tip to Solve: First compare the two phenols using the methyl group, then place the carboxylic acid at the strongest end.

3(a). Write IUPAC name of the complex $[\text{Co}(\text{en})_2(\text{H}_2\text{O})(\text{CN})]^{2+}$.

[1 mark]

Solution:

Concept:

- Neutral ligands aqua and ethane-1,2-diamine contribute zero charge, while cyanido has charge -1 .
- Ligand names are written alphabetically, ignoring multiplicative prefixes; the oxidation state follows the metal name.

Step 1: Determine the oxidation state Let the oxidation state of cobalt be x . The two en ligands and the water ligand are neutral, and the cyanido ligand has charge -1 . The complex has charge $+2$, hence

$$x + 0 + 0 - 1 = +2 \Rightarrow x = +3.$$

The positively charged complex therefore uses the metal name cobalt, rather than cobaltate.

Step 2: Arrange the ligand names The ligand names in alphabetical order are aqua, cyanido and ethane-1,2-diamine. There are two ethane-1,2-diamine ligands, so use bis with this compound ligand name enclosed in parentheses. Finish with cobalt and its oxidation state in Roman numerals.

Step 3: Conclusion The name is aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion.

Quick Tip to Solve: Find cobalt(III) from the single negative cyanido ligand before alphabetising aqua, cyanido and ethane-1,2-diamine.

OR

3(b). Using IUPAC norms, write the formula of Ammonium tetrafluoridocobaltate(II).

[1 mark]

Solution:

Concept:

- In tetrafluoridocobaltate(II), cobalt has oxidation state $+2$ and each fluorido ligand has charge -1 .
- A neutral salt must contain enough NH_4^+ ions to balance the complex anion charge.

Step 1: Calculate the charge of the complex The prefix tetra specifies four fluorido ligands around cobalt. Combining cobalt(II) with four fluoride ions gives

$$q = +2 + 4(-1) = -2.$$

Thus the coordination entity is $[\text{CoF}_4]^{2-}$; the ending cobaltate agrees with its negative charge.

Quick Tip to Solve: Calculate the complex charge first: cobalt(II) plus four fluoride ligands requires two ammonium counterions.

Step 2: Balance the counterions Each ammonium ion, NH_4^+ , has charge +1. Two ammonium ions are therefore required for every one complex anion, since $2(+1) + (-2) = 0$. Enclose ammonium in parentheses when writing its subscript, and retain square brackets around the coordination entity.

Step 3: Conclusion The formula is $(\text{NH}_4)_2[\text{CoF}_4]$.

Quick Tip to Solve: Calculate the complex charge first: cobalt(II) plus four fluoride ligands requires two ammonium counterions.

4(a). What is the difference between a glycosidic linkage and a peptide linkage?

[1 mark]

Solution:

Concept:

- A condensation reaction joins two units with loss of water.
- The linkage is identified by the functional groups and atoms joining the units.

Step 1: Identify a glycosidic linkage A glycosidic linkage joins monosaccharide units through an oxygen atom, normally involving the anomeric carbon of one sugar and a hydroxyl group of another. It is a C–O–C linkage, as found between the two sugar units of a disaccharide.

Step 2: Identify a peptide linkage A peptide linkage joins amino acid units. The carboxyl group of one amino acid reacts with the amino group of another, eliminating water to form the amide linkage –CO–NH–. This bond forms the backbone of peptides and proteins; it is different from the oxygen bridge between sugars.

Step 3: Conclusion A glycosidic linkage is the C–O–C bond joining sugar units, whereas a peptide linkage is the –CO–NH– bond joining amino acid units.

Quick Tip to Solve: Identify the units being joined: sugars use an oxygen bridge, while amino acids use the carbonyl-nitrogen amide bond.

OR

4(b). What is the difference between Nucleotide and Nucleoside?

[1 mark]

Solution:

Concept:

- A nitrogenous base and a pentose sugar together form a nucleoside.
- Addition of a phosphate group to a nucleoside forms a nucleotide.

Step 1: State the composition of a nucleoside A nucleoside contains a nitrogenous base attached to a pentose sugar by a glycosidic bond. The sugar is ribose in an RNA nucleoside or deoxyribose in a DNA nucleoside. A nucleoside does not contain a phosphate group.

Step 2: State the additional component of a nucleotide A nucleotide contains all the components of a nucleoside and, in addition, a phosphate group attached to the sugar. For example, adenosine

Quick Tip to Solve: Check for phosphate: base plus sugar alone is a nucleoside; adding phosphate gives a nucleotide.

is a nucleoside, while adenosine monophosphate is a nucleotide. The phosphate component is the distinguishing feature required in this comparison.

Step 3: Conclusion Nucleoside = nitrogenous base + pentose sugar; nucleotide = nitrogenous base + pentose sugar + phosphate group.

Quick Tip to Solve: Check for phosphate: base plus sugar alone is a nucleoside; adding phosphate gives a nucleotide.

5. Why is chloroform kept in dark coloured bottles?

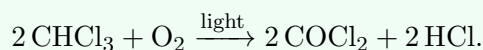
[1 mark]

Solution:

Concept:

- Chloroform, CHCl_3 , is oxidised slowly by oxygen in the presence of light.
- The oxidation product phosgene, COCl_2 , is highly poisonous.

Step 1: Identify the harmful change When chloroform is exposed to air and light, atmospheric oxygen oxidises it to carbonyl chloride, commonly called phosgene. The balanced reaction is



Phosgene is a highly poisonous gas, so its formation during storage must be prevented.

Step 2: Explain the dark bottle A dark-coloured bottle reduces the amount of light reaching the chloroform. Since light promotes the oxidation, excluding light suppresses the conversion to phosgene and makes storage safer. The purpose of the coloured bottle is therefore connected to the chemical action of light on chloroform.

Step 3: Conclusion Chloroform is kept in dark-coloured bottles to suppress its light-assisted oxidation to poisonous phosgene.

Quick Tip to Solve: Connect the bottle colour to exclusion of light, then name the dangerous oxidation product phosgene.

Section B (14 marks)

6(a). What happens when AgCl is doped with CdCl_2 ? What is the name of this defect?

[2 marks]

Solution:

Concept:

- An impurity defect arises when ions of another substance enter an ionic crystal. Electrical neutrality must still be maintained.
- In AgCl , the host cation is Ag^+ , whereas the dopant supplies Cd^{2+} ; the unequal cation charges cause vacancies.

Step 1: Replacement of silver ions When AgCl is doped with a small amount of CdCl_2 , some Cd^{2+}

Quick Tip to Solve: Compare dopant and host charges: a $+2$ dopant replacing $+1$ ions needs one cation vacancy per dopant ion.

ions occupy normal silver-ion sites in the crystal lattice. A cadmium ion has twice the positive charge of one silver ion. Therefore, introducing one cadmium ion in place of a silver ion contributes one extra positive charge relative to the original lattice.

Step 2: Formation of a cation vacancy To compensate for this extra positive charge, another Ag^+ ion is absent from its normal lattice site. Thus, one Cd^{2+} ion effectively replaces two Ag^+ ions: it occupies one cation site and leaves the other vacant. One silver-ion vacancy is produced for each cadmium ion incorporated. The crystal remains electrically neutral, and the defect is an impurity defect with cation vacancies.

Step 3: Conclusion AgCl develops an impurity defect: each incorporated Cd^{2+} ion creates one Ag^+ -site vacancy to maintain electrical neutrality.

Quick Tip to Solve: Compare dopant and host charges: a +2 dopant replacing +1 ions needs one cation vacancy per dopant ion.

OR

6(b). What type of defect is shown by NaCl in

(a) stoichiometric defects, and

(b) non-stoichiometric defects?

[2 marks]

Solution:

Concept:

- Stoichiometric defects preserve the cation-to-anion ratio and the overall electrical neutrality of an ionic solid.
- A non-stoichiometric defect changes the relative composition; an electron trapped in an anion vacancy is called an F-centre.

Step 1: Stoichiometric defect in NaCl NaCl shows the Schottky defect. Equal numbers of Na^+ and Cl^- ions are missing from their respective lattice sites. Because one positive ion and one negative ion are removed together, electrical neutrality and the 1:1 ion ratio are preserved. The number of ions in a given crystal volume decreases, so its density decreases. This defect is favoured in NaCl because its cations and anions have comparable sizes.

Step 2: Non-stoichiometric defect in NaCl NaCl shows a metal-excess defect due to anion vacancies. When heated in sodium vapour, sodium atoms provide electrons, and chloride-ion vacancies become occupied by those electrons. The trapped electrons compensate for the missing negative ions, maintaining electrical neutrality. These electron-containing anion vacancies are F-centres; they impart a yellow colour to the crystal. The resulting crystal has excess metal relative to chlorine.

Step 3: Conclusion (a) Schottky defect. (b) Metal-excess defect due to anion vacancies containing electrons (F-centres).

Quick Tip to Solve: Distinguish missing ion pairs in Schottky defects from electron-filled chloride vacancies in metal-excess NaCl .

7. (a) Out of 0.1 molal aqueous solution of glucose and 0.1 molal aqueous solution of KCl, which one will have higher boiling point and why?

(b) Predict whether van't Hoff factor, (i) is less than one or greater than one in the following:

(i) CH_3COOH dissolved in water

(ii) CH_3COOH dissolved in benzene

[2 marks]

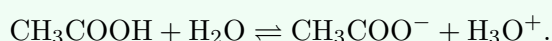
Solution:

Concept:

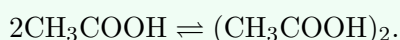
- Boiling-point elevation is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent constant and m molality.
- Dissociation increases the number of solute particles and gives $i > 1$; association reduces their number and gives $i < 1$.

Step 1: Compare the boiling points Both aqueous solutions have the same molality, 0.1 mol kg^{-1} , and the same solvent, so K_b is common. Glucose does not dissociate in water and has $i = 1$. KCl dissociates as $\text{KCl} \rightarrow \text{K}^+ + \text{Cl}^-$, giving more dissolved particles and a van't Hoff factor greater than one (ideally close to 2). Hence $iK_b m$, and therefore boiling-point elevation, is larger for KCl.

Step 2: Acetic acid in the two solvents In water, acetic acid partially ionises:



The increase in particle number gives $i > 1$. In benzene, acetic acid molecules associate through hydrogen bonding to form dimers:



The decrease in particle number gives $i < 1$. Partial ionisation does not require $i = 2$, and partial dimerisation does not require $i = 1/2$.

Step 3: Conclusion (a) The 0.1 molal KCl solution has the higher boiling point. (b) For acetic acid, $i > 1$ in water and $i < 1$ in benzene.

Quick Tip to Solve: At equal molality in the same solvent, compare particle counts: ions raise i , whereas dimers lower i .

8(a). Complete and balance the following equations:

(a) $\text{C} + \text{H}_2\text{SO}_4 (\text{conc.}) \rightarrow$

(b) $\text{XeF}_2 + \text{PF}_5 \rightarrow$

[2 marks]

Solution:

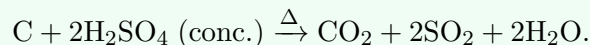
Concept:

- Hot concentrated sulphuric acid acts as an oxidising agent; carbon is oxidised to carbon dioxide while sulphur is reduced from +6 to +4.
- PF_5 is a Lewis acid that accepts a fluoride ion from XeF_2 , producing an ionic fluoride-transfer

Quick Tip to Solve: For the fluoride-transfer equation, count all seven fluorine atoms and retain the charges on both product ions.

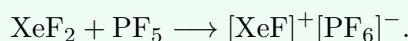
product.

Step 1: Carbon with concentrated sulphuric acid Carbon is oxidised from oxidation state 0 to +4 in CO_2 , losing four electrons. Each sulphur atom is reduced from +6 in sulphuric acid to +4 in SO_2 , gaining two electrons. Two acid molecules are therefore required per carbon atom. Balancing hydrogen and oxygen then gives



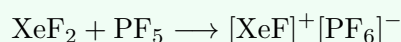
Each side contains one C, two S, four H and eight O atoms.

Step 2: Xenon difluoride with phosphorus pentafluoride One fluoride ion transfers from XeF_2 to PF_5 . The former becomes $[\text{XeF}]^+$, while the latter becomes $[\text{PF}_6]^-$. Hence the balanced equation is



The product is an ionic salt. One xenon atom, one phosphorus atom and seven fluorine atoms occur on each side, and the oppositely charged ions give an electrically neutral product.

Step 3: Conclusion



Quick Tip to Solve: For the fluoride-transfer equation, count all seven fluorine atoms and retain the charges on both product ions.

OR

8(b). Write balanced chemical equations involved in the following reactions:

(a) Fluorine gas reacts with water.

(b) Phosphine gas is absorbed in copper sulphate solution.

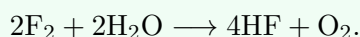
[2 marks]

Solution:

Concept:

- Fluorine oxidises water to oxygen and is itself reduced to fluoride in hydrogen fluoride.
- Phosphine reacts with copper sulphate solution to form copper phosphide, which removes phosphine from the gas stream.

Step 1: Fluorine gas with water Fluorine is a strong oxidising agent. Oxygen in water changes from oxidation state -2 to 0, while fluorine changes from 0 to -1. Two water molecules supply one oxygen molecule; their four hydrogen atoms form four HF molecules, requiring two fluorine molecules. The balanced equation is

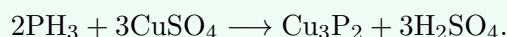


The equation conserves four F atoms, four H atoms and two O atoms, and represents the oxidation of

Quick Tip to Solve: Balance Cu_3P_2 first: its formula fixes three CuSO_4 and two PH_3 , after which three H_2SO_4 completes the equation.

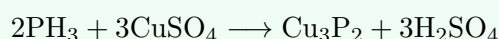
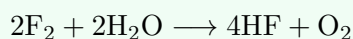
water by fluorine.

Step 2: Phosphine absorbed in copper sulphate solution Phosphine is removed by reaction with aqueous copper sulphate, forming copper phosphide. The balanced equation is



The three copper atoms and two phosphorus atoms form Cu_3P_2 . The six hydrogen atoms from two phosphine molecules combine with the three sulphate groups to give three sulphuric acid molecules. Thus the equation conserves all atoms and explains why copper sulphate solution absorbs phosphine.

Step 3: Conclusion



Quick Tip to Solve: Balance Cu_3P_2 first: its formula fixes three CuSO_4 and two PH_3 , after which three H_2SO_4 completes the equation.

9. Draw structures of the following:

(a) $\text{H}_2\text{S}_2\text{O}_7$

(b) HClO_3

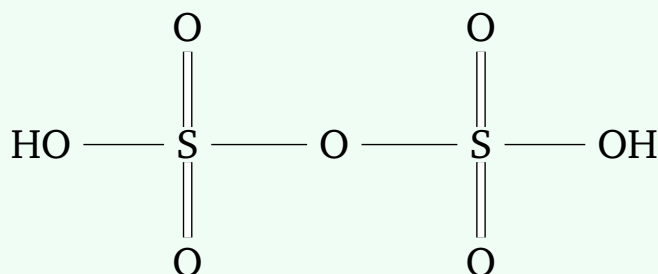
[2 marks]

Solution:

Concept:

- Disulphuric acid, $\text{H}_2\text{S}_2\text{O}_7$, has two sulphur atoms in oxidation state +6, joined through a bridging oxygen atom.
- Chloric acid, HClO_3 , has chlorine in oxidation state +5. In an oxoacid, the acidic hydrogen is bonded to oxygen.

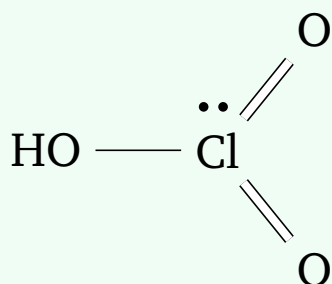
Step 1: Draw disulphuric acid Each sulphur atom is bonded to two terminal oxygen atoms by double bonds, one hydroxyl oxygen by a single bond, and the common bridging oxygen by a single bond. Thus its connectivity is $\text{HO} - \text{S}(=\text{O})_2 - \text{O} - \text{S}(=\text{O})_2 - \text{OH}$. Count the oxygen atoms: four terminal oxo atoms, two hydroxyl atoms and one bridge give seven in total. The two hydroxyl groups supply the two acidic hydrogens.



Structure of disulphuric acid

Quick Tip to Solve: Count all oxygen atoms after drawing: disulphuric acid has one S-O-S bridge; chloric acid has one O-H group.

Step 2: Draw chloric acid The chlorine atom is bonded to two oxygen atoms by double bonds and to one hydroxyl oxygen by a single bond. Its connectivity is $\text{HO} - \text{Cl}(=\text{O})_2$. This gives three oxygen atoms and one acidic hydrogen, matching HClO_3 . Chlorine also carries one lone pair, so the arrangement about chlorine is pyramidal rather than planar.



Structure of chloric acid; dots show the chlorine lone pair

Step 3: Conclusion The required structures are $\text{HO} - \text{S}(=\text{O})_2 - \text{O} - \text{S}(=\text{O})_2 - \text{OH}$ and $\text{HO} - \text{Cl}(=\text{O})_2$, as drawn.

Quick Tip to Solve: Count all oxygen atoms after drawing: disulphuric acid has one S-O-S bridge; chloric acid has one O-H group.

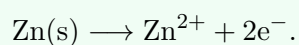
10. Write anode and cathode reactions that occur in dry cell. How does a dry cell differ from a mercury cell? [2 marks]

Solution:

Concept:

- A dry cell is a primary cell: zinc undergoes oxidation at the anode, while manganese dioxide is reduced at the cathode.
- The dry-cell electrolyte is a moist paste of NH_4Cl and ZnCl_2 ; its carbon rod acts as a current collector.

Step 1: Write the dry-cell half-reactions The zinc container supplies electrons through oxidation:



At the cathode, manganese dioxide reacts with ammonium ions and the incoming electron:

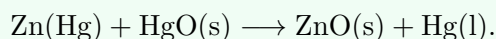


The cathode equation is written per electron; it must be doubled when combined with the anode reaction. Both mass and charge are conserved.

Step 2: Compare with a mercury cell A mercury cell uses a zinc-mercury amalgam anode, a mercury(II)

Quick Tip to Solve: For the dry-cell cathode, balance one electron with one ammonium ion; for mercury-cell constancy, inspect the overall reaction for electrolyte ions.

oxide cathode and an alkaline paste of KOH and ZnO. Its overall reaction is



Since the overall mercury-cell reaction does not involve electrolyte ions whose concentration changes, its potential remains nearly constant at about 1.35 V. A dry cell initially gives about 1.5 V, but its potential declines during use as reactants are consumed and electrolyte conditions change.

Step 3: Conclusion The zinc anode is oxidised and manganese dioxide is reduced according to the half-reactions above. Compared with the dry cell, the Zn(Hg)/HgO mercury cell has an alkaline electrolyte and gives a nearly constant potential of 1.35 V.

Quick Tip to Solve: For the dry-cell cathode, balance one electron with one ammonium ion; for mercury-cell constancy, inspect the overall reaction for electrolyte ions.

11. Account for the following:

- (a) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.
(b) On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali. [2 marks]

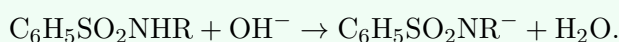
Solution:

Concept:

- Gabriel synthesis requires nucleophilic substitution of a halide by the phthalimide anion, followed by hydrolysis.
- In the Hinsberg test, alkali solubility depends on whether the sulphonamide product retains an acidic N-H bond.

Step 1: Explain the limitation of Gabriel synthesis An aromatic primary amine would require an aryl halide, $\text{Ar}-\text{X}$, to react with potassium phthalimide. Aryl halides do not undergo the ordinary nucleophilic substitution used in Gabriel synthesis: the halogen is attached directly to an sp^2 -hybridised carbon, and resonance gives the C-X bond partial double-bond character. Consequently, the phthalimide anion cannot replace the halogen under the normal synthesis conditions. The method therefore prepares aliphatic primary amines, rather than aromatic primary amines.

Step 2: Explain the difference in alkali solubility A primary amine gives $\text{C}_6\text{H}_5\text{SO}_2\text{NHR}$ with benzene sulphonyl chloride. This sulphonamide retains an N-H bond; the strongly electron-withdrawing sulphonyl group makes its hydrogen acidic. Alkali removes that proton, forming an ionic, alkali-soluble salt:



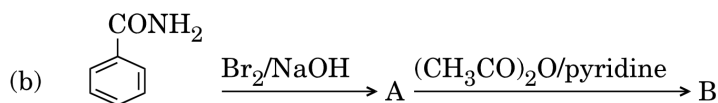
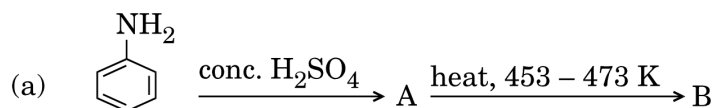
A secondary amine gives $\text{C}_6\text{H}_5\text{SO}_2\text{NR}_2$, which has no N-H bond. It cannot form this salt by deprotonation and remains insoluble in alkali.

Step 3: Conclusion (a) Aryl halides resist the substitution required by Gabriel synthesis. (b) The primary-amine sulphonamide has an acidic N-H bond and forms a soluble salt; the secondary-amine product has no N-H bond.

Quick Tip to Solve: In a Hinsberg product, count hydrogens still bonded to nitrogen: an N-H bond permits salt formation with alkali.

12. Write structures of compounds A and B in each of the following reactions:

[2 marks]

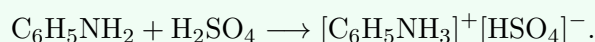


Solution:

Concept:

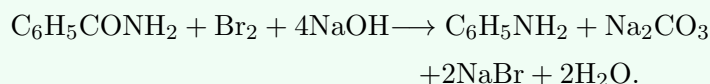
- Aniline first forms anilinium hydrogen sulphate with concentrated sulphuric acid; heating produces sulphanilic acid by para sulphonation.
- Hofmann bromamide degradation converts an amide to a primary amine with one fewer carbon atom. Acetic anhydride then acetylates the amine nitrogen.

Step 1: Identify A and B in reaction (a) Aniline accepts a proton from concentrated H_2SO_4 , giving the salt



Thus A is anilinium hydrogen sulphate. On heating at 453 – 473 K, it forms sulphanilic acid, $\text{p} - \text{H}_2\text{N} - \text{C}_6\text{H}_4 - \text{SO}_3\text{H}$: the amino and sulphonic acid groups occupy opposite (para) positions on the benzene ring. Sulphanilic acid also exists as the zwitterion $\text{p} - ^+\text{H}_3\text{N} - \text{C}_6\text{H}_4 - \text{SO}_3^-$.

Step 2: Identify A and B in reaction (b) Benzamide undergoes Hofmann bromamide degradation with Br_2/NaOH :



Therefore A is aniline, $\text{C}_6\text{H}_5 - \text{NH}_2$. Treatment with acetic anhydride in pyridine introduces an acetyl group on nitrogen:



Thus B is acetanilide, whose structure is $\text{C}_6\text{H}_5 - \text{NH} - \text{C}(=\text{O}) - \text{CH}_3$.

Step 3: Conclusion (a) $A = [\text{C}_6\text{H}_5\text{NH}_3]^+ [\text{HSO}_4]^-$; $B = \text{p} - \text{H}_2\text{N} - \text{C}_6\text{H}_4 - \text{SO}_3\text{H}$. (b) $A = \text{C}_6\text{H}_5 - \text{NH}_2$; $B = \text{C}_6\text{H}_5 - \text{NH} - \text{C}(=\text{O}) - \text{CH}_3$.

Quick Tip to Solve: Distinguish acid treatment from heating in (a); in (b), remove the carbonyl carbon during Hofmann degradation before acetylating nitrogen.

Section C (36 marks)

13. (a) Following reaction takes place in the cell:



Calculate $\Delta_r G^\circ$ of the reaction.

[Given: $E^\circ_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$, $E^\circ_{(\text{Ag}^+/\text{Ag})} = 0.80 \text{ V}$, $1 \text{ F} = 96,500 \text{ C mol}^{-1}$]

(b) How can you determine limiting molar conductivity, (Λ_m°) for strong electrolyte and weak electrolyte? [3 marks]

Solution:

Concept:

- Standard Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n counts transferred electrons and F is the Faraday constant.
- Kohlrausch's law expresses limiting molar conductivity as the sum of limiting ionic conductivities with their stoichiometric coefficients.

Step 1: (a) Use the supplied potentials Zinc changes from oxidation state zero to +2; therefore the reaction transfers $n = 2$ electrons. Subtract the anode reduction potential from the cathode reduction potential:

$$E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56 \text{ V}.$$

The supplied values therefore give

$$\Delta_r G^\circ = -2(96500)(1.56) = -301080 \text{ J mol}^{-1} = -301.08 \text{ kJ mol}^{-1}.$$

A negative Gibbs energy corresponds to a favourable cell reaction. Strictly, the supplied silver potential refers to Ag^+/Ag , whereas the written cathode reactant is Ag_2O . Its exact Gibbs energy requires the oxide cathode potential or equivalent thermodynamic data. The calculation above gives the expected numerical result from the supplied potentials.

Step 2: (b) Strong electrolyte: extrapolate to zero concentration Measure molar conductivity Λ_m at several low concentrations c . For a strong electrolyte the dilute-solution relation is $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$. Plot Λ_m against $\sqrt{c}$, and extrapolate the straight line to $\sqrt{c} = 0$. Its vertical intercept is the limiting molar conductivity Λ_m° , corresponding to infinite dilution.

Step 3: (b) Weak electrolyte: apply Kohlrausch's law A weak electrolyte ionises increasingly upon dilution, producing a strongly curved conductivity plot which cannot be extrapolated reliably. Combine limiting conductivities of suitable strong electrolytes instead. For acetic acid,

$$\begin{aligned}\Lambda_m^\circ(\text{CH}_3\text{COOH}) &= \Lambda_m^\circ(\text{HCl}) \\ &\quad + \Lambda_m^\circ(\text{CH}_3\text{COONa}) \\ &\quad - \Lambda_m^\circ(\text{NaCl}).\end{aligned}$$

Sodium and chloride contributions cancel, leaving only hydrogen and acetate ionic contributions.

Step 4: Conclusion The supplied potentials yield $-301.08 \text{ kJ mol}^{-1}$. Determine Λ_m° by extrapolation for strong electrolytes and by Kohlrausch's law for weak electrolytes.

Quick Tip to Solve: Count two electrons for zinc and subtract reduction potentials; cancel common ions when combining limiting conductivities.

14(a). Define the following with a suitable example, of each:

(a) Coagulation

(b) Multimolecular colloid

(c) Gel

[3 marks]

Solution:

Concept:

- Colloidal particles remain dispersed through stabilising effects such as their charge and interaction with the dispersion medium.
- Colloids can be classified by how their particles form and by the physical states of their dispersed phase and dispersion medium.

Step 1: (a) Coagulation Coagulation is the aggregation and precipitation of colloidal particles. When an electrolyte is added to a charged sol, oppositely charged ions can neutralise the particles' charge. Their repulsion decreases, allowing particles to combine into larger aggregates which separate from the dispersion medium. For example, adding sodium chloride to a ferric hydroxide sol can cause coagulation: chloride ions neutralise the positively charged colloidal particles.

Step 2: (b) Multimolecular colloid A multimolecular colloid is formed when many atoms or small molecules aggregate to produce particles whose sizes lie in the colloidal range. The individual constituent atoms or molecules are smaller than a colloidal particle; the aggregate, held together by weak intermolecular forces, is colloidal. Gold sol is an example, since each colloidal particle contains many gold atoms. Sulphur sol is another example, with aggregates of sulphur molecules.

Step 3: (c) Gel A gel is a colloidal system in which a liquid is dispersed in a solid dispersion medium. The solid forms a network that immobilises the liquid, giving a semisolid appearance despite the substantial liquid content. Jelly is a suitable example; cheese is another familiar example of this liquid-in-solid class. This phase arrangement distinguishes a gel from a sol, which usually has a solid dispersed in a liquid.

Step 4: Conclusion Coagulation is colloidal aggregation and precipitation, as for ferric hydroxide sol with an electrolyte. Gold sol is a multimolecular colloid, and jelly is a gel with liquid dispersed in a solid.

Quick Tip to Solve: Give both the defining feature and an example: particle aggregation, aggregates of small units, and liquid-in-solid respectively.

14(b). (a) Out of starch and ferric hydroxide sol, which one can easily be coagulated and why?

(b) What is observed when an emulsion is centrifuged?

(c) What is the role of promoters and poisons in catalysis?

[3 marks]

Solution:

Concept:

- Lyophilic sols are stabilised by solvation as well as charge; lyophobic sols depend mainly on the electrical charge of their particles.
- Centrifugation accelerates separation of dispersed phases. Catalyst activity can be increased by promoters or decreased by poisons.

Step 1: (a) Compare the two sols Ferric hydroxide sol is more easily coagulated. It is lyophobic: its dispersed particles have little affinity for water and depend largely on their electrical charge for stability. Adding a suitable electrolyte neutralises their charge, reduces electrostatic repulsion and allows aggregation and precipitation. Starch sol is lyophilic; its particles are strongly hydrated and have a protective solvation layer in addition to charge. This additional stabilisation makes starch sol more resistant to coagulation by small quantities of electrolyte.

Step 2: (b) Centrifuge an emulsion On centrifugation, the emulsion separates into its two constituent liquids as distinct layers. An emulsion consists of droplets of one liquid dispersed in another immiscible liquid. Centrifugation accelerates separation according to their density difference, so the dispersed droplets collect and the two liquid phases separate. Thus the observation is breaking of the emulsion and formation of separate liquid layers.

Step 3: (c) Explain promoters and poisons A promoter increases the activity of a catalyst. For example, molybdenum promotes the iron catalyst used in the Haber process for ammonia synthesis. A poison decreases or destroys catalytic activity, commonly by binding strongly to active surface sites and preventing reactants from using them. For example, arsenic compounds poison the platinum catalyst in the Contact process. The terms describe effects on catalytic activity rather than changes to the reaction's equilibrium constant.

Step 4: Conclusion Ferric hydroxide sol coagulates more readily because it is lyophobic. Centrifugation separates an emulsion into its liquids. Promoters increase catalytic activity, while poisons decrease or destroy it.

Quick Tip to Solve: Identify hydration as starch's extra protection, describe separate liquid layers, and give opposite effects for promoter and poison.

15. (a) An element crystallises in bcc lattice with a cell edge of 3×10^{-8} cm. The density of the element is 6.89 g cm^{-3} . Calculate the molar mass of the element. ($N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$)

(b) What type of semiconductor is obtained when

(i) Ge is doped with In?

(ii) Si is doped with P?

[3 marks]

Solution:

Concept:

- Unit-cell density is $\rho = zM/(a^3N_A)$, where z is atoms per cell, M the molar mass and a the cell edge. A bcc cell has $z = 2$.
- Trivalent dopants create holes in tetravalent crystals (p-type), while pentavalent dopants supply extra electrons (n-type).

Step 1: (a) Determine the cell volume and atom count Eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom; the body-centred atom contributes one whole atom. Thus the bcc cell contains two atoms. Using centimetres to match the density,

$$a^3 = (3 \times 10^{-8})^3 = 27 \times 10^{-24} = 2.7 \times 10^{-23} \text{ cm}^3.$$

The cell mass is ρa^3 ; in terms of molar mass it is $2M/N_A$. Equating the two expressions gives $M = \rho a^3 N_A / 2$.

Step 2: (a) Calculate the molar mass

$$M = \frac{6.89 \times 2.7 \times 10^{-23} \times 6.022 \times 10^{23}}{2} = 56.014 \text{ g mol}^{-1}.$$

The powers of ten cancel. Density multiplied by cell volume gives grams per cell; multiplying by Avogadro's constant and dividing by two converts this to grams per mole of atoms.

Step 3: (b) Identify the charge carriers (i) Ge has four valence electrons and In has three. Replacing Ge by In leaves one covalent bond deficient in an electron. These vacancies, called holes, are the majority carriers; hence Ge doped with In is p-type.

(ii) Si has four valence electrons and P has five. Four electrons form covalent bonds and the fifth is available for conduction. Electrons are the majority carriers; hence Si doped with P is n-type.

Step 4: Conclusion (a) The molar mass is approximately 56.0 g mol^{-1} . (b) (i) Ge doped with In is p-type; (ii) Si doped with P is n-type.

Quick Tip to Solve: Use two atoms per bcc cell; a dopant with one fewer valence electron creates holes, whereas one extra supplies electrons.

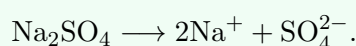
16. A solution 0.1 M of Na_2SO_4 is dissolved to the extent of 95%. What would be its osmotic pressure at 27°C ? ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$) [3 marks]

Solution:

Concept:

- Osmotic pressure of an electrolyte is $\pi = iCRT$, where C is its analytical molarity, T the absolute temperature and i the van't Hoff factor.
- If a fraction α dissociates into n ions per formula unit, then $i = 1 + (n - 1)\alpha$; count undissociated molecules as well as ions.

Step 1: Interpret the electrolyte dissociation The stated extent of 95 percent is used as the degree of dissociation of dissolved sodium sulphate, so $\alpha = 0.95$. Its dissociation is



Each dissociated formula unit produces three ions, so $n = 3$. Starting with one mole of formula units, $1 - \alpha$ mole remains undissociated, while 2α mole of sodium ions and α mole of sulphate ions are formed.

Step 2: Find the effective particle concentration The total number of moles of solute particles per initial mole is

$$i = (1 - \alpha) + 2\alpha + \alpha = 1 + 2\alpha = 1 + 2(0.95) = 2.90.$$

Thus the particle concentration is $iC = 2.90(0.1) = 0.290 \text{ mol L}^{-1}$. Using $i = 3$ would incorrectly assume complete dissociation; using $i = 0.95$ would omit the multiple ions produced.

Step 3: Substitute in the osmotic-pressure equation Convert the temperature to kelvin: $T = 27 + 273 = 300 \text{ K}$. The given value of R uses litres and atmospheres and therefore matches the concentration in moles per litre:

$$\pi = 2.90 \times 0.1 \times 0.0821 \times 300 = 7.1427 \text{ atm}.$$

The litre, mole and kelvin factors cancel, leaving pressure in atmospheres.

Step 4: Conclusion The osmotic pressure is $\pi \approx 7.14 \text{ atm}$.

Quick Tip to Solve: Sodium sulphate gives three ions, so use $i = 1 + 2\alpha$ and convert Celsius to kelvin before substituting.

17(a). Write down the reactions taking place in blast furnace related to the metallurgy of iron in the temperature range $500 \text{ K} - 800 \text{ K}$. What is the role of limestone in the metallurgy of iron? [3 marks]

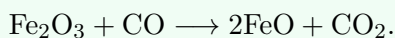
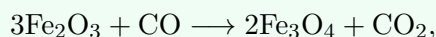
Solution:

Concept:

- In the upper, relatively cooler region of the blast furnace, carbon monoxide acts as the reducing agent and removes oxygen from iron oxides as carbon dioxide.
- Limestone is a flux: its decomposition produces basic calcium oxide, which combines with acidic silica gangue to form a fusible slag.

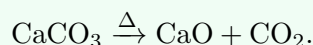
Quick Tip to Solve: Separate the functions: CO removes oxygen from iron oxides, while limestone supplies CaO to remove silica as slag.

Step 1: Give the reactions at 500–800 K In this temperature range, carbon monoxide reduces the iron oxides. The reactions conventionally listed for the upper zone of the blast furnace are

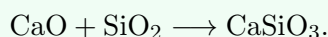


These show reduction of hematite to magnetite or ferrous oxide and reduction of magnetite to iron. In each equation, CO is oxidised to carbon dioxide while the iron oxide loses oxygen. Each equation conserves the numbers of iron, carbon and oxygen atoms.

Step 2: Explain the role of limestone Limestone, CaCO_3 , is added as a flux. On heating in the hotter region of the furnace, it decomposes:



The basic oxide CaO reacts with the acidic silica impurity in the ore:



Calcium silicate is a fusible slag. It separates from the denser molten iron and can be removed, thereby eliminating silica gangue. Limestone therefore helps purify the metal through slag formation; it is not the reducing agent in the above reactions.

Step 3: Conclusion At 500–800 K, CO reduces iron oxides through the three reactions given above. Limestone supplies CaO, which removes silica as calcium silicate slag, CaSiO_3 .

Quick Tip to Solve: Separate the functions: CO removes oxygen from iron oxides, while limestone supplies CaO to remove silica as slag.

OR

17(b). What happens when

- (a) Silver is leached with NaCN in the presence of air?
- (b) Copper matte is charged into silica lined converter and hot air blast is blown?
- (c) NaCN is added in an ore containing PbS and ZnS during concentration by froth floatation method?

[3 marks]

Solution:

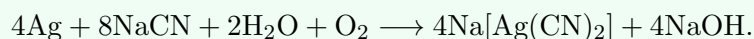
Concept:

- Cyanide leaching dissolves silver as the soluble complex $[\text{Ag}(\text{CN})_2]^-$; oxygen from air acts as the oxidant.
- Copper matte contains Cu_2S and FeS . Air oxidises sulphides, silica removes iron oxide as slag, and copper is formed by self-reduction.
- A depressant selectively prevents one sulphide from entering the froth, allowing two sulphide ores

Quick Tip to Solve: Match each reagent to its role: air oxidises, silica removes FeO, and NaCN selectively depresses ZnS.

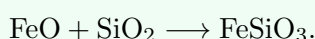
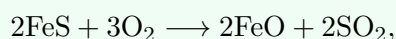
to be separated.

Step 1: (a) Leaching silver in the presence of air Silver dissolves in aqueous sodium cyanide because the silver(I) ions formed by oxidation are stabilised as dicyanidoargentate(I). The balanced reaction is

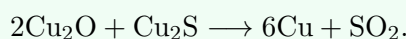
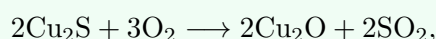


Thus silver passes into the leach solution as a soluble complex, while insoluble impurities remain behind. The presence of air supplies the oxygen needed for dissolution.

Step 2: (b) Conversion of copper matte into copper On blowing hot air, iron sulphide is oxidised first. The iron oxide reacts with the silica lining to form iron silicate slag:



Some copper(I) sulphide is then oxidised to copper(I) oxide. The oxide reacts with the remaining sulphide, giving copper by self-reduction:



Escaping sulphur dioxide produces blisters on solidification, so the product is called blister copper.

Step 3: (c) Selective depression of zinc sulphide Sodium cyanide acts as a depressant for ZnS . It prevents zinc sulphide from collecting with the froth, whereas PbS remains floatable and is carried into the froth. Consequently lead sulphide is separated from zinc sulphide, which remains in the aqueous pulp.

Step 4: Conclusion (a) Silver forms soluble $\text{Na}[\text{Ag}(\text{CN})_2]$. (b) Iron is removed as FeSiO_3 slag and blister copper is obtained. (c) NaCN depresses ZnS , allowing PbS to float.

Quick Tip to Solve: Match each reagent to its role: air oxidises, silica removes FeO , and NaCN selectively depresses ZnS .

18. Give reasons for the following:

(a) Dioxygen is a gas but sulphur a solid.

(b) NO(g) released by jet aeroplanes is slowly depleting the ozone layer.

(c) Interhalogens are more reactive than pure halogens.

[3 marks]

Solution:

Concept:

- Physical state depends on molecular size and the strength of intermolecular attractions, whereas the molecular form also depends on the ability to form multiple bonds.
- A catalyst can destroy many ozone molecules when it is regenerated in successive reaction steps.
- Interhalogen bonds are generally weaker than the corresponding halogen-halogen bonds; fluorine

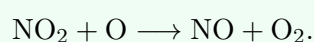
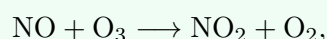
Quick Tip to Solve: Distinguish the intramolecular bond that determines O_2 or S_8 from the intermolecular forces that determine their physical states.

is the exception to the usual reactivity comparison.

Step 1: (a) Compare dioxygen and sulphur Oxygen atoms are small and form a strong $p\pi-p\pi$ double bond, so elemental oxygen exists as discrete O_2 molecules. These small molecules have weak intermolecular dispersion forces and a low boiling point; dioxygen is therefore a gas at ordinary temperature.

Sulphur has larger atoms, whose orbitals do not overlap effectively enough to favour the analogous multiple bond. It instead forms puckered S_8 rings with single S–S bonds. The larger, more polarisable S_8 molecules have much stronger intermolecular dispersion forces than O_2 , so sulphur is a solid at ordinary temperature.

Step 2: (b) Explain catalytic destruction of ozone by NO Nitric oxide released by jet aeroplanes reacts with ozone to form nitrogen dioxide and oxygen. The nitrogen dioxide then reacts with atomic oxygen, regenerating nitric oxide:



Adding the reactions gives $O_3 + O \longrightarrow 2O_2$. Because NO is regenerated, it acts as a catalyst and can repeatedly destroy ozone, gradually depleting the ozone layer.

Step 3: (c) Compare interhalogens with pure halogens An interhalogen contains two different halogen atoms. Their differing sizes and orbital energies generally make the bond between them weaker than the bond in the corresponding pure halogen molecule. The interhalogen bond is therefore more readily broken during reaction, accounting for its greater reactivity. The usual statement excludes F_2 , which is exceptionally reactive because its F–F bond is unusually weak.

Step 4: Conclusion Dioxygen has small molecules with weak intermolecular attractions, whereas sulphur has larger S_8 rings with stronger attractions. NO catalytically converts ozone into oxygen. Interhalogens generally react more readily because their bonds are weaker, with F_2 the standard exception.

Quick Tip to Solve: Distinguish the intramolecular bond that determines O_2 or S_8 from the intermolecular forces that determine their physical states.

19(a). Write the structures of monomers used to obtain the following polymers:

(a) Neoprene

(b) PHBV

(c) Bakelite

[3 marks]

Solution:

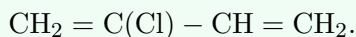
Concept:

- Addition polymers arise from unsaturated monomers: the carbon-carbon double bonds provide sites for linking units into a chain.
- Condensation polymers arise from monomers with suitable functional groups. Hydroxy acids can

Quick Tip to Solve: For PHBV, count the $COOH$ carbon as carbon 1 and place OH on carbon 3 in both four-carbon and five-carbon acids.

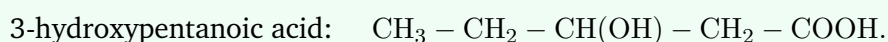
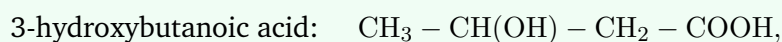
form ester links, while phenol and formaldehyde form a resin with methylene bridges.

Step 1: (a) Monomer of neoprene Neoprene is obtained by addition polymerisation of chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its structural formula is



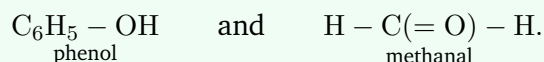
The chlorine atom is attached to the second carbon of the conjugated diene. During polymerisation the diene units join to form the polychloroprene chain; the chlorine substituent remains attached to the chain.

Step 2: (b) Monomers of PHBV PHBV is poly(β -hydroxybutyrate-co- β -hydroxyvalerate), a copolymer formed from two hydroxy acids:



These are also called β -hydroxybutyric acid and β -hydroxyvaleric acid. Numbering begins at the carboxyl carbon, so the hydroxyl group is on carbon 3 in each structure. Their hydroxyl and carboxyl groups form ester links in the copolymer.

Step 3: (c) Monomers of Bakelite Bakelite is produced from phenol and formaldehyde (methanal). Their structures are



In phenol, the OH group is bonded directly to a benzene-ring carbon; C_6H_5 denotes that phenyl ring. Reaction with formaldehyde introduces links at the ortho and para positions, ultimately giving the cross-linked phenol-formaldehyde resin.

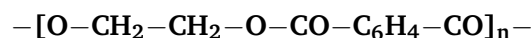
Step 4: Conclusion Neoprene: $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$. PHBV: $\text{CH}_3 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{COOH}$ and $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{OH}) - \text{CH}_2 - \text{COOH}$. Bakelite: phenol $\text{C}_6\text{H}_5 - \text{OH}$ and formaldehyde $\text{H} - \text{C}(=\text{O}) - \text{H}$.

Quick Tip to Solve: For PHBV, count the COOH carbon as carbon 1 and place OH on carbon 3 in both four-carbon and five-carbon acids.

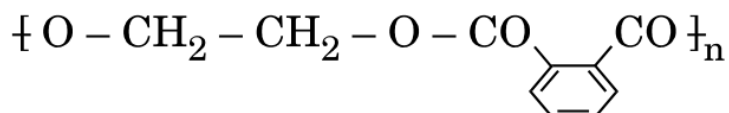
19(b). (a) Arrange the following polymers in decreasing order of their intermolecular forces:

Bakelite, Polythene, Buna-S, Nylon-6,6

(b) Write the monomers of the following polymer:



(c) What is the structural difference between high density polythene (HDP) and low density polythene (LDP)? [3 marks]

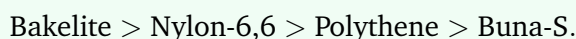


Solution:

Concept:

- Polymer strength depends on the links between chains: cross-links give a rigid network, hydrogen bonds strengthen fibres, and weaker dispersion forces occur in thermoplastics and elastomers.
- An ester linkage $-\text{COO}-$ is formed by condensation of a carboxylic acid group and an alcohol group with loss of water.

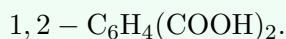
Step 1: (a) Compare the forces between polymer chains Bakelite is a highly cross-linked thermosetting network. Nylon-6,6 has strong hydrogen bonding between its amide groups. Polythene chains have weaker van der Waals forces, while Buna-S is an elastomer whose chains are held together relatively weakly so that they can stretch. Thus the decreasing order is



Step 2: (b) Identify the two condensation monomers Break each ester bond conceptually into an alcohol group and a carboxylic acid group. The $-\text{OCH}_2\text{CH}_2\text{O}-$ segment comes from ethylene glycol,



In the printed ring diagram the two carbonyl groups are attached to adjacent carbon atoms of benzene. Therefore the acid monomer is benzene-1,2-dicarboxylic acid (phthalic acid),



The diol and diacid form ester links by condensation with loss of water.

Step 3: (c) Relate branching to density High density polythene has predominantly linear, unbranched chains. These chains pack closely, giving higher density. Low density polythene has branched chains; the branches prevent close packing, giving lower density.

Step 4: Conclusion (a) Bakelite $>$ Nylon-6,6 $>$ Polythene $>$ Buna-S. (b) Ethylene glycol and phthalic acid. (c) HDP is predominantly linear, whereas LDP is branched.

Quick Tip to Solve: Locate the two ring attachment positions before naming a polyester acid monomer; adjacent and opposite substituents give different acids.

20(a). Why are metal hydroxides better alternatives than sodium hydrogen carbonate in antacids?

(b) Why is aspirin used in the prevention of heart-attacks?

(c) Why antihistamines do not affect the secretion of acid in stomach?

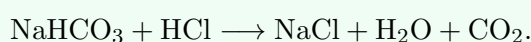
[3 marks]

Solution:

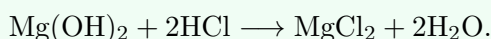
Concept:

- Antacids neutralise excess gastric hydrochloric acid. Their usefulness also depends on avoiding excessive alkalinity and unwanted gaseous products.
- Aspirin inhibits platelet aggregation, while the action of an antihistamine depends on which histamine receptor it blocks.

Step 1: (a) Compare antacid action Sodium hydrogen carbonate neutralises acid rapidly, but an excessive amount can make the stomach alkaline and stimulate further acid secretion. It also releases carbon dioxide, which may cause discomfort:



Sparingly soluble metal hydroxides, such as magnesium hydroxide and aluminium hydroxide, neutralise excess acid more gradually and do not raise the pH excessively because of their limited solubility. They do not release carbon dioxide. For example,



Step 2: (b) Explain aspirin's preventive action Aspirin has an anti-blood-clotting or antiplatelet action: it inhibits aggregation of blood platelets. Reduced platelet aggregation lowers the likelihood of a clot forming in a coronary artery and obstructing blood flow to the heart muscle. This explains its use in the prevention of heart attacks; the relevant property here is its antiplatelet action, rather than merely its ability to relieve pain.

Step 3: (c) Distinguish histamine receptors Histamine has different effects through different types of receptors. The conventional antihistamines used to control allergic responses act on H_1 receptors. Gastric acid secretion is stimulated through H_2 receptors in the stomach. Since these receptors differ, the anti-allergy antihistamines do not block the stomach receptors and therefore do not suppress gastric acid secretion. Drugs such as cimetidine inhibit the gastric H_2 receptors and can reduce acid secretion.

Step 4: Conclusion (a) Sparingly soluble metal hydroxides avoid excessive alkalinity and carbon dioxide formation. (b) Aspirin prevents platelet aggregation and helps reduce clot formation. (c) Anti-allergy antihistamines act on H_1 receptors, whereas gastric acid secretion involves H_2 receptors.

Quick Tip to Solve: For the antihistamine part, distinguish the allergy receptor from the gastric receptor before explaining the drug's selectivity.

20(b). Define the following terms with a suitable example of each:

(a) Tranquilizers

(b) Antibiotics

(c) Non-ionic detergents

[3 marks]

Solution:

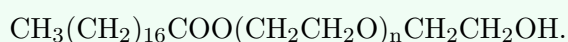
Concept:

- Drugs are classified by their therapeutic action. Tranquilizers act on the nervous system, whereas antibiotics act against microorganisms.
- Detergents contain a hydrophobic hydrocarbon portion and a hydrophilic portion; the charge on the hydrophilic portion determines their classification.

Step 1: (a) Define tranquilizers and give an example Tranquilizers are drugs used to treat stress, fatigue and mild or severe mental disorders. They act on the central nervous system to produce a feeling of well-being and relieve anxiety or tension. Diazepam is a suitable example of a tranquilizer. Its calming action identifies the therapeutic category requested in this part.

Step 2: (b) Define antibiotics and give an example Antibiotics are chemical substances which, in low concentrations, kill microorganisms or inhibit their growth by interfering with their metabolic processes. They were originally obtained from microorganisms; synthetic modifications of such substances are also used as antibiotics. Penicillin is a suitable example. It acts against susceptible bacteria by interfering with bacterial cell-wall formation, thereby illustrating the antimicrobial action in the definition.

Step 3: (c) Define non-ionic detergents and give an example Non-ionic detergents are detergents which do not contain any ion in their constitution and do not form an ionic head group in water. Their uncharged polar groups provide the hydrophilic part, while the long hydrocarbon chain provides the hydrophobic part. A suitable example is the detergent formed by reaction of stearic acid with polyethylene glycol:



The ester and ether oxygen atoms interact with water, while the long hydrocarbon chain interacts with grease. This permits cleansing without a charged detergent ion.

Step 4: Conclusion Tranquilizers relieve anxiety and mental stress, for example diazepam. Antibiotics kill or inhibit microorganisms at low concentrations, for example penicillin. Non-ionic detergents have an uncharged hydrophilic portion, for example the stearic acid–polyethylene glycol ester.

Quick Tip to Solve: Give both the defining action or structural feature and one named example for every requested class; examples alone are incomplete.

21. (a) Out of cyclohexyl chloride ($C_6H_{11}Cl$) and cyclohexylmethyl chloride ($C_6H_{11}CH_2Cl$), which one is more reactive towards S_N2 reaction and why?
- (b) Out of chlorobenzene (C_6H_5Cl) and para-nitrochlorobenzene ($p-O_2NC_6H_4Cl$), which one is more reactive towards nucleophilic substitution reaction and why?
- (c) Out of $HOCH_2CH_2CH(CH_3)_2$ and $CH_3CH(OH)CH(CH_3)CH_3$, which one is optically active and why? [3 marks]

Solution:

Concept:

- An S_N2 substitution proceeds by simultaneous backside attack of the nucleophile and departure of the leaving group; crowding at the carbon carrying chlorine reduces its rate.
- An electron-withdrawing nitro group at the ortho or para position stabilises the anionic intermediate in nucleophilic aromatic substitution.
- A tetrahedral carbon bonded to four different groups is a chiral centre; a compound with one such centre can show optical activity.

Step 1: (a) Compare crowding at the reacting carbon In cyclohexyl chloride, the carbon bonded to chlorine is secondary and lies in the ring; the neighbouring carbon groups obstruct backside attack. In cyclohexylmethyl chloride, chlorine is attached to an external primary $-CH_2Cl$ carbon. That site is less hindered, so the nucleophile can approach it more readily. Thus $C_6H_{11}CH_2Cl$ undergoes S_N2 substitution faster than $C_6H_{11}Cl$.

Step 2: (b) Examine the para nitro group Chlorobenzene resists nucleophilic substitution because its carbon-chlorine bond has partial double-bond character. In para-nitrochlorobenzene, the $-NO_2$ group withdraws electron density and stabilises the negative charge of the intermediate by resonance. Nucleophilic attack followed by chloride loss is therefore easier, making $p-O_2NC_6H_4Cl$ more reactive.

Step 3: (c) Identify the stereogenic carbon In $HOCH_2CH_2CH(CH_3)_2$, the branched carbon has two identical methyl groups, and the remaining carbons are CH_2 or CH_3 . It has no chiral centre. In $CH_3CH(OH)CH(CH_3)CH_3$, the carbon bearing OH is attached to OH, H, CH_3 , and $CH(CH_3)_2$: four different groups. Its enantiomers rotate plane-polarised light; the second structure is the optically active compound (an individual enantiomer, rather than a racemic mixture).

Step 4: Conclusion (a) Cyclohexylmethyl chloride is more reactive in S_N2 owing to less steric hindrance. (b) Para-nitrochlorobenzene is more reactive owing to resonance stabilisation of the intermediate. (c) 3-Methylbutan-2-ol is optically active because carbon 2 is chiral.

Quick Tip to Solve: Inspect the carbon bearing the leaving group for substitution, and list all four groups on a candidate carbon before calling it chiral.

22. What happens when

(a) Salicylic acid is treated with $(\text{CH}_3\text{CO})_2\text{O}/\text{H}^+$?

(b) Phenol is oxidised with $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$?

(c) Anisole is treated with $\text{CH}_3\text{Cl}/\text{anhydrous AlCl}_3$?

Write chemical equation in support of your answer.

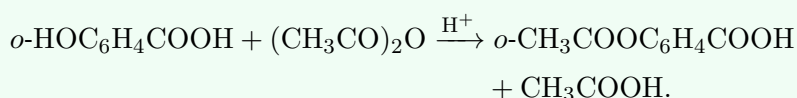
[3 marks]

Solution:

Concept:

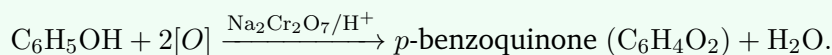
- Acid-catalysed acetylation with acetic anhydride converts a phenolic hydroxyl group into an acetate ester.
- Acidified dichromate oxidises phenol to benzoquinone; $[\text{O}]$ in a reaction equation denotes an oxygen equivalent supplied by the oxidising agent.
- Anisole undergoes Friedel-Crafts alkylation. Its electron-donating methoxy group activates the aromatic ring and directs substitution to ortho and para positions.

Step 1: (a) Acetylation of salicylic acid The phenolic $-\text{OH}$ group of salicylic acid is acetylated by acetic anhydride in the presence of acid. The carboxylic acid group remains intact. The product is 2-acetoxybenzoic acid, commonly called acetylsalicylic acid or aspirin:



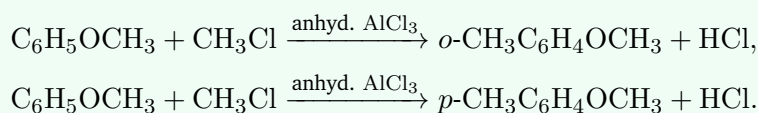
Acetic acid is the accompanying product; acetylation replaces the hydrogen of the phenolic hydroxyl group by $\text{CH}_3\text{CO}-$.

Step 2: (b) Oxidation of phenol Acidified sodium dichromate oxidises phenol to para-benzoquinone (1,4-benzoquinone). The two carbonyl groups are at opposite positions in the six-membered ring:



This equation balances carbon, hydrogen and oxygen when the oxidant is represented by oxygen equivalents.

Step 3: (c) Friedel-Crafts methylation of anisole Methyl chloride in the presence of anhydrous aluminium chloride introduces a methyl group into the ring. Resonance donation from $-\text{OCH}_3$ directs attack to the ortho and para positions, yielding 2-methylanisole and 4-methylanisole, with the para product predominating because it has less steric crowding:



The two equations show the alternative substitution pathways, each consuming one molecule of anisole.

Step 4: Conclusion (a) Aspirin is formed by acetylation. (b) Phenol gives para-benzoquinone on oxidation. (c) Anisole gives ortho- and para-methylanisole, with para-methylanisole as the major

Quick Tip to Solve: Match each reagent to its role: anhydride acetylates the hydroxyl group, dichromate oxidises, and methyl chloride with aluminium chloride alkylates the ring.

product.

Quick Tip to Solve: Match each reagent to its role: anhydride acetylates the hydroxyl group, dichromate oxidises, and methyl chloride with aluminium chloride alkylates the ring.

23. (a) Give one chemical test as an evidence to show that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ are ionisation isomers.
- (b) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why? (Atomic no. of Ni = 28)
- (c) Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (i) strong field ligand, and (ii) weak field ligand. (Atomic no. of Fe = 26)

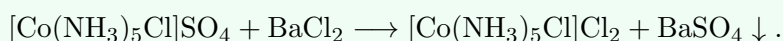
[3 marks]

Solution:

Concept:

- Ionisation isomers exchange a ligand inside the coordination sphere with a counter-ion outside it. Chemical tests detect the free counter-ion in aqueous solution.
- Unpaired electrons cause paramagnetism; a configuration with all electrons paired is diamagnetic. Determine the metal oxidation state before counting its d electrons.
- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. Strong-field ligands favour pairing, whereas weak-field ligands favour the high-spin arrangement.

Step 1: (a) Test for the free sulfate ion Add aqueous barium chloride to separate freshly prepared aqueous solutions of the two complexes. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ gives a white precipitate of barium sulfate because sulfate is outside its coordination sphere:



$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ does not give this immediate sulfate precipitate, because its sulfate is coordinated to cobalt. The different ions liberated in solution demonstrate ionisation isomerism. Conversely, its free chloride gives an immediate white AgCl precipitate with silver nitrate.

Step 2: (b) Compare the nickel electron counts Nickel has ground-state configuration $[\text{Ar}]3d^84s^2$. In $[\text{NiCl}_4]^{2-}$, four chloride ligands contribute a total charge of -4 , so nickel is $+2$, with a $3d^8$ configuration. Chloride is a weak-field ligand and the tetrahedral complex has two unpaired electrons; hence it is paramagnetic. In $[\text{Ni}(\text{CO})_4]$, neutral CO ligands leave nickel in oxidation state zero. The metal has a filled $3d^{10}$ configuration in this complex, with all electrons paired, so it is diamagnetic. Both have tetrahedral geometry (sp^3 hybridisation in the valence-bond description), but their electron counts differ.

Step 3: (c) Fill the octahedral levels for iron(III) Iron has configuration $[\text{Ar}]3d^64s^2$. Removal of two $4s$ electrons and one $3d$ electron gives Fe^{3+} the configuration $3d^5$. For a strong-field ligand, the octahedral splitting Δ_o exceeds the pairing energy P , so electrons pair in the lower set:

(i) Strong field: $t_{2g}^5 e_g^0$ (low spin; one unpaired electron).

Quick Tip to Solve: First determine the oxidation state and d-electron count; then use the geometry and field strength to decide pairing and magnetism.

For a weak-field ligand, $\Delta_o < P$, so electrons occupy all five orbitals singly before pairing:

(ii) Weak field: $t_{2g}^3 e_g^2$ (high spin; five unpaired electrons).

Step 4: Conclusion (a) Only $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ gives an immediate BaSO_4 precipitate with BaCl_2 . (b) The chloride complex has two unpaired electrons, whereas nickel carbonyl has none. (c) Strong field: $t_{2g}^5 e_g^0$; weak field: $t_{2g}^3 e_g^2$.

Quick Tip to Solve: First determine the oxidation state and d-electron count; then use the geometry and field strength to decide pairing and magnetism.

24. Define the following terms with a suitable example of each:

(a) Anomers

(b) Essential amino acids

(c) Denaturation of protein

[3 marks]

Solution:

Concept:

- The properties of biomolecules depend on their stereochemistry, nutritional availability and three-dimensional structure.
- An anomeric carbon is the carbonyl carbon of the open-chain sugar that becomes a new stereocentre on ring formation.
- Protein function depends on its native conformation; denaturation disrupts this conformation without normally breaking peptide bonds.

Step 1: (a) Anomers Anomers are cyclic stereoisomers of a sugar that differ only in the configuration at the anomeric carbon. For glucose this is carbon 1, which was the aldehyde carbon in the open-chain form. For example, α -D-glucopyranose and β -D-glucopyranose are anomers. In the usual Haworth representation, the anomeric hydroxyl group is on the opposite side to the CH_2OH group in the α form and on the same side in the β form.

Step 2: (b) Essential amino acids Essential amino acids are amino acids that the human body cannot synthesise in sufficient amounts to meet its requirements and hence must obtain through the diet. Valine is a suitable example; lysine is another. They are required for protein synthesis, just as other amino acids are, but their dietary supply is essential.

Step 3: (c) Denaturation of protein Denaturation is the loss of the native secondary and tertiary structure of a protein, and consequently of its biological activity, under the action of heat, changes in pH or suitable chemicals. The primary structure, namely the amino-acid sequence linked by peptide bonds, remains intact in ordinary denaturation. A suitable example is coagulation of egg-white protein on boiling: heat unfolds the protein and the unfolded molecules aggregate into a solid mass.

Step 4: Conclusion Examples are α - and β -D-glucopyranose for anomers, valine for an essential amino acid, and coagulation of egg white on boiling for protein denaturation.

Quick Tip to Solve: Pair each definition with its own example, and distinguish loss of protein conformation from breaking its peptide bonds.

Section D (15 marks)

25(a). Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction?

(b) A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction. [5 marks]

Solution:

Concept:

- For a rate law $r = k[A]^m[B]^n$, the overall order is $m + n$; the exponents are determined experimentally.
- Molecularity is the number of reacting species taking part in one elementary reaction step.
- For a first-order reaction, $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$ and $t_{1/2} = \frac{0.693}{k}$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations.

Step 1: (a) Define order of reaction The order of a reaction is the sum of the powers of the reactant concentrations in the experimentally determined rate law. Thus, if $r = k[A]^m[B]^n$, the order is $m + n$. It is a kinetic quantity and cannot generally be read from the coefficients of the overall balanced chemical equation. The order may be zero, fractional or an integer, depending on the observed rate law.

Step 2: Compare order and molecularity for a complex reaction A complex reaction proceeds through two or more elementary steps. Its overall order is obtained experimentally from the rate law and depends on its mechanism, particularly the rate-controlling step and any preceding equilibria. Molecularity counts the reacting atoms, molecules or ions participating in a single elementary step. It is always a positive integer and is never zero or fractional. Hence an overall order can be assigned to a complex reaction, but molecularity has meaning only for its individual elementary steps, not for the complex reaction as a whole. Order and molecularity need not be equal.

Step 3: (b) Find the first-order rate constant At 50% completion, half the initial reactant remains, so the stated time is the half-life: $t_{1/2} = 25$ min. Therefore,

$$k = \frac{0.693}{25} = 0.02772 \text{ min}^{-1}.$$

Equivalently, $k = (2.303/25) \log 2$. The units are inverse minutes because all times are expressed in minutes.

Step 4: Calculate the time for 80 percent completion At 80% completion, 20% of the initial reactant remains. Thus $[A]_t = 0.20[A]_0$ and $[A]_0/[A]_t = 5$, not $1/0.80$. Substituting into the integrated

Quick Tip to Solve: Convert percentage completion into the fraction remaining before using the first-order law; here 80 percent completion means 20 percent remains.

first-order law gives

$$\begin{aligned}t_{80} &= \frac{2.303}{k} \log 5 \\&= 25 \frac{\log 5}{\log 2} \\&= 25 \frac{0.6990}{0.3010} \\&\approx 58.06 \text{ min.}\end{aligned}$$

The result exceeds two half-lives (50 minutes), which leave 25% reactant, and is below three half-lives (75 minutes), which leave 12.5%; hence it is consistent with 20% remaining.

Step 5: Conclusion (a) Order is the sum of the concentration exponents in the experimental rate law; molecularity applies only to an elementary step of a complex reaction. (b) The time required for 80% completion is 58.06 min, approximately 58.1 min.

Quick Tip to Solve: Convert percentage completion into the fraction remaining before using the first-order law; here 80 percent completion means 20 percent remains.

OR

25(b). (a) The decomposition of a hydrocarbon has value of rate constant as $2.5 \times 10^4 \text{ s}^{-1}$ at 27°C . At what temperature would rate constant be $7.5 \times 10^4 \text{ s}^{-1}$ if energy of activation is $19.147 \times 10^3 \text{ J mol}^{-1}$?

(b) Write a condition under which a bimolecular reaction is kinetically first order. Give an example of such a reaction.

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 5 = 0.6990$)

[5 marks]

Solution:

Concept:

- Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy and T the absolute temperature.
- For two temperatures, $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$, with $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$.
- A bimolecular reaction behaves as pseudo first order when one reactant is in large excess, so its concentration remains effectively constant during the reaction.

Step 1: (a) Convert the temperature and compare rate constants The initial absolute temperature is $T_1 = 27 + 273 = 300 \text{ K}$. Both rate constants have the same units, so their ratio is dimensionless:

$$\frac{k_2}{k_1} = \frac{7.5 \times 10^4}{2.5 \times 10^4} = 3, \quad \log \frac{k_2}{k_1} = 0.4771.$$

Use $E_a = 19.147 \times 10^3 = 19147 \text{ J mol}^{-1}$, keeping the energy unit consistent with the gas constant. Since the rate constant increases and the activation energy is positive, the required temperature must exceed 300 K.

Quick Tip to Solve: Cancel the common powers of ten before using Arrhenius: the rate ratio is 3. Always use kelvin in reciprocal-temperature calculations.

Step 2: Substitute into the two-temperature Arrhenius equation Taking common logarithms of the Arrhenius equation at the two temperatures and subtracting eliminates the unchanged frequency factor:

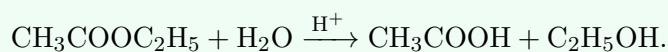
$$0.4771 = \frac{19147}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{T_2} \right).$$

The coefficient is approximately 1000 K. Therefore,

$$\begin{aligned} \frac{1}{T_2} &= \frac{1}{300} - \frac{0.4771}{1000} \\ &= 0.0028562 \text{ K}^{-1}, \\ T_2 &\approx 350.1 \text{ K}. \end{aligned}$$

The corresponding Celsius temperature is $350.1 - 273 \approx 77.1^\circ\text{C}$. This is higher than the initial temperature, as expected.

Step 3: (b) State the condition and explain an example For a bimolecular reaction with rate $r = k[A][B]$, take B in a very large excess. Its consumption makes a negligible fractional change in $[B]$; thus $k' = k[B]$ is effectively constant and $r = k'[A]$. The observed kinetics are first order in the reactant whose concentration changes, although the reaction involves both reactants. Hydrolysis of ethyl acetate in excess water at a fixed acid concentration is an example:



Water is the solvent and is present in a much larger amount than the ester, so its concentration is effectively constant. The measured rate then depends on the first power of the ester concentration. This is called a pseudo first-order reaction.

Step 4: Conclusion (a) The required temperature is approximately 350 K, or 77°C . (b) A bimolecular reaction is kinetically first order when one reactant is in large excess; hydrolysis of ethyl acetate in excess water is an example.

Quick Tip to Solve: Cancel the common powers of ten before using Arrhenius: the rate ratio is 3. Always use kelvin in reciprocal-temperature calculations.

26(a). Predict the main product of the following reactions:

(i) The formyl-substituted cyclohexanone with Tollens' reagent, as shown in the figure.

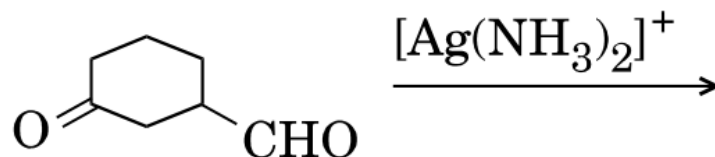
(ii) $\text{CH}_3\text{COCH}_2\text{COOCH}_3$ with (i) NaBH_4 , (ii) H^+ .

(iii) $\text{C}_6\text{H}_5\text{CHO} + \text{CH}_3\text{CHO}$ with dilute NaOH .

(b) Give a simple chemical test to distinguish between $\text{C}_6\text{H}_5\text{COCH}_3$ and $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$.

(c) Why is alpha (α) hydrogen of carbonyl compounds acidic in nature?

[5 marks]



Solution:

Concept:

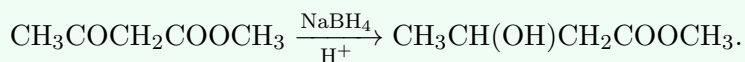
- Tollens' reagent oxidises an aldehyde group to a carboxylate group and is reduced to metallic silver. An ordinary ketone group remains unchanged.
- Sodium borohydride, NaBH_4 , reduces aldehydes and ketones to alcohols but normally leaves an ester group unchanged.
- Aldehydes with alpha hydrogen undergo aldol addition in dilute alkali; dehydration of the beta-hydroxy product gives an alpha,beta-unsaturated carbonyl compound.
- A methyl ketone, RCOCH_3 , gives the iodoform test. Alpha hydrogen is acidic because its removal produces a resonance-stabilised enolate ion.

Step 1: (a)(i) Oxidise only the aldehyde group The drawn molecule has a cyclohexanone ring bearing a $-\text{CHO}$ substituent. Tollens' reagent converts this substituent into $-\text{COO}^-$, while the carbonyl within the ring remains a ketone. Thus the product is 3-oxocyclohexanecarboxylate, conventionally represented as 3-oxocyclohexanecarboxylic acid after acidification. The ring connectivity and the relative positions of the two groups are retained. The balanced ionic reaction for the aldehyde group is



Here R denotes the unchanged ketone-containing ring residue. Silver forms a mirror; oxidation does not convert the ring ketone into an alcohol or carboxyl group.

Step 2: (a)(ii) Reduce the ketone carbonyl The substrate is methyl acetoacetate, $\text{CH}_3\text{COCH}_2\text{COOCH}_3$. Hydride from NaBH_4 attacks the ketone carbonyl; the acid work-up protonates the alkoxide. The ester is not reduced under these conditions:

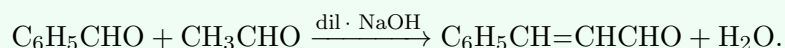


The product is methyl 3-hydroxybutanoate. Only the ketone $\text{C}=\text{O}$ becomes $\text{CH}(\text{OH})$; the terminal COOCH_3 group is retained.

Step 3: (a)(iii) Form the crossed aldol product Benzaldehyde has no alpha hydrogen, while ethanal has alpha hydrogen and forms the enolate in dilute NaOH . The ethanal enolate attacks the benzaldehyde carbonyl, yielding the crossed aldol $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_2\text{CHO}$. This beta-hydroxy aldehyde loses water

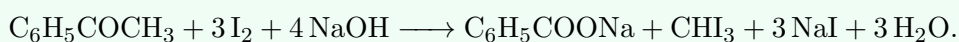
Quick Tip to Solve: Identify each functional group before selecting a product: Tollens oxidises CHO , borohydride reduces the ketone but preserves the ester, and iodoform detects COCH_3 .

readily to give the conjugated main condensation product, cinnamaldehyde:



The remaining aldehyde group belongs to ethanal; the new carbon-carbon bond joins its alpha carbon to the former benzaldehyde carbonyl carbon.

Step 4: (b) Apply the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$, contains the methyl ketone group and produces a yellow precipitate of iodoform, CHI_3 :



Benzophenone, $\text{C}_6\text{H}_5\text{COC}_6\text{H}_5$, has no COCH_3 group and gives no yellow iodoform precipitate. This observation distinguishes the two ketones directly.

Step 5: (c) Explain the acidity of alpha hydrogen An alpha hydrogen is bonded to the carbon adjacent to the carbonyl group. The electron-withdrawing carbonyl group polarises the neighbouring carbon-hydrogen bond. Removal of this hydrogen as a proton leaves an enolate ion whose negative charge is delocalised between the alpha carbon and the electronegative oxygen:



These are resonance contributors of the same ion. Stabilisation of the conjugate base makes proton removal easier than from an ordinary alkane, where the resulting carbanion lacks this carbonyl-assisted delocalisation.

Step 6: Conclusion (a) The products are (i) the carboxylate corresponding to the drawn aldehyde (3-oxocyclohexanecarboxylic acid after acidification), (ii) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOCH}_3$, and (iii) cinnamaldehyde, $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$. (b) Acetophenone gives a yellow iodoform precipitate; benzophenone does not. (c) Alpha hydrogen is acidic because deprotonation gives a resonance-stabilised enolate ion.

Quick Tip to Solve: Identify each functional group before selecting a product: Tollens oxidises CHO, borohydride reduces the ketone but preserves the ester, and iodoform detects COCH_3 .

26(b). (a) Write the main product formed when propanal reacts with the following reagents:

(i) 2 moles of CH_3OH in presence of dry HCl

(ii) Dilute NaOH

(iii) $\text{H}_2\text{N}-\text{NH}_2$ followed by heating with KOH in ethylene glycol

(b) Arrange the following compounds in increasing order of their property as indicated:

(i) $\text{F}-\text{CH}_2\text{COOH}$, $\text{O}_2\text{N}-\text{CH}_2\text{COOH}$, CH_3COOH , HCOOH — acid character

(ii) Acetone, Acetaldehyde, Benzaldehyde, Acetophenone — reactivity towards addition of HCN

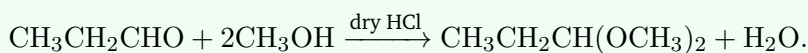
[5 marks]

Solution:

Concept:

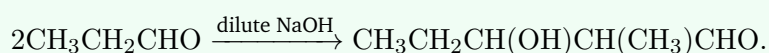
- Aldehydes form acetals with two molecules of an alcohol in an acidic medium. An aldehyde having an alpha hydrogen also undergoes aldol addition in dilute alkali.
- Wolff-Kishner reduction converts the carbonyl group into a methylene group. Electron-withdrawing groups increase carboxylic acid strength by stabilising the carboxylate ion.
- HCN adds by nucleophilic attack on the carbonyl carbon; electron donation, steric hindrance and resonance with an aromatic ring reduce its reactivity.

Step 1: (a)(i) Acetal formation Propanal first forms a hemiacetal, and the second molecule of methanol replaces the hydroxyl group under acid catalysis. The main product is 1,1-dimethoxypropane:



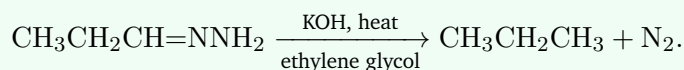
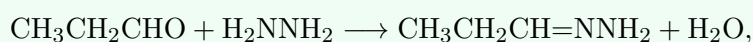
The two methoxy groups are attached to the original carbonyl carbon.

Step 2: (a)(ii) Aldol addition Propanal contains alpha hydrogens. Dilute NaOH produces a small concentration of its enolate, which attacks the carbonyl group of another propanal molecule. Protonation gives the beta-hydroxy aldehyde, 3-hydroxy-2-methylpentanal:



The stated dilute-alkali conditions give the aldol addition product; dehydration requires further heating.

Step 3: (a)(iii) Wolff-Kishner reduction Hydrazine converts propanal into its hydrazone. Heating with KOH in ethylene glycol removes nitrogen and reduces the carbonyl carbon to a methylene group:



Thus the carbon chain is retained and propane is formed.

Step 4: (b)(i) Increasing acid character The methyl group has a positive inductive effect and destabilises the acetate ion compared with formate, so ethanoic acid is weaker than methanoic acid.

Quick Tip to Solve: For propanal's aldol, retain one CHO group and place OH on the carbonyl carbon of the second molecule; count all six carbons before naming the product.

Both fluorine and the nitro group withdraw electrons from the alpha carbon and stabilise the conjugate base. The nitro group has the stronger withdrawing influence in this comparison. Hence:



Step 5: (b)(ii) Increasing reactivity towards HCN addition Ketones are less reactive than corresponding aldehydes because a second carbon substituent supplies electron density and adds steric hindrance. Conjugation with a phenyl ring further lowers carbonyl electrophilicity in aromatic carbonyl compounds. Acetophenone combines both these effects and is least reactive. Acetone is more reactive than acetophenone because it lacks conjugation with a phenyl ring. Benzaldehyde, being an aldehyde with less steric hindrance and only one carbon substituent, is more reactive than acetone in this comparison. Acetaldehyde is most reactive because it is an aliphatic aldehyde without phenyl-ring conjugation. The order is:



Step 6: Conclusion (a) The products are (i) 1,1-dimethoxypropane, (ii) 3-hydroxy-2-methylpentanal and (iii) propane. (b) The increasing acid order is ethanoic acid, methanoic acid, fluoroethanoic acid, nitroethanoic acid. HCN-addition reactivity increases as acetophenone, acetone, benzaldehyde, acetaldehyde.

Quick Tip to Solve: For propanal's aldol, retain one CHO group and place OH on the carbonyl carbon of the second molecule; count all six carbons before naming the product.

27(a). Account for the following:

(i) Manganese shows maximum number of oxidation states in 3d series.

(ii) E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(iii) Ti^{4+} is colourless whereas V^{4+} is coloured in an aqueous solution.

(b) Write the chemical equations for the preparation of KMnO_4 from MnO_2 . Why does purple colour of acidified permanganate solution decolourise when it oxidises Fe^{2+} to Fe^{3+} ? [5 marks]

Solution:

Concept:

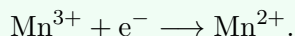
- The small energy difference between the 3d and 4s orbitals allows both sets of electrons to participate in bonding. Especially stable electronic configurations influence reduction potentials.
- Aqueous transition-metal ions show colour when visible light causes transitions between split d orbitals; a d^0 ion cannot undergo a d-d transition.
- Oxidation of manganese dioxide in alkaline medium produces manganate, which is then oxidised to permanganate. In acid, permanganate accepts five electrons to form Mn^{2+} .

Step 1: (a)(i) Oxidation states of manganese Manganese has the electronic configuration $[\text{Ar}]3d^54s^2$. Its five 3d electrons and two 4s electrons can participate in bonding because these subshells have comparable energies. It therefore exhibits oxidation states from +2 to +7, the widest range in the 3d

Quick Tip to Solve: Write the d-electron counts first: $\text{Mn(III)}/\text{Mn(II)}$ is d^4/d^5 , $\text{Cr(III)}/\text{Cr(II)}$ is d^3/d^4 , and $\text{Ti(IV)}/\text{V(IV)}$ is d^0/d^1 ; these directly explain the three observations.

series. In the highest oxidation state all seven valence electrons participate, as in MnO_4^- .

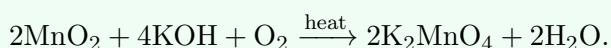
Step 2: (a)(ii) Comparison of reduction potentials Reduction of Mn^{3+} , which is $3d^4$, produces Mn^{2+} , with the particularly stable half-filled $3d^5$ configuration:



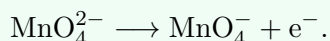
This makes reduction strongly favourable and gives a large positive standard reduction potential. By contrast, Cr^{3+} has a stable $3d^3$ configuration, including a stable t_{2g}^3 arrangement in its aqueous octahedral complex. Reduction gives Cr^{2+} , which is $3d^4$, and loses this stability. Thus E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is much more positive than for $\text{Cr}^{3+}/\text{Cr}^{2+}$.

Step 3: (a)(iii) Colour of the aqueous ions Titanium has configuration $[\text{Ar}]3d^24s^2$, so Ti^{4+} is $3d^0$. It has no d electron available for a d–d transition and its aqueous ion is colourless. Vanadium is $[\text{Ar}]3d^34s^2$, so V^{4+} is $3d^1$. Its d electron can absorb visible light and move between the ligand-field-split d levels; its aqueous species is therefore coloured.

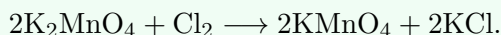
Step 4: (b) Preparation of potassium permanganate Fuse manganese dioxide with potassium hydroxide in the presence of air or oxygen. This oxidises manganese from +4 to +6, giving green potassium manganate:



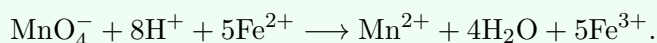
Oxidise manganate electrolytically in alkaline solution. The anode reaction is:



The resulting potassium permanganate is obtained from the solution. A chemical oxidation route is also represented by the balanced equation



Step 5: (b) Decolourisation during oxidation of iron(II) Each Fe^{2+} ion loses one electron to become Fe^{3+} , while one permanganate ion accepts five electrons in acidic solution. Combining the half-reactions gives:



The intensely purple permanganate ion is consumed and forms Mn^{2+} , whose very pale pink colour is effectively invisible in dilute solution. Hence the purple colour disappears while sufficient iron(II) remains. Once iron(II) is exhausted, an excess drop of permanganate gives a persistent pale pink endpoint.

Step 6: Conclusion Mn's seven available valence electrons explain its many oxidation states; stable d^5 Mn^{2+} explains the large positive reduction potential. Ti^{4+} is d^0 and colourless whereas V^{4+} is d^1 and coloured. Alkaline oxidation of MnO_2 gives manganate and further oxidation gives KMnO_4 ; reduction of purple permanganate to Mn^{2+} explains decolourisation by Fe^{2+} .

Quick Tip to Solve: Write the d-electron counts first: Mn(III)/Mn(II) is d^4/d^5 , Cr(III)/Cr(II) is d^3/d^4 , and Ti(IV)/V(IV) is d^0/d^1 ; these directly explain the three observations.

- 27(b). (a) Write one difference between transition elements and p-block elements with reference to variability of oxidation states.
- (b) Why do transition metals exhibit higher enthalpies of atomization?
- (c) Name an element of lanthanoid series which is well known to shown +4 oxidation state. Is it a strong oxidising agent or reducing agent?
- (d) What is lanthanoid contraction? Write its one consequence.
- (e) Write the ionic equation showing the oxidation of Fe(II) salt by acidified dichromate solution.

[5 marks]

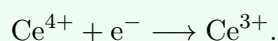
Solution:**Concept:**

- Transition elements can use both $(n - 1)d$ and ns electrons in bonding because their energies are comparable. This permits several oxidation states.
- Enthalpy of atomization is the energy required to form gaseous atoms from the element. Strong metallic bonding produces a high value.
- The poor shielding of nuclear charge by $4f$ electrons causes a gradual decrease in lanthanoid radii. In a redox equation, both atoms and total charge must balance.

Step 1: (a) Compare variability of oxidation states Transition elements commonly show oxidation states differing by one unit, such as Fe^{2+} and Fe^{3+} , because both the outer ns and inner $(n - 1)d$ electrons can participate in bonding. In contrast, the common oxidation states of p-block elements generally differ by two units, for example +3 and +5 for phosphorus. This reflects the involvement or non-involvement of the outer ns^2 electron pair. Thus, successive oxidation states differing by one unit are characteristic of transition elements, whereas a difference of two is common in the p-block.

Step 2: (b) Explain the high enthalpies of atomization Transition metals have strong metallic bonds. A relatively large number of electrons, including unpaired d electrons as well as s electrons, participate in metallic bonding. The resulting strong attraction between metal centres and the bonding electrons requires considerable energy to separate the solid into individual gaseous atoms. Hence, transition metals generally exhibit high enthalpies of atomization; the values vary with the number of electrons available for bonding.

Step 3: (c) Identify the lanthanoid and its oxidising behaviour Cerium, Ce, is well known for the +4 oxidation state. The species Ce^{4+} is a strong oxidising agent because it readily accepts an electron and changes to the more stable, usual lanthanoid oxidation state +3:



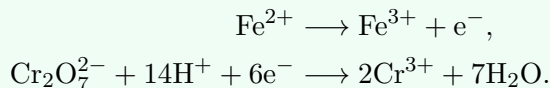
While undergoing reduction itself, Ce^{4+} oxidises the other reactant. The oxidising character refers to cerium in its +4 state.

Step 4: (d) Define lanthanoid contraction and give a consequence Lanthanoid contraction is the gradual decrease in atomic radii and in the ionic radii of Ln^{3+} ions with increasing atomic number across the lanthanoid series. As nuclear charge increases, the added $4f$ electrons shield it poorly, so the effective nuclear attraction increases and the electron cloud contracts. One consequence is the

Quick Tip to Solve: For acidified dichromate, remember that each dichromate ion accepts six electrons, so it oxidises six Fe(II) ions; then check both atoms and charge.

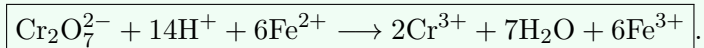
almost equal sizes of zirconium and hafnium: the contraction preceding hafnium offsets the expected size increase from an additional shell. Consequently, Zr and Hf have very similar chemical properties and are difficult to separate.

Step 5: (e) Balance oxidation of Fe(II) by acidified dichromate Iron(II) loses one electron per ion, while one dichromate ion accepts six electrons in acidic solution:



Multiply the iron half-reaction by six and add, cancelling the electrons. There are two Cr atoms, seven O atoms and fourteen H atoms on each side. The total charge is +24 on each side, which verifies the ionic equation.

Step 6: Conclusion (a) Transition-element oxidation states commonly differ by one unit; common p-block states differ by two. (b) Strong metallic bonding gives high atomization enthalpies. (c) Cerium exhibits +4, and Ce^{4+} is a strong oxidising agent. (d) Lanthanoid contraction is the gradual decrease in radii across the series; it makes Zr and Hf almost equal in size. (e) The required equation is



Quick Tip to Solve: For acidified dichromate, remember that each dichromate ion accepts six electrons, so it oxidises six Fe(II) ions; then check both atoms and charge.