

CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-2

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) Questions number 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Questions number 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Questions number 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Question number 23 is a value based question and carries 4 marks.
- (vi) Questions number 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables, if necessary. Use of calculators is not allowed.

1. What is the effect of adding a catalyst on

(a) Activation energy (E_a), and

(b) Gibbs energy (ΔG) of a reaction?

[1 mark]

Solution:

Concept:

- Activation energy E_a is the energy barrier between reactants and the transition state; a catalyst supplies an alternative pathway with a lower barrier.
- The reaction Gibbs energy is $\Delta G = G_{\text{products}} - G_{\text{reactants}}$; it depends on the initial and final states, not on the pathway.

Step 1: (a) Compare the activation barriers Adding a catalyst changes the reaction mechanism to one having a lower activation-energy barrier. A greater fraction of reacting molecules can therefore react at the same temperature, so the reaction becomes faster.

Step 2: (b) Compare the initial and final states The catalyst does not change the Gibbs energies of the reactants or products. Hence their difference remains the same. It speeds up approach to equilibrium but changes neither the equilibrium constant nor the thermodynamic feasibility of the reaction.

Step 3: Conclusion (a) Activation energy E_a decreases. (b) The Gibbs energy change ΔG remains unchanged.

Quick Tip to Solve: For a catalyst, distinguish the kinetic barrier from the thermodynamic end-point difference: only the barrier falls.

2. What type of colloid is formed when a solid is dispersed in a liquid? Give an example.

[1 mark]

Solution:

Concept:

- A colloid is classified using the physical states of its dispersed phase and dispersion medium.
- A sol has solid colloidal particles dispersed throughout a liquid medium.

Step 1: Identify the two phases The question gives solid as the dispersed phase and liquid as the dispersion medium. This combination is called a sol. It is different from an emulsion, in which both phases are liquids, and a gel, in which a liquid is dispersed in a solid.

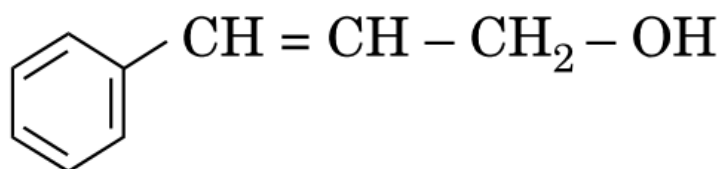
Step 2: Give an example Gold sol is a suitable example: very small solid gold particles form the dispersed phase, while water forms the liquid dispersion medium. The dispersed particles are colloidal rather than individual dissolved gold atoms or ions.

Step 3: Conclusion The colloid is a **sol**; an example is gold sol (solid gold dispersed in water).

Quick Tip to Solve: Read the dispersed phase first: solid in liquid means sol; liquid in solid means gel.

3. Write the IUPAC name of the following compound:

[1 mark]



Solution:

Concept:

- The alcohol group is the principal functional group and determines the suffix and the direction of numbering.
- Choose the three-carbon unsaturated chain containing OH ; the benzene ring is a phenyl substituent on this chain.

Step 1: Choose and number the parent chain The displayed structure is $\text{C}_6\text{H}_5\text{—CH=CH—CH}_2\text{OH}$. Number the three-carbon chain from the CH_2OH end, so the hydroxyl group has locant 1. The double bond then lies between carbons 2 and 3, giving the parent name prop-2-en-1-ol.

Step 2: Locate the ring substituent The phenyl group $\text{C}_6\text{H}_5\text{—}$ is attached to carbon 3 of the numbered parent chain. Place its locant and name before the parent name. The ring is aromatic, so the substituent is phenyl, not cyclohexyl; no double-bond stereodescriptor is specified by this drawing.

Step 3: Conclusion The IUPAC name is **3-phenylprop-2-en-1-ol**.

Quick Tip to Solve: Number from the alcohol end before locating the double bond: OH is at 1, the double bond at 2 and phenyl at 3.

4. Write the formula of the compound of sulphur which is obtained when conc. HNO_3 oxidises S_8 .

[1 mark]

Solution:

Concept:

- Concentrated nitric acid is a strong oxidising agent and oxidises elemental sulphur to sulphuric acid.
- Sulphur changes from oxidation state 0 in S_8 to +6 in H_2SO_4 .

Step 1: Identify the oxidation product On treatment with concentrated HNO_3 , sulphur is oxidised to its higher oxidation state, +6. The sulphur-containing product is sulphuric acid, rather than sulphurous acid, in which sulphur would have oxidation state +4.

Step 2: Confirm the product with the reaction The balanced overall reaction is



Nitric acid is reduced to nitrogen dioxide while sulphur is oxidised. The equation conserves sulphur, nitrogen, hydrogen and oxygen atoms.

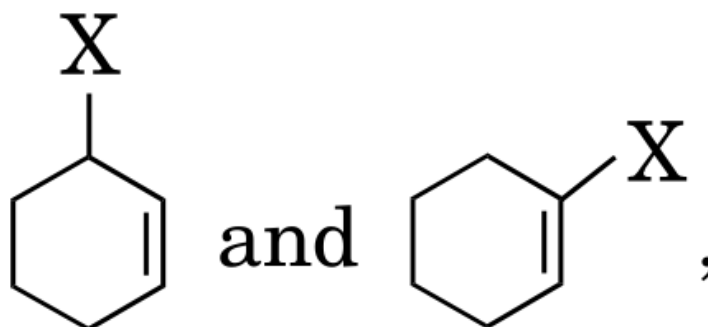
Quick Tip to Solve: With concentrated nitric acid, take sulphur to its +6 oxidation state: the product is sulphuric acid.

Step 3: Conclusion The formula of the sulphur compound is H_2SO_4 (sulphuric acid).

Quick Tip to Solve: With concentrated nitric acid, take sulphur to its +6 oxidation state: the product is sulphuric acid.

5. Out of the two compounds shown below, which is an example of a vinylic halide?

[1 mark]



Solution:

Concept:

- A vinylic halide has its halogen directly bonded to an sp^2 -hybridised carbon of a carbon-carbon double bond.
- An allylic halide has the halogen bonded to an sp^3 -hybridised carbon adjacent to the double bond.

Step 1: Examine the first compound In the first, left-hand ring, the carbon bearing X is the saturated carbon immediately next to the double bond. It is not one of the two doubly bonded carbon atoms. The compound is therefore an allylic halide, rather than a vinylic halide.

Step 2: Examine the second compound In the second, right-hand ring, X is directly bonded to the upper carbon of the drawn double bond. This carbon is sp^2 -hybridised, and the carbon-halogen bond is directly attached to the alkene unit, satisfying the definition of a vinylic halide.

Step 3: Conclusion The **second (right-hand) compound** is the vinylic halide.

Quick Tip to Solve: Locate the carbon actually bonded to X : on the double bond means vinylic; beside it means allylic.

6. Using IUPAC norms write the formulae for the following:

(a) Tris(ethane-1,2-diamine)chromium(III) chloride

(b) Potassium tetrahydroxozincate(II)

[2 marks]

Solution:

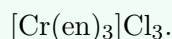
Concept:

- In a complex, add the oxidation state of the metal to the charges of its ligands to obtain the complex-ion charge.

Quick Tip to Solve: Neutral en leaves chromium at charge +3; four hydroxido ligands turn zinc(II) into a 2-complex. Then balance counterions.

- Ethane-1,2-diamine, denoted en, is a neutral bidentate ligand; each hydroxido ligand OH^- carries charge -1.
- Write the coordination entity inside square brackets and add enough counterions outside the brackets to make the complete salt electrically neutral.

Step 1: (a) Form the chromium coordination entity Tris specifies three ethane-1,2-diamine ligands. As each ligand is neutral and chromium is in oxidation state +3, the complex is $[\text{Cr}(\text{en})_3]^{3+}$. Three chloride counterions, each carrying charge -1, are needed outside the coordination sphere. Hence the formula is

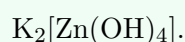


The three bidentate ligands provide six donor nitrogen atoms; chloride is a counterion, not a ligand inside the brackets.

Step 2: (b) Balance the zincate ion with potassium Tetrahydroxo specifies four OH^- ligands, and zinc(II) has oxidation state +2. The charge on the coordination entity is therefore

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

Two potassium ions K^+ balance the anion $[\text{Zn}(\text{OH})_4]^{2-}$. Hence the complete formula is



Step 3: Conclusion (a) $[\text{Cr}(\text{en})_3]\text{Cl}_3$, where en is ethane-1,2-diamine. (b) $\text{K}_2[\text{Zn}(\text{OH})_4]$.

Quick Tip to Solve: Neutral en leaves chromium at charge +3; four hydroxido ligands turn zinc(II) into a 2-complex. Then balance counterions.

7. Draw the structures of the following:

(a) $\text{H}_2\text{S}_2\text{O}_8$

(b) ClF_3

[2 marks]

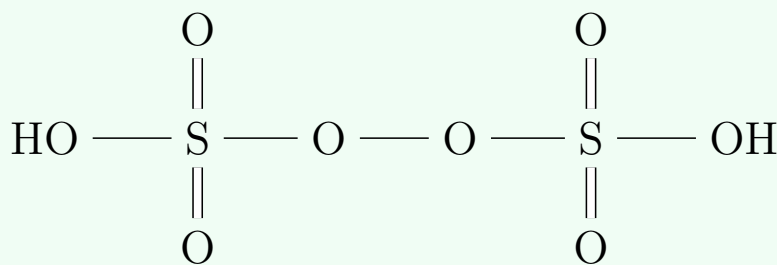
Solution:

Concept:

- Peroxodisulphuric acid, $\text{H}_2\text{S}_2\text{O}_8$, contains a peroxide linkage $-\text{O}-\text{O}-$ joining two sulphur-containing groups.
- VSEPR theory predicts the shape from bonding pairs and lone pairs around the central atom. In ClF_3 , chlorine has three bonding pairs and two lone pairs.

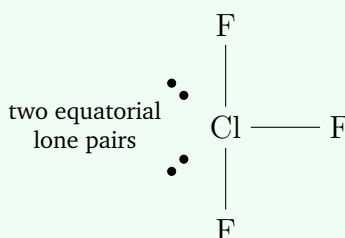
Step 1: (a) Draw peroxodisulphuric acid Each sulphur atom is bonded to two terminal oxygen atoms by double bonds, to one hydroxyl group and to one oxygen of the peroxide bridge. Thus its structural formula is $\text{HO}-\text{S}(=\text{O})_2-\text{O}-\text{O}-\text{S}(=\text{O})_2-\text{OH}$. The drawing shows all eight oxygen atoms: four terminal oxo oxygens, two hydroxyl oxygens and the two oxygens of the bridge. The acidic hydrogen atoms are attached to oxygen, not sulphur.

Quick Tip to Solve: Count eight oxygen atoms in the acid; for ClF_3 place both lone pairs equatorially before drawing the three Cl-F bonds.



(a) Peroxodisulphuric acid: the central O-O bond is the peroxide linkage.

Step 2: (b) Draw chlorine trifluoride Chlorine has seven valence electrons. Formation of three Cl – F bonds leaves two lone pairs on chlorine, giving five electron-pair domains. Their electron-pair arrangement is trigonal bipyramidal, conventionally described by sp^3d hybridisation. Both lone pairs occupy equatorial positions to minimise repulsion. The remaining three fluorine atoms therefore give a T-shaped molecule, with two axial fluorines and one equatorial fluorine.



(b) T-shaped ClF_3 ; the pairs of dots represent equatorial lone pairs.

Step 3: Conclusion $\text{H}_2\text{S}_2\text{O}_8$ has the peroxide-bridged structure shown above; ClF_3 is T-shaped with two equatorial lone pairs on chlorine.

Quick Tip to Solve: Count eight oxygen atoms in the acid; for ClF_3 place both lone pairs equatorially before drawing the three Cl-F bonds.

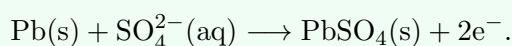
8. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell. [2 marks]

Solution:

Concept:

- A lead storage battery is a rechargeable secondary cell. During discharge, chemical energy is converted into electrical energy.
- Oxidation occurs at the anode and reduction at the cathode. Dilute sulphuric acid supplies the H^+ and SO_4^{2-} ions involved in the electrode reactions.

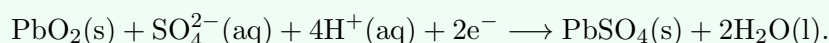
Step 1: Identify the cell and write the anode reaction The cell generally used in inverters is the lead storage cell (lead-acid battery). During discharge, the lead electrode acts as the anode. Lead is oxidised from oxidation state zero to +2, releasing two electrons and forming lead sulphate:



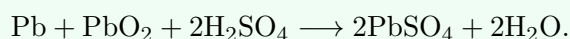
Quick Tip to Solve: For discharge, remember Pb loses two electrons and PbO_2 gains two; both electrodes form PbSO_4 .

This electrode supplies the electrons that flow through the external circuit.

Step 2: Write the cathode reaction during discharge The lead dioxide electrode acts as the cathode. Lead in PbO_2 is reduced from +4 to +2. It consumes the electrons delivered by the external circuit:



Adding the two half-reactions cancels the electrons and gives



Both electrodes become coated with lead sulphate as the cell discharges; the reactions reverse on charging.

Step 3: Conclusion The inverter uses a lead storage battery. Its discharge anode reaction is oxidation of Pb to PbSO_4 , and its cathode reaction is reduction of PbO_2 to PbSO_4 , as balanced above.

Quick Tip to Solve: For discharge, remember Pb loses two electrons and PbO_2 gains two; both electrodes form PbSO_4 .

9. Calculate the number of unit cells in 8.1 g of aluminium if it crystallizes in a face-centred cubic (f.c.c.) structure. (Atomic mass of Al = 27 g mol⁻¹) [2 marks]

Solution:

Concept:

- The amount of substance is $n = m/M$, where m is the sample mass and M is its molar mass. The number of atoms is $N = nN_A$, with $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$.
- A face-centred cubic unit cell contains $Z = 4$ atoms. Hence the number of unit cells is the total number of atoms divided by four.

Step 1: Count the atoms contributed to one f.c.c. unit cell A corner atom is shared by eight neighbouring unit cells, so the eight corners together contribute $8 \times \frac{1}{8} = 1$ atom. A face-centred atom is shared by two cells, so the six faces together contribute $6 \times \frac{1}{2} = 3$ atoms. Therefore

$$Z = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4.$$

We must divide the atom count by this number, because four aluminium atoms belong to each complete unit cell.

Step 2: Convert the sample mass to the number of unit cells Using the given atomic molar mass,

$$n = \frac{8.1 \text{ g}}{27 \text{ g mol}^{-1}} = 0.30 \text{ mol}.$$

The total number of aluminium atoms is

$$N = 0.30 \times 6.022 \times 10^{23} = 1.8066 \times 10^{23}.$$

Quick Tip to Solve: Use $N_{\text{cells}} = m N_A / (4M)$ directly for an f.c.c. solid; do not multiply the atom count by four.

Thus the number of unit cells is

$$N_{\text{cells}} = \frac{N}{Z} = \frac{1.8066 \times 10^{23}}{4} = 4.5165 \times 10^{22}.$$

The result is a count, so it has no physical unit. It is smaller than the atom count by the factor four.

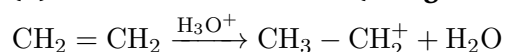
Step 3: Conclusion The sample contains approximately 4.52×10^{22} f.c.c. unit cells (or 4.5×10^{22} to two significant figures).

Quick Tip to Solve: Use $N_{\text{cells}} = m \text{ NA} / (4M)$ directly for an f.c.c. solid; do not multiply the atom count by four.

10(a). Arrange the following compounds in the increasing order of their acid strength:

p-cresol, p-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction:



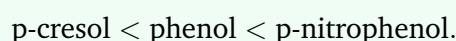
[2 marks]

Solution:

Concept:

- The acid strength of a phenol increases when its conjugate base, the phenoxide ion, is stabilised by an electron-withdrawing substituent.
- A curved arrow starts at an electron pair and ends where that pair forms a bond or becomes a lone pair. An alkene pi bond supplies electrons to an electrophile such as a proton.

Step 1: (a) Compare the stability of the conjugate bases The para-methyl group of p-cresol donates electron density by its +I effect and hyperconjugation, making its phenoxide ion less stable than that from phenol. The para-nitro group withdraws electron density by both -I and resonance effects. It stabilises the negative charge of p-nitrophenoxide, so p-nitrophenol releases a proton most readily. The increasing order of acid strength is therefore

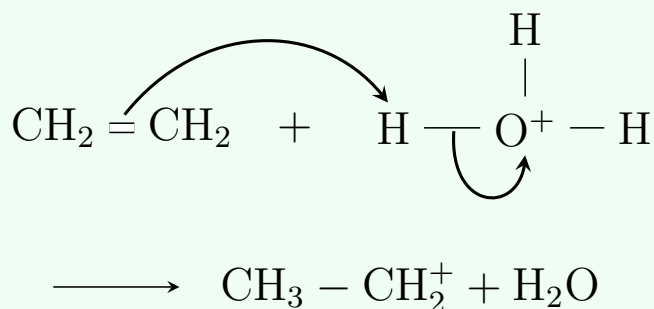


Step 2: (b) Show the electron flow in protonation of ethene In the printed reaction, ethene reacts with hydronium ion to form the ethyl carbocation and water. Draw one curved arrow from the alkene pi bond to a hydrogen atom of H_3O^+ . Simultaneously draw a second curved arrow from that O-H bond back to oxygen. The first arrow forms a C-H bond; the second breaks the O-H bond and gives water. The other alkene carbon is left electron deficient, carrying the positive charge:



Since ethene is symmetrical, protonation at either end gives the same carbocation.

Quick Tip to Solve: For acidity compare conjugate-base stability; in protonation start the curved arrows at the pi bond and the O-H bond.



Curved-arrow mechanism for formation of the ethyl carbocation.

Step 3: Conclusion (a) p-cresol < phenol < p-nitrophenol. (b) The alkene pi electrons form a C-H bond while the hydronium O-H bond electrons return to oxygen, producing $\text{CH}_3 - \text{CH}_2^+$ and H_2O .

Quick Tip to Solve: For acidity compare conjugate-base stability; in protonation start the curved arrows at the pi bond and the O-H bond.

OR

10(b). Write the structures of the products when Butan-2-ol reacts with the following:

(a) CrO_3

(b) SOCl_2

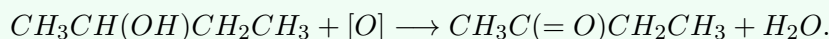
[2 marks]

Solution:

Concept:

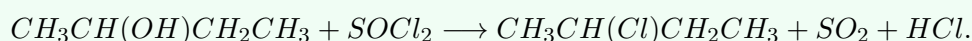
- Butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, is a secondary alcohol: its hydroxyl-bearing carbon is attached to two carbon groups.
- Oxidation of a secondary alcohol gives a ketone. Thionyl chloride, SOCl_2 , replaces the hydroxyl group by chlorine without changing the carbon skeleton.

Step 1: (a) Reaction with chromium trioxide CrO_3 is an oxidising agent. The carbon bearing the hydroxyl group loses its hydrogen, while the oxygen becomes part of a carbonyl group. Thus the carbonyl carbon stays at position 2 in the four-carbon chain:



The product structure is $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_3$, called butan-2-one. A secondary alcohol forms a ketone, rather than the aldehyde obtained from a primary alcohol.

Step 2: (b) Reaction with thionyl chloride Here the hydroxyl group at carbon 2 is replaced by chlorine. The balanced reaction is



The required product structure is $\text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$, called 2-chlorobutane. Sulphur dioxide and

Quick Tip to Solve: Mark carbon 2 first: oxidation changes its $\text{CH}(\text{OH})$ group to $\text{C}(=\text{O})$, whereas SOCl_2 changes it to $\text{CH}(\text{Cl})$.

hydrogen chloride are gaseous by-products; the carbon chain remains intact.

Step 3: Conclusion (a) CrO_3 : butan-2-one, $CH_3C(=O)CH_2CH_3$.

(b) $SOCl_2$: 2-chlorobutane, $CH_3CH(Cl)CH_2CH_3$.

Quick Tip to Solve: Mark carbon 2 first: oxidation changes its $CH(OH)$ group to $C(=O)$, whereas $SOCl_2$ changes it to $CH(Cl)$.

11. (a) Write the principle of vapour phase refining.

(b) Write the role of dilute $NaCN$ in the extraction of silver.

(c) What is the role of collectors in the froth floatation process? Give an example of a collector.

[3 marks]

Solution:

Concept:

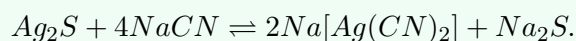
- Refining separates a metal from impurities by exploiting a difference in their chemical or physical behaviour.
- Cyanide leaching selectively dissolves silver through formation of a soluble coordination complex, $[Ag(CN)_2]^-$.
- Froth floatation separates sulphide ore particles from gangue by making the ore surface preferentially wetted by oil and attached to air bubbles.

Step 1: (a) Principle of vapour phase refining Convert the impure metal into a volatile compound by reacting it with a suitable reagent. Separate this volatile compound from the non-volatile impurities and then decompose it to obtain pure metal. The essential conditions are that the metal readily forms a volatile compound and that this compound decomposes easily to regenerate the metal. For example, in the Mond process nickel forms volatile nickel tetracarbonyl:



Heating the separated vapour at a higher temperature decomposes it into pure nickel and carbon monoxide.

Step 2: (b) Role of dilute sodium cyanide Dilute $NaCN$ acts as the leaching agent. It dissolves silver from its ore by forming the soluble dicyanidoargentate(I) complex. For silver sulphide, the complex-forming step is



Thus silver enters the aqueous solution as $[Ag(CN)_2]^-$, while insoluble gangue is removed by filtration. Silver is subsequently recovered from the complex solution, for example by displacement with zinc. Cyanide therefore helps extract silver by selective complex formation, rather than serving as the metal deposited at this stage.

Step 3: (c) Role and example of a collector Collectors increase the non-wettability of sulphide ore particles by water. Their adsorption makes the ore surface water-repelling, so the particles attach to

Quick Tip to Solve: Link each reagent to its purpose: volatile compound for refining, soluble cyanide complex for leaching, and a water-repelling ore surface for floatation.

air bubbles and rise with the froth, whereas water-wetted gangue remains behind. A suitable example is a xanthate, such as potassium ethyl xanthate, $C_2H_5OCS_2K$. Collectors promote attachment of ore to bubbles; the production and stabilisation of the froth are separate functions.

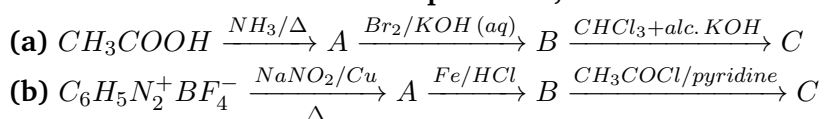
Step 4: Conclusion (a) Form, separate and decompose a volatile metal compound to obtain pure metal.

(b) Dilute $NaCN$ leaches silver as soluble $[Ag(CN)_2]^-$.

(c) Collectors make sulphide ore particles less wettable by water; potassium ethyl xanthate is an example.

Quick Tip to Solve: Link each reagent to its purpose: volatile compound for refining, soluble cyanide complex for leaching, and a water-repelling ore surface for flotation.

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



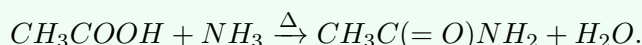
[3 marks]

Solution:

Concept:

- Heating a carboxylic acid with ammonia produces an amide. Hofmann bromamide degradation converts $RCONH_2$ to RNH_2 , removing the carbonyl carbon.
- A primary amine reacts with chloroform and alcoholic potassium hydroxide to form an isocyanide, $R-N \equiv C$, in the carbylamine reaction.
- Replacement of the diazonium group by $-NO_2$, reduction of $-NO_2$ to $-NH_2$, and acylation of the amino group identify the compounds in the second sequence.

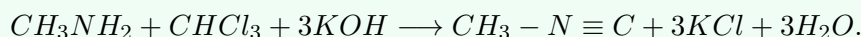
Step 1: (a) Identify A, B and C from ethanoic acid Ethanoic acid first forms ammonium ethanoate with ammonia. On heating, this salt loses water to give ethanamide (acetamide):



Hence $A = CH_3C(=O)NH_2$. With Br_2 and aqueous KOH , the amide undergoes Hofmann degradation. Removal of the carbonyl carbon gives methylamine:



Thus $B = CH_3NH_2$, methanamine (methylamine). This primary amine undergoes the carbylamine reaction:



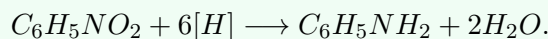
Therefore $C = CH_3-N \equiv C$, methyl isocyanide. It has a methyl-to-nitrogen bond, unlike the nitrile $CH_3-C \equiv N$.

Step 2: (b) Identify A, B and C from the diazonium salt Heating benzenediazonium tetrafluoroborate with $NaNO_2$ in the presence of copper replaces the diazonium group by a nitro group. Therefore

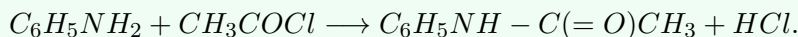
Quick Tip to Solve: Count carbons in the Hofmann step and check which atom bonds to methyl in the carbylamine product: the final linkage is $CH_3-N \equiv C$.

$A = C_6H_5NO_2$, nitrobenzene.

Iron and hydrochloric acid reduce the nitro group to an amino group:



Thus $B = C_6H_5NH_2$, aniline. Ethanoyl chloride in pyridine acylates the amino group:



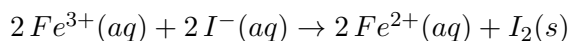
Pyridine takes up the hydrogen chloride. Hence $C = C_6H_5NH - C(=O)CH_3$, acetanilide.

Step 3: Conclusion (a) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3 - N \equiv C$.

(b) $A = C_6H_5NO_2$, $B = C_6H_5NH_2$, $C = C_6H_5NHCOCH_3$.

Quick Tip to Solve: Count carbons in the Hofmann step and check which atom bonds to methyl in the carbylamine product: the final linkage is $CH_3 - N \equiv C$.

13. (a) A cell in which the following reaction occurs:



has $E_{cell}^{\circ} = 0.236$ V at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given: $1 F = 96,500$ C mol⁻¹)

(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: $1 F = 96,500$ C mol⁻¹) [3 marks]

Solution:

Concept:

- Standard Gibbs energy and cell potential are related by $\Delta_r G^{\circ} = -nFE_{cell}^{\circ}$, where n is the number of moles of electrons transferred per mole of the reaction as written and F is the Faraday constant.
- A current I flowing for time t carries charge $Q = It$. Since one mole of electrons carries charge F , the number of electrons is $N = (Q/F)N_A$, where $N_A = 6.022 \times 10^{23}$ mol⁻¹.

Step 1: (a) Identify the electron transfer The reduction half-reaction is $2Fe^{3+} + 2e^{-} \rightarrow 2Fe^{2+}$. The oxidation half-reaction is $2I^{-} \rightarrow I_2 + 2e^{-}$. Thus the balanced overall reaction transfers two electrons, so $n = 2$. The electron number is taken from the reaction as written; it is not the total number of ions present.

Step 2: (a) Substitute in the Gibbs energy relation At 298 K, use the given standard cell potential and Faraday constant:

$$\begin{aligned}\Delta_r G^{\circ} &= -(2)(96500)(0.236) \text{ J mol}^{-1} \\ &= -45548 \text{ J mol}^{-1} \\ &= -45.548 \text{ kJ mol}^{-1}.\end{aligned}$$

Here $C \times V = J$. The negative sign is consistent with the positive standard cell potential and indicates a spontaneous cell reaction under standard conditions.

Step 3: (b) Calculate charge and convert it into electrons Express time in seconds before using

Quick Tip to Solve: Count electrons from balanced half-reactions for Gibbs energy, and always convert hours to seconds before calculating charge from amperes.

current in amperes: $t = 2 \times 60 \times 60 = 7200$ s. Then

$$\begin{aligned}Q &= It = (0.5)(7200) = 3600 \text{ C}, \\n(e^-) &= \frac{3600}{96500} = 0.03731 \text{ mol}, \\N &= \frac{3600}{96500}(6.022 \times 10^{23}) \\&\approx 2.25 \times 10^{22} \text{ electrons}.\end{aligned}$$

The Faraday constant converts charge to moles of electrons; multiplication by Avogadro's constant converts those moles to the actual number of electrons.

Step 4: Conclusion (a) $\Delta_r G^\circ = -45.548 \text{ kJ mol}^{-1}$ for the reaction as written.

(b) $N \approx 2.25 \times 10^{22}$ electrons flow through the wire.

Quick Tip to Solve: Count electrons from balanced half-reactions for Gibbs energy, and always convert hours to seconds before calculating charge from amperes.

14. Give reasons for the following:

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.

(c) Although $-\text{NH}_2$ is o/p directing group, yet aniline on nitration gives a significant amount of m-nitroaniline. [3 marks]

Solution:

Concept:

- The availability of the nitrogen lone pair controls both the basicity of an amine and its ability to donate electron density to an aromatic ring by resonance.
- An electron-donating +I alkyl group increases electron density on nitrogen, whereas delocalisation of its lone pair reduces its availability for accepting a proton.
- Electrophilic substitution depends on the substituent present under the reaction conditions. Strong acid can convert an amino group into an anilinium group with different directing behaviour.

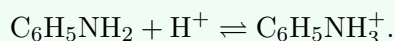
Step 1: (a) Effect of acetylation on ring activation Acetylation converts aniline, $\text{C}_6\text{H}_5\text{NH}_2$, into acetanilide, $\text{C}_6\text{H}_5\text{NHCOCH}_3$. In aniline the nitrogen lone pair is readily donated into the benzene ring, strongly increasing its electron density and activating it towards electrophilic substitution. In acetanilide the same lone pair is also delocalised towards the carbonyl group of the acetyl substituent. It is therefore less available for donation into the ring. Consequently $-\text{NHCOCH}_3$ activates the ring less strongly than $-\text{NH}_2$, although it still directs substitution to the ortho and para positions.

Step 2: (b) Compare methylamine and aniline In methylamine, CH_3NH_2 , the methyl group exhibits the electron-releasing +I effect, increasing electron density on nitrogen. The nitrogen lone pair is localised and available to bind H^+ . In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, this lone pair is delocalised into the benzene ring by resonance and is less available for protonation. The phenyl group also has an electron-withdrawing inductive effect. Thus methylamine accepts a proton more readily and is more

Quick Tip to Solve: First identify whether nitrogen's lone pair is localised, resonance-delocalised, or consumed in protonation; this resolves all three comparisons.

basic than aniline.

Step 3: (c) Explain meta substitution during nitration The nitrating mixture contains concentrated nitric acid and concentrated sulphuric acid. In this strongly acidic medium, aniline is protonated:



The anilinium group $-\text{NH}_3^+$ has no nitrogen lone pair available for donation into the ring and strongly withdraws electron density. It is a deactivating, meta-directing group. Nitration of this protonated form therefore produces a significant amount of meta-nitroaniline after work-up. The directing effect of free $-\text{NH}_2$ alone cannot predict the product mixture in this acidic medium.

Step 4: Conclusion (a) Acetylation reduces lone-pair donation to the ring through competition with the carbonyl group. (b) The localised lone pair and methyl $+I$ effect make methylamine more basic. (c) Protonation produces the meta-directing anilinium ion during nitration.

Quick Tip to Solve: First identify whether nitrogen's lone pair is localised, resonance-delocalised, or consumed in protonation; this resolves all three comparisons.

15. Give reasons for the following:

- (a) Red phosphorus is less reactive than white phosphorus.
- (b) Electron gain enthalpies of halogens are largely negative.
- (c) N_2O_5 is more acidic than N_2O_3 .

[3 marks]

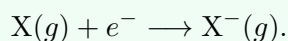
Solution:

Concept:

- The reactivity of an allotrope depends on its structure and stability: highly strained bonding generally makes a structure more reactive.
- Electron gain enthalpy is the enthalpy change for addition of an electron to an isolated gaseous atom. A negative value means that the process releases energy.
- For oxides of the same non-metal, acidic character generally increases as the oxidation state of the central element increases. Their corresponding oxyacids help explain this comparison.

Step 1: (a) Compare the structures of phosphorus allotropes White phosphorus consists of discrete tetrahedral P_4 molecules. The $\text{P}-\text{P}-\text{P}$ bond angles are only 60° , producing considerable angular strain in the molecule. This strained structure is relatively unstable and reacts readily. Red phosphorus has a polymeric structure in which linked phosphorus units form a more stable extended arrangement. Its bonding has much less angular strain than the discrete tetrahedra of white phosphorus. Consequently red phosphorus is less reactive than white phosphorus.

Step 2: (b) Explain electron gain by halogens Halogens have the valence-shell configuration ns^2np^5 . Addition of just one electron completes their outer shell, giving the stable noble-gas configuration ns^2np^6 :

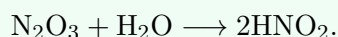
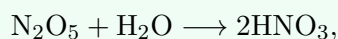


Their high effective nuclear attraction and strong tendency to complete the octet make electron

Quick Tip to Solve: For two oxides of the same non-metal, compare the central atom's oxidation states and write their corresponding acids before judging acidity.

addition strongly favourable. A large amount of energy is generally released in this process, so their electron gain enthalpies are largely negative. The negative sign refers to energy released on electron addition; it does not mean that energy must be supplied.

Step 3: (c) Compare the acidic character of the nitrogen oxides In N_2O_5 , nitrogen has oxidation state +5, whereas in N_2O_3 it has oxidation state +3. The oxide with nitrogen in the higher oxidation state shows stronger acidic character. The corresponding reactions with water are



Nitric acid is stronger than nitrous acid. The extra oxygen in nitric acid strengthens electron withdrawal and its conjugate base has greater stabilisation. Thus N_2O_5 , the anhydride of nitric acid, is more acidic than N_2O_3 , the anhydride of nitrous acid.

Step 4: Conclusion (a) Red phosphorus has a more stable, less strained polymeric structure. (b) Halogens release substantial energy on gaining an electron to complete their octet. (c) The higher nitrogen oxidation state and formation of the stronger acid make N_2O_5 more acidic.

Quick Tip to Solve: For two oxides of the same non-metal, compare the central atom's oxidation states and write their corresponding acids before judging acidity.

16. Define the following:

(a) Anionic detergents

(b) Narrow spectrum antibiotics

(c) Antacids

[3 marks]

Solution:

Concept:

- Detergents are cleansing agents with a long hydrophobic hydrocarbon chain and a hydrophilic head; classification as anionic depends on the charge of the active cleansing ion.
- The spectrum of an antibiotic is the range of bacteria against which it is effective. Antacids instead act chemically to neutralise excess stomach acid.

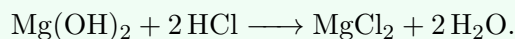
Step 1: Define anionic detergents (a) Anionic detergents are detergents in which the negatively charged ion is responsible for cleansing action. They are commonly sodium salts of long-chain alkyl hydrogen sulphates or alkylbenzene sulphonic acids. For example, sodium lauryl sulphate is $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$; its active ion is $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-$. The hydrocarbon chain interacts with grease while the charged head interacts with water, allowing the grease to be washed away.

Step 2: Define narrow spectrum antibiotics (b) Narrow spectrum antibiotics are antibiotics effective against a limited range of bacteria, typically either Gram-positive or Gram-negative bacteria, rather than both groups. Penicillin G is a standard example. Here, narrow spectrum describes the restricted range of susceptible bacteria, not the amount or strength of the antibiotic administered.

Step 3: Define antacids (c) Antacids are substances that neutralise excess hydrochloric acid in the

Quick Tip to Solve: For these definitions, identify the active ion's charge, the antibiotic's bacterial range, and the antacid's acid-neutralising action, respectively.

stomach and relieve acidity. Mild bases such as magnesium hydroxide and aluminium hydroxide are used as antacids. Their action can be illustrated by



Neutralisation reduces excess acidity without requiring complete removal of the acid needed for digestion.

Step 4: Conclusion Anionic detergents cleanse through a negatively charged active ion; narrow spectrum antibiotics act against a limited range of bacteria; antacids neutralise excess stomach acid.

Quick Tip to Solve: For these definitions, identify the active ion's charge, the antibiotic's bacterial range, and the antacid's acid-neutralising action, respectively.

17. Write the structures of the monomers used for getting the following polymers:

(a) Polyvinyl chloride (PVC)

(b) Melamine-formaldehyde polymer

(c) Buna-N

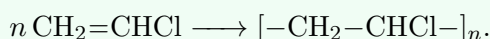
[3 marks]

Solution:

Concept:

- Addition polymerisation joins unsaturated monomers without eliminating small molecules. PVC uses one monomer; Buna-N uses two different monomers.
- Melamine-formaldehyde is a condensation polymer made from melamine and formaldehyde. Its monomers have functional groups that form cross-links.

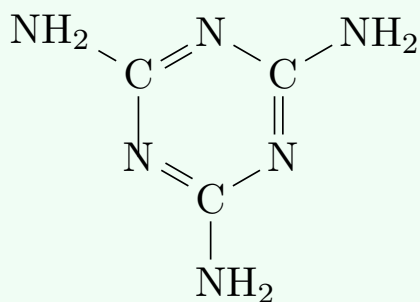
Step 1: Identify the monomer of PVC (a) The monomer is vinyl chloride, also called chloroethene. Its structure is $\text{CH}_2=\text{CHCl}$. Its double bond opens during addition polymerisation:



The monomer is unsaturated; the repeating unit is saturated.

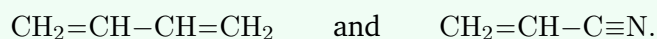
Step 2: Give both monomers of melamine-formaldehyde polymer (b) The monomers are melamine (2,4,6-triamino-1,3,5-triazine) and formaldehyde (methanal). Melamine has an alternating carbon-nitrogen six-membered ring, with one NH_2 group on each of its three carbon atoms. Its structural formula is shown below. Formaldehyde has the structure $\text{H}-\text{C}(=\text{O})-\text{H}$. Its amino groups react with formaldehyde to produce a cross-linked thermosetting polymer.

Quick Tip to Solve: Restore the double bond to identify an addition monomer; remember that the N in Buna-N points to the nitrile-containing monomer acrylonitrile.



Structure of melamine

Step 3: Give both monomers of Buna-N (c) Buna-N is formed by copolymerisation of buta-1,3-diene and acrylonitrile (prop-2-enenitrile). Their structures are, respectively,



Their carbon-carbon double bonds participate in polymerisation, while the nitrile group remains attached to the chain.

Step 4: Conclusion PVC uses vinyl chloride; melamine-formaldehyde uses melamine and formaldehyde; Buna-N uses buta-1,3-diene and acrylonitrile, with structures given above.

Quick Tip to Solve: Restore the double bond to identify an addition monomer; remember that the N in Buna-N points to the nitrile-containing monomer acrylonitrile.

18. The following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

(a) Write the compound which is most reactive towards $\text{S}_{\text{N}}2$ reaction.

(b) Write the compound which is optically active.

(c) Write the compound which is most reactive towards β -elimination reaction.

[3 marks]

Solution:

Concept:

- In an $\text{S}_{\text{N}}2$ reaction, the nucleophile attacks the carbon bearing the leaving group from the opposite side. Steric hindrance reduces the rate, giving the general order primary > secondary > tertiary alkyl halides.
- A chiral carbon has four different groups attached to it. A single enantiomer of a chiral compound rotates plane-polarised light; a racemic mixture does not show net optical rotation.
- In the usual comparison of alkyl halides for β -elimination, tertiary halides react most readily, followed by secondary and primary halides; more substituted alkenes are generally more stable.

Step 1: Compare substitution reactivity (a) 1-Bromopentane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, is a primary halide. 2-Bromopentane, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_2\text{CH}_3$, is secondary, whereas 2-bromo-2-methylbutane, $\text{CH}_3\text{C}(\text{Br})(\text{CH}_3)\text{CH}_2\text{CH}_3$, is tertiary. Since backside attack is least hindered at a primary carbon, 1-bromopentane is the most reactive towards $\text{S}_{\text{N}}2$. The greater crowding around the carbon bearing

Quick Tip to Solve: First classify the brominated carbon as primary, secondary or tertiary; then separately check whether it bears four different groups to decide chirality.

bromine makes the other two compounds less favourable for this mechanism.

Step 2: Identify the compound with a chiral carbon (b) In 2-bromopentane, carbon 2 is attached to four different groups: Br, H, CH₃, and CH₂CH₂CH₃. Thus it is a stereogenic carbon and the compound can be optically active. In 1-bromopentane, the carbon bearing bromine has two identical hydrogen atoms. In 2-bromo-2-methylbutane, that carbon has two identical methyl groups. Neither of these compounds has a chiral carbon. The requested compound is therefore 2-bromopentane, with optical activity understood for an enantiomerically enriched sample.

Step 3: Compare reactivity towards beta-elimination (c) The tertiary halide, 2-bromo-2-methylbutane, is the most reactive towards β -elimination in the standard alkyl-halide comparison. Elimination removes a hydrogen from a carbon adjacent to the carbon bearing bromine, together with the leaving group, to form a carbon-carbon double bond. This substrate can give the more substituted alkene 2-methylbut-2-ene, (CH₃)₂C=CHCH₃, as the major product under usual dehydrohalogenation conditions. Tertiary substitution favours elimination relative to the primary and secondary compounds listed.

Step 4: Conclusion (a) Most reactive towards S_N2: 1-bromopentane. (b) Optically active compound: 2-bromopentane. (c) Most reactive towards β -elimination: 2-bromo-2-methylbutane.

Quick Tip to Solve: First classify the brominated carbon as primary, secondary or tertiary; then separately check whether it bears four different groups to decide chirality.

19. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

[3 marks]

Solution:

Concept:

- For a first order reaction, $kt = 2.303 \log([A]_0/[A]_t)$, where k is the rate constant and $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.
- If a fraction f has decomposed, the fraction remaining is $1 - f$. Thus, percentage completion must first be converted into the amount of reactant left.

Step 1: Determine the rate constant from 25 percent decomposition Take the initial amount as 100 units. After 20 minutes, 25 units have decomposed and 75 units remain. The first order equation gives

$$k = \frac{2.303}{20} \log \frac{100}{75} = \frac{2.303}{20} \log \frac{4}{3}.$$

Using the logarithms supplied in the question,

$$\log \frac{4}{3} = \log 4 - \log 3 = 0.6021 - 0.4771 = 0.1250, \quad k = 0.01439375 \text{ min}^{-1}.$$

The same value of k applies throughout this first order reaction.

Step 2: Calculate the time for 75 percent completion At 75 percent completion, 25 units remain out

Quick Tip to Solve: Use the fraction remaining, not the fraction decomposed, inside the first order logarithm; taking a ratio of times cancels both k and 2.303.

of the initial 100 units. Consequently,

$$\begin{aligned} t_{75} &= \frac{2.303}{k} \log \frac{100}{25} = \frac{2.303}{k} \log 4 \\ &= 20 \frac{\log 4}{\log(4/3)} = 20 \frac{0.6021}{0.1250} = 96.336 \text{ min.} \end{aligned}$$

This is the total time measured from the start of the reaction. Multiplying 20 minutes by three would be incorrect because the reaction rate decreases as the reactant concentration falls.

Step 3: Conclusion The time required for 75 percent completion is 96.34 minutes, approximately.

Quick Tip to Solve: Use the fraction remaining, not the fraction decomposed, inside the first order logarithm; taking a ratio of times cancels both k and 2.303.

20(a). Write one difference in each of the following:

(a) Multimolecular colloid and Associated colloid

(b) Coagulation and Peptization

(c) Homogeneous catalysis and Heterogeneous catalysis

[3 marks]

Solution:

Concept:

- Colloids are classified by how their dispersed particles form. Multimolecular particles are aggregates of small molecules or atoms; associated colloids form micelles from surfactant molecules under suitable conditions.
- Coagulation and peptization describe opposite changes between a colloidal dispersion and a precipitate. Catalysis is classified as homogeneous or heterogeneous by the phases of the catalyst and reactants.

Step 1: (a) Multimolecular and associated colloids In a multimolecular colloid, many small molecules or atoms aggregate to form particles of colloidal dimensions. Gold sol and sulphur sol are examples. In an associated colloid, substances such as soap behave as ordinary electrolytes at low concentrations but form colloidal aggregates called micelles above the critical micelle concentration and above the Kraft temperature. Thus, the distinguishing feature is aggregation of small atoms or molecules in the former versus concentration-dependent micelle formation by surfactant molecules in the latter.

Step 2: (b) Coagulation and peptization Coagulation is the conversion of a colloidal sol into a precipitate, commonly by adding an electrolyte that neutralises the charge on colloidal particles and permits their aggregation. Peptization is the conversion of a freshly prepared precipitate into a colloidal sol by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte, called the peptizing agent. Hence, coagulation removes colloidal stability, whereas peptization produces a stable colloidal dispersion from a precipitate.

Step 3: (c) Homogeneous and heterogeneous catalysis In homogeneous catalysis, the catalyst and reactants are in the same phase; for example, acid-catalysed hydrolysis of an ester in aqueous solution. In heterogeneous catalysis, the catalyst and reactants are in different phases; for example, gaseous

Quick Tip to Solve: Compare colloids by particle formation, coagulation and peptization by direction of conversion, and catalysis by the phases involved.

nitrogen and hydrogen react over solid iron in the Haber process. The distinction concerns phase, not whether the catalyst is consumed: in both cases the catalyst is regenerated during the reaction.

Step 4: Conclusion (a) Multimolecular colloids contain aggregates of small atoms or molecules; associated colloids contain micelles formed under suitable concentration and temperature conditions. (b) Coagulation converts a sol into a precipitate; peptization converts a fresh precipitate into a sol. (c) Homogeneous catalysis involves the same phase; heterogeneous catalysis involves different phases.

Quick Tip to Solve: Compare colloids by particle formation, coagulation and peptization by direction of conversion, and catalysis by the phases involved.

OR

20(b). (a) Write the dispersed phase and dispersion medium of milk.

(b) Write one similarity between physisorption and chemisorption.

(c) Write the chemical method by which $\text{Fe}(\text{OH})_3$ sol is prepared from FeCl_3 .

[3 marks]

Solution:

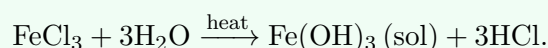
Concept:

- An emulsion contains droplets of one liquid dispersed in another liquid. The droplets constitute the dispersed phase, while the continuous surrounding liquid is the dispersion medium.
- Adsorption is the accumulation of molecules at a surface; both physical and chemical adsorption release heat. Colloidal ferric hydroxide can be prepared by a chemical condensation method involving hydrolysis of ferric chloride.

Step 1: (a) Identify the phases of milk Milk is an oil-in-water emulsion. Its liquid fat droplets are distributed throughout the continuous aqueous phase. Therefore, the dispersed phase is liquid fat (oil), and the dispersion medium is water. Naming both as liquids alone would not identify which component forms the droplets and which forms the surrounding medium.

Step 2: (b) State a similarity between the two types of adsorption Both physisorption and chemisorption are exothermic processes: adsorption is accompanied by the release of heat, so $\Delta H_{\text{ads}} < 0$. Physisorption involves weak intermolecular attractions, whereas chemisorption involves chemical bond formation with the surface; this difference in binding does not alter the shared fact that heat is released on adsorption. The heat of adsorption is generally larger for chemisorption.

Step 3: (c) Prepare ferric hydroxide sol from ferric chloride The chemical method is hydrolysis. Add a small quantity of dilute ferric chloride solution to boiling water. Ferric chloride hydrolyses to form a reddish-brown colloidal sol of ferric hydroxide:



This is a condensation method because the chemical reaction produces insoluble ferric hydroxide particles that grow to colloidal dimensions. The small concentration of ferric chloride and the use of hot water favour formation of a sol rather than a bulk precipitate; excess electrolyte should be avoided because it can cause coagulation.

Quick Tip to Solve: For milk, identify fat as the droplets and water as the continuous phase; for ferric hydroxide sol, recall hydrolysis of ferric chloride in boiling water.

Step 4: Conclusion (a) Dispersed phase: liquid fat (oil); dispersion medium: water. (b) Both physisorption and chemisorption are exothermic. (c) $\text{Fe}(\text{OH})_3$ sol is prepared from FeCl_3 by hydrolysis in boiling water.

Quick Tip to Solve: For milk, identify fat as the droplets and water as the continuous phase; for ferric hydroxide sol, recall hydrolysis of ferric chloride in boiling water.

21. (a) What type of isomerism is shown by the complex $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$?

(b) Why is $[\text{NiCl}_4]^{2-}$ paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic? (Atomic number of Ni = 28)

(c) Why are low spin tetrahedral complexes rarely observed?

[3 marks]

Solution:

Concept:

- Linkage isomerism arises when an ambidentate ligand can coordinate to the same metal through either of two different donor atoms. Thiocyanate, SCN^- , can bind through sulphur or nitrogen.
- The magnetic behaviour of a complex depends on its unpaired electrons: unpaired electrons produce paramagnetism, while complete pairing produces diamagnetism. Ligand field strength can change electron pairing and geometry.
- A low-spin arrangement requires the crystal-field splitting energy to exceed the electron-pairing energy P . Tetrahedral splitting Δ_t is generally too small to fulfil this condition.

Step 1: (a) Identify the isomerism The ligand SCN^- is ambidentate. In $[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$, it can attach through S; in the corresponding $[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$ complex, it attaches through N. The composition is unchanged but the donor atom changes. Therefore, the complex shows linkage isomerism.

Step 2: (b) Compare the nickel complexes In both complexes, each ligand has charge -1 , so nickel has oxidation state $+2$: $x - 4 = -2$, giving $x = +2$. Neutral nickel has configuration $[\text{Ar}]3d^84s^2$, and Ni^{2+} is $[\text{Ar}]3d^8$.

Cl^- is a weak-field ligand and does not cause pairing of the two unpaired $3d$ electrons. Thus $[\text{NiCl}_4]^{2-}$ is a tetrahedral, sp^3 -hybridised complex with two unpaired electrons and is paramagnetic.

CN^- is a strong-field ligand and causes the $3d$ electrons to pair, leaving one $3d$ orbital available for dsp^2 hybridisation. Thus $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar, has no unpaired electrons and is diamagnetic.

Step 3: (c) Explain the rarity of low-spin tetrahedral complexes Tetrahedral crystal-field splitting is small; for the same metal ion and ligand, Δ_t is approximately $\frac{4}{9}\Delta_o$. Usually $\Delta_t < P$, so occupying a higher-energy orbital costs less energy than pairing electrons in a lower-energy orbital. Electrons therefore remain unpaired wherever possible, giving high-spin complexes. Low-spin tetrahedral complexes are consequently rarely observed.

Step 4: Conclusion (a) Linkage isomerism. (b) $[\text{NiCl}_4]^{2-}$ has two unpaired electrons and is paramagnetic; square-planar $[\text{Ni}(\text{CN})_4]^{2-}$ has all electrons paired and is diamagnetic. (c) Small tetrahedral splitting generally cannot overcome the pairing energy.

Quick Tip to Solve: First find Ni^{2+} as d^8 ; then use weak Cl^- versus strong CN^- to distinguish tetrahedral and square-planar behaviour.

22. (a) Based on the nature of intermolecular forces, classify the following solids:

Benzene, Silver

(b) AgCl shows Frenkel defect while NaCl does not. Give reason.

(c) What type of semiconductor is formed when Ge is doped with Al?

[3 marks]

Solution:

Concept:

- Solids are classified according to their constituent particles and the forces holding those particles together. Non-polar molecules are held by dispersion forces; metal atoms form a lattice held by metallic bonding.
- In a Frenkel defect, a small ion leaves its normal lattice site and occupies an interstitial site. This produces a vacancy-interstitial pair without changing the stoichiometry or the total number of ions in the crystal.
- Doping a group 14 semiconductor with a group 13 element introduces an electron deficiency, or hole. Holes are the majority charge carriers in a p-type semiconductor.

Step 1: (a) Classify benzene and silver Benzene consists of non-polar C_6H_6 molecules. In solid benzene, the molecules are held together mainly by London dispersion forces. It is therefore a non-polar molecular solid.

Silver is a metallic solid. Its metal cores are held together by attraction to the delocalised valence electrons, that is, metallic bonding. It is not classified as a molecular solid because its lattice is not made of separate silver molecules.

Step 2: (b) Explain the difference between AgCl and NaCl A Frenkel defect requires a cation to fit into an interstitial space after leaving its normal lattice position. In AgCl, the size difference between Ag^+ and Cl^- is sufficiently large: the relatively small silver ion can occupy an interstitial site, leaving a vacancy at its original site. Hence AgCl shows Frenkel defects.

In NaCl, the Na^+ ion is not sufficiently small relative to Cl^- to occupy the available interstitial spaces readily. Thus NaCl does not show Frenkel defects; it instead commonly shows Schottky defects involving paired cation and anion vacancies.

Step 3: (c) Determine the semiconductor type Germanium is tetravalent and normally forms four covalent bonds with neighbouring atoms. Aluminium is trivalent. When an Al atom substitutes for a Ge atom, it has only three valence electrons and therefore leaves an electron deficiency in the bonding arrangement. This deficiency is a hole. Aluminium acts as an acceptor impurity, and holes become the majority carriers, so the doped germanium is a p-type semiconductor.

Step 4: Conclusion (a) Benzene: non-polar molecular solid; silver: metallic solid. (b) Relatively small Ag^+ ions can occupy interstitial sites, whereas Na^+ ions cannot do so readily. (c) Ge doped with Al forms a p-type semiconductor.

Quick Tip to Solve: For Ge doping, compare valence electrons: trivalent Al supplies one fewer electron than Ge, creating holes and therefore p-type conduction.

23. After watching a programme on TV about the presence of carcinogens (cancer causing agents) Potassium bromate and Potassium iodate in bread and other bakery products, Rupali a Class XII student decided to make others aware about the adverse effects of these carcinogens in foods. She consulted the school principal and requested him to instruct the canteen contractor to stop selling sandwiches, pizzas, burgers and other bakery products to the students. The principal took an immediate action and instructed the canteen contractor to replace the bakery products with some protein and vitamin rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and the students.

After reading the above passage, answer the following questions:

- (a) What are the values (at least two) displayed by Rupali?
- (b) Which polysaccharide component of carbohydrates is commonly present in bread?
- (c) Write the two types of secondary structures of proteins.
- (d) Give two examples of water soluble vitamins.

[4 marks]

Solution:

Concept:

- Social responsibility and concern for others' health are shown when a person uses scientific awareness to seek a practical improvement for the community.
- Starch is a plant storage polysaccharide made from glucose units; it is a major carbohydrate in cereal grains and the flour used to make bread.
- Secondary protein structure is the regular folding of a polypeptide backbone, stabilised mainly by hydrogen bonds between peptide groups. The two standard forms are the α -helix and the β -pleated sheet.
- Vitamins are classified by solubility. The B-group vitamins and vitamin C are water soluble, while vitamins A, D, E and K are fat soluble.

Step 1: (a) Identify the values shown by Rupali Rupali displays **social responsibility** and **concern for the health and welfare of others**. She does not keep the information to herself: she tries to protect fellow students by bringing the matter to the principal's attention. Her request for a change in canteen food also shows initiative and scientific awareness. Any two of these values, supported by the actions described in the passage, answer this part.

Step 2: (b) Identify the polysaccharide in bread Bread is normally prepared from cereal flour, whose principal storage carbohydrate is **starch**. Starch is a polysaccharide composed of many glucose units and contains amylose and amylopectin. Thus starch, rather than a simple sugar such as glucose, is the polysaccharide asked for here.

Step 3: (c) Name the two secondary structures of proteins The two types are the α -**helix** and the β -**pleated sheet**. In the α -helix the polypeptide chain coils, with hydrogen bonds stabilising the turns. In the β -pleated sheet, extended chain segments lie alongside one another and are linked by hydrogen bonds. These describe backbone folding, whereas the amino-acid sequence is the primary structure.

Step 4: (d) Give two water-soluble vitamins Two examples are **vitamin B₁ (thiamine)** and **vitamin C (ascorbic acid)**. Both belong to the water-soluble class. Naming a specific B vitamin avoids treating the entire B complex as one individual vitamin. Vitamins A, D, E and K would not be suitable examples because they are fat soluble.

Quick Tip to Solve: Recall starch for cereal foods, alpha and beta for protein secondary structure, and B plus C for water-soluble vitamins.

Step 5: Conclusion (a) Social responsibility and concern for others' health; (b) starch; (c) α -helix and β -pleated sheet; (d) vitamin B₁ and vitamin C.

Quick Tip to Solve: Recall starch for cereal foods, alpha and beta for protein secondary structure, and B plus C for water-soluble vitamins.

24(a). A 10% solution (by mass) of sucrose in water has a freezing point of 269.15 K. Calculate the freezing point of 10% glucose in water if the freezing point of pure water is 273.15 K.

Given:

(Molar mass of sucrose = 342 g mol⁻¹)

(Molar mass of glucose = 180 g mol⁻¹)

(b) Define the following terms:

(i) Molality (m)

(ii) Abnormal molar mass

[5 marks]

Solution:

Concept:

- For a non-volatile, non-electrolyte solute, depression in freezing point is $\Delta T_f = T_f^0 - T_f = K_f m$, where T_f^0 is the freezing point of pure solvent, K_f its molal depression constant and m the molality of the solution. Sucrose and glucose neither dissociate nor associate in the aqueous solutions considered here, so their van't Hoff factor is $i = 1$.
- A 10% solution by mass contains 10 g of solute in 100 g of solution. Thus the mass of water is 90 g = 0.090 kg, not 100 g. Molality is calculated using the mass of the solvent.
- For the same solvent, equal solute masses and equal solvent masses give $\Delta T_f \propto 1/M$, where M is the solute molar mass. Colligative properties depend on the number of solute particles, so glucose produces a larger depression than sucrose at the same mass percentage.

Step 1: (a) Find the depression and molality of the sucrose solution Choose 100 g of each solution as the calculation basis. The sucrose solution contains 10 g sucrose and 90 g water. Its freezing-point depression is

$$\Delta T_{f,s} = 273.15 - 269.15 = 4.00 \text{ K.}$$

The amount of sucrose and the corresponding molality are

$$n_s = \frac{10}{342} \text{ mol}, \quad m_s = \frac{10/342}{0.090} = 0.3249 \text{ mol kg}^{-1}.$$

Thus the given sucrose solution supplies the relation $K_f m_s = 4.00 \text{ K}$. We use this relation directly, since both solutions contain the same solvent.

Step 2: (a) Compare glucose with sucrose and calculate its freezing point The glucose solution also contains 10 g solute and 0.090 kg water. Therefore

$$m_g = \frac{10/180}{0.090} = 0.6173 \text{ mol kg}^{-1}.$$

Quick Tip to Solve: For equal mass percentages of two non-electrolytes in the same solvent, multiply the known freezing-point depression by the ratio of their molar masses; subtract the resulting depression from the pure solvent's freezing point.

Dividing the freezing-point depression equations cancels K_f :

$$\begin{aligned}\frac{\Delta T_{f,g}}{\Delta T_{f,s}} &= \frac{m_g}{m_s} = \frac{(10/180)/0.090}{(10/342)/0.090} = \frac{342}{180} = 1.90, \\ \Delta T_{f,g} &= 4.00 \times 1.90 = 7.60 \text{ K}, \\ T_{f,g} &= 273.15 - 7.60 = 265.55 \text{ K}.\end{aligned}$$

The freezing point must be lower than that of the sucrose solution: glucose has the smaller molar mass and hence provides more solute molecules for the same solute mass.

Step 3: (b)(i) Define molality Molality, denoted by m , is the number of moles of solute present in one kilogram of solvent:

$$m = \frac{\text{amount of solute in mol}}{\text{mass of solvent in kg}}.$$

Its unit is mol kg^{-1} . Since it uses masses rather than the volume of solution, molality does not change merely because the solution temperature changes, provided no material is lost.

Step 4: (b)(ii) Define abnormal molar mass Abnormal molar mass is the molar mass determined from a colligative property that differs from the normal molar mass of the solute because the solute undergoes association or dissociation in solution. Association reduces the number of independently moving solute particles and gives a higher apparent molar mass; dissociation increases their number and gives a lower apparent molar mass.

$$i = \frac{\text{normal molar mass}}{\text{observed molar mass}}.$$

Here i is the van't Hoff factor, which measures the effective change in the number of solute particles relative to the number expected without association or dissociation.

Step 5: Conclusion (a) The freezing point of the 10% glucose solution is 265.55 K. (b)(i) Molality is the number of moles of solute per kilogram of solvent. (ii) Abnormal molar mass is the colligative-property molar mass that differs from the normal value owing to solute association or dissociation.

Quick Tip to Solve: For equal mass percentages of two non-electrolytes in the same solvent, multiply the known freezing-point depression by the ratio of their molar masses; subtract the resulting depression from the pure solvent's freezing point.

24(b). (a) 30 g of urea ($M = 60 \text{ g mol}^{-1}$) is dissolved in 846 g of water. Calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298 K is 23.8 mm Hg.

(b) Write two differences between ideal solutions and non-ideal solutions.

[5 marks]

Solution:

Concept:

- Raoult's law for a solution of a non-volatile solute: $p_w = x_w p_w^0$, where x_w is the mole fraction of water and p_w^0 is the vapour pressure of pure water at the same temperature.
- The solvent mole fraction is $x_w = n_w / (n_w + n_u)$. Urea is a non-electrolyte and does not dissociate.
- Ideal solutions obey Raoult's law throughout the composition range. Their enthalpy and volume changes on mixing, ΔH_{mix} and ΔV_{mix} , are zero.

Step 1: (a) Convert the masses into moles The molar mass of water is 18 g mol^{-1} , and that of urea is 60 g mol^{-1} . Therefore,

$$n_u = \frac{30 \text{ g}}{60 \text{ g mol}^{-1}} = 0.50 \text{ mol},$$

$$n_w = \frac{846 \text{ g}}{18 \text{ g mol}^{-1}} = 47.0 \text{ mol}.$$

Urea is non-volatile, so only water contributes to the vapour pressure. Both substances enter the mole-fraction calculation.

Step 2: (a) Apply Raoult's law to water The mole fraction of water is

$$x_w = \frac{47}{47 + 0.5} = \frac{94}{95} = 0.98947.$$

At 298 K, use the supplied pure-water vapour pressure:

$$p_w = \frac{94}{95} \times 23.8 = 23.5495 \text{ mm Hg}.$$

The solution pressure is below that of pure water, as expected for addition of a non-volatile solute.

Step 3: (b) Compare ideal and non-ideal solutions **First difference: vapour-pressure behaviour.**

An ideal solution obeys Raoult's law over the entire composition range: each volatile component has partial pressure $p_i = x_i p_i^0$. A non-ideal solution deviates positively or negatively from these predicted pressures because unlike-molecule interactions differ from the corresponding like-molecule interactions.

Second difference: changes on mixing. For an ideal solution, $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$: mixing produces neither heat absorption/evolution nor volume change. For a non-ideal solution these mixing changes are generally non-zero.

Step 4: Conclusion (a) The vapour pressure of water above the urea solution at 298 K is 23.55 mm Hg.
(b) Ideal solutions obey Raoult's law at all compositions and have zero enthalpy and volume changes on mixing; non-ideal solutions deviate from Raoult's law and generally have non-zero mixing changes.

Quick Tip to Solve: Convert both masses to moles first: the solvent mole fraction here is $47 / (47 + 0.5)$, not the mass fraction $846 / (846 + 30)$.

25(a). Write the product(s) in the following reactions:

(i) Cyclohexanone + HCN $\rightarrow$?

(ii) Sodium benzoate + NaOH $\xrightarrow[\Delta]{CaO}$?

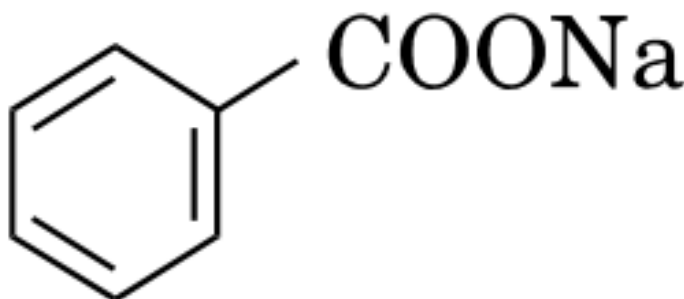
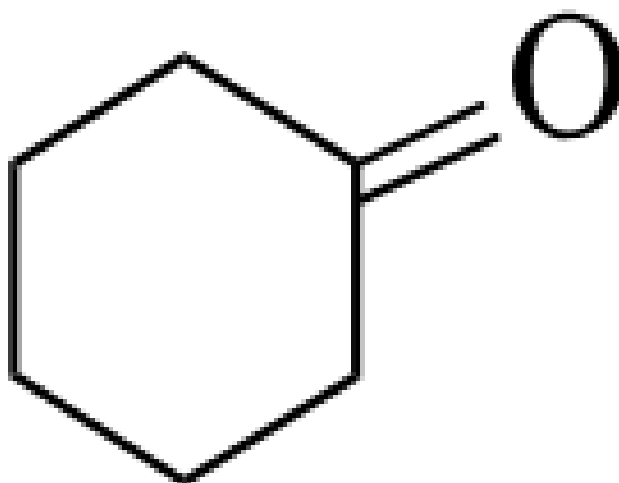
(iii) $CH_3-CH=CH-CN \xrightarrow[(b) H_2O]{(a) DIBAL-H}$?

(b) Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Butanal and Butan-2-one

(ii) Benzoic acid and Phenol

[5 marks]



Solution:

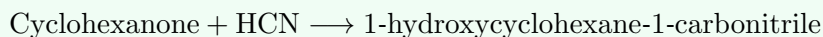
Concept:

- Hydrogen cyanide adds across the carbonyl group: the carbonyl carbon receives CN, while its oxygen becomes an OH group. The product is a cyanohydrin.
- Heating a sodium carboxylate with soda lime, NaOH/CaO, causes decarboxylation. The organic product has one carbon atom fewer than the carboxylate.
- DIBAL-H partially reduces a nitrile group to an intermediate which, on hydrolysis, gives an aldehyde. Under these conditions the carbon-carbon double bond is retained.
- Aldehydes reduce Tollens' reagent, whereas ordinary ketones do not. Carboxylic acids release

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, whereas DIBAL-H retains the nitrile carbon as CHO. Use Tollens' reagent for aldehyde versus ketone and bicarbonate for carboxylic acid versus phenol.

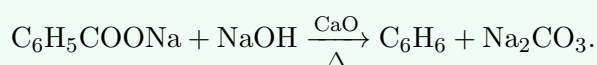
carbon dioxide from sodium hydrogen carbonate, whereas phenol does not.

Step 1: (a)(i) Addition of HCN to cyclohexanone The nucleophile CN^- attacks the electrophilic carbonyl carbon. Protonation of the resulting oxygen anion gives the cyanohydrin. Thus the carbon that originally belonged to the $\text{C}=\text{O}$ group now carries both OH and CN, while the six-membered ring remains intact.



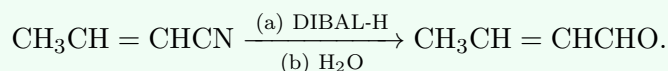
This product is also called cyclohexanone cyanohydrin. The hydroxy and cyano groups are attached to the same ring carbon.

Step 2: (a)(ii) Soda-lime decarboxylation of sodium benzoate Heating sodium benzoate with sodium hydroxide in the presence of calcium oxide removes its carboxylate carbon as sodium carbonate. Hydrogen takes the place of the carboxylate group on the benzene ring:



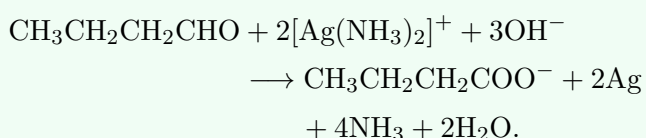
The organic product is benzene. Calcium oxide is part of soda lime and is written over the arrow; it is not consumed in the balanced equation.

Step 3: (a)(iii) Partial reduction of the unsaturated nitrile DIBAL-H reduces the terminal $-\text{C}\equiv\text{N}$ group partially. Subsequent hydrolysis converts the intermediate to $-\text{CHO}$, without reducing the $\text{C}=\text{C}$ bond:



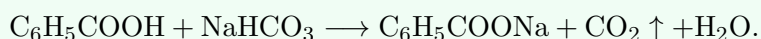
The product is but-2-enal (crotonaldehyde). The nitrile carbon becomes the aldehyde carbon, so the four-carbon chain is retained.

Step 4: (b)(i) Distinguish butanal and butan-2-one Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Butanal gives a silver mirror on the inner wall of the test tube, because its aldehyde group reduces silver(I) to silver metal. Butan-2-one gives no silver mirror under these conditions.



The positive observation identifies butanal; the negative observation identifies butan-2-one.

Step 5: (b)(ii) Distinguish benzoic acid and phenol Add aqueous sodium hydrogen carbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide:



The gas turns limewater milky. Phenol gives no effervescence with sodium hydrogen carbonate because it is too weak an acid to liberate carbon dioxide from this reagent. This test therefore distinguishes the carboxylic acid from phenol directly.

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, whereas DIBAL-H retains the nitrile carbon as CHO. Use Tollens' reagent for aldehyde versus ketone and bicarbonate for carboxylic acid versus phenol.

Step 6: Conclusion (a) The products are (i) cyclohexanone cyanohydrin, (ii) benzene (with sodium carbonate), and (iii) but-2-enal, $\text{CH}_3\text{CH}=\text{CHCHO}$. (b) Butanal gives a Tollens' silver mirror while butan-2-one does not; benzoic acid gives CO_2 effervescence with NaHCO_3 , while phenol does not.

Quick Tip to Solve: Track the functional-group carbon: soda lime removes it, whereas DIBAL-H retains the nitrile carbon as CHO . Use Tollens' reagent for aldehyde versus ketone and bicarbonate for carboxylic acid versus phenol.

OR

25(b). (a) Write the reactions involved in the following:

(i) Etard reaction

(ii) Stephen reduction

(b) How will you convert the following in not more than two steps:

(i) Benzoic acid to Benzaldehyde

(ii) Acetophenone to Benzoic acid

(iii) Ethanoic acid to 2-Hydroxyethanoic acid

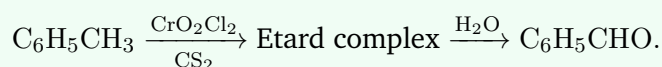
[5 marks]

Solution:

Concept:

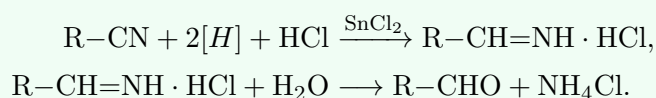
- Etard oxidation changes the methyl side chain of toluene into an aldehyde using chromyl chloride, CrO_2Cl_2 , followed by hydrolysis of the intermediate complex.
- Stephen reduction converts a nitrile $\text{R}-\text{CN}$ into an iminium salt with SnCl_2/HCl ; hydrolysis then gives the aldehyde $\text{R}-\text{CHO}$.
- Rosenmund reduction converts an acid chloride into an aldehyde using hydrogen and poisoned palladium on barium sulphate. The haloform reaction cleaves a methyl ketone, while the Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen.

Step 1: (a)(i) Etard reaction Toluene is treated with chromyl chloride in a non-aqueous solvent such as carbon disulphide. An Etard complex forms at the benzylic carbon; hydrolysis of this complex produces benzaldehyde. The reaction sequence is



Thus the side chain changes from $-\text{CH}_3$ to $-\text{CHO}$, while the benzene ring is retained. The hydrolysis is essential for releasing the aldehyde from the complex.

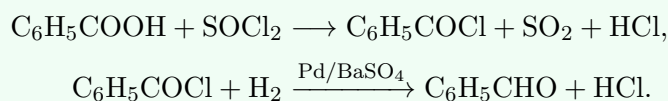
Step 2: (a)(ii) Stephen reduction A nitrile is partially reduced with stannous chloride and hydrochloric acid to its iminium chloride, which is hydrolysed to an aldehyde. Using $[\text{H}]$ to denote reducing hydrogen supplied by the reagent, the stages are



Quick Tip to Solve: For these conversions, identify the group first: acid to aldehyde needs an acid chloride; a methyl ketone permits haloform cleavage; an alpha hydroxyl group can be introduced through an alpha halo acid.

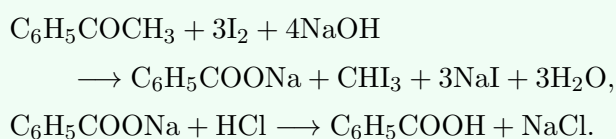
The carbon of the nitrile group becomes the aldehyde carbon, so the carbon skeleton is unchanged. For example, ethanenitrile gives ethanal by this sequence.

Step 3: (b)(i) Benzoic acid to benzaldehyde First convert benzoic acid into benzoyl chloride with thionyl chloride. Next carry out Rosenmund reduction of the acid chloride:



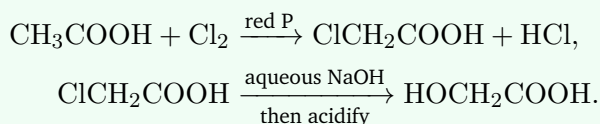
The poisoned catalyst moderates the reduction so that benzaldehyde is obtained. A strong reducing reagent such as LiAlH_4 would instead give benzyl alcohol and is unsuitable for the required conversion.

Step 4: (b)(ii) Acetophenone to benzoic acid Acetophenone contains the methyl-ketone group $-\text{COCH}_3$. Treat it with iodine and sodium hydroxide to obtain sodium benzoate by the haloform reaction, then acidify:



The carbonyl carbon remains in the benzoate group and the methyl carbon leaves as yellow iodoform, CHI_3 . Acidification converts the carboxylate salt to the required free carboxylic acid.

Step 5: (b)(iii) Ethanoic acid to 2-hydroxyethanoic acid Introduce chlorine at the alpha carbon by the Hell–Volhard–Zelinsky reaction using chlorine and red phosphorus. Hydrolyse the resulting chloroethanoic acid with aqueous alkali, followed by acid work-up:



The second transformation replaces $-\text{Cl}$ by $-\text{OH}$; acid work-up restores the free acid from its sodium salt. The product is 2-hydroxyethanoic acid, also called glycolic acid. These are two synthetic transformations: alpha chlorination and hydrolysis with its work-up.

Step 6: Conclusion Etard oxidation gives benzaldehyde from toluene; Stephen reduction gives an aldehyde from a nitrile. The required conversions use, respectively, benzoyl chloride followed by Rosenmund reduction, haloform cleavage followed by acidification, and alpha chlorination followed by hydrolysis to HOCH_2COOH .

Quick Tip to Solve: For these conversions, identify the group first: acid to aldehyde needs an acid chloride; a methyl ketone permits haloform cleavage; an alpha hydroxyl group can be introduced through an alpha halo acid.

26(a). Account for the following:

(i) Transition metals show variable oxidation states.

(ii) Zn, Cd and Hg are soft metals.

(iii) E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive (+1.57 V) as compared to $\text{Cr}^{3+}/\text{Cr}^{2+}$.

(b) Write one similarity and one difference between the chemistry of lanthanoid and actinoid elements.

[5 marks]

Solution:

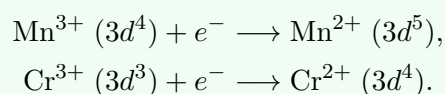
Concept:

- The outer ns and inner $(n-1)d$ orbitals of transition metals have comparable energies, so different numbers of electrons can participate in bonding.
- Metallic bonding depends on the availability of electrons for bonding; a completely filled d^{10} subshell contributes much less than a partly filled d subshell.
- A positive standard reduction potential, E° , indicates a favourable tendency for reduction under standard conditions. The stability of the resulting electronic configuration affects this tendency.
- Lanthanoids and actinoids are inner-transition elements involving the progressive filling of $4f$ and $5f$ orbitals, respectively.

Step 1: (a)(i) Explain variable oxidation states The energy separation between the $(n-1)d$ and ns orbitals is small. Therefore, besides the outer ns electrons, different numbers of $(n-1)d$ electrons can also take part in bond formation. Removal or sharing of different numbers of these electrons produces different oxidation states. For example, iron forms Fe^{2+} and Fe^{3+} , while manganese exhibits several oxidation states. Thus, variable oxidation states follow from the comparable energies of the orbitals available for bonding.

Step 2: (a)(ii) Explain the softness of Zn, Cd and Hg Zinc, cadmium and mercury have the outer electronic configuration $(n-1)d^{10}ns^2$. Their d subshells are completely filled and contain no unpaired d electrons. The filled d subshells do not contribute effectively to strong metallic bonding in the way that partly filled d subshells do in many other metals of the d -block. Consequently, their interatomic metallic bonding is relatively weak, accounting for their softness. Mercury has exceptionally weak bonding and is liquid at room temperature.

Step 3: (a)(iii) Compare the two standard reduction potentials The relevant changes in electronic configuration are



Reduction of Mn^{3+} produces the especially stable half-filled $3d^5$ configuration of Mn^{2+} . Hence Mn^{3+} has a strong tendency to accept an electron, consistent with the highly positive $E^\circ = +1.57\text{ V}$. In contrast, Cr^{3+} has a particularly stable $3d^3$ configuration; in an octahedral aqueous complex it gives a stable t_{2g}^3 arrangement. Reduction to Cr^{2+} , with $3d^4$, loses this stability. Therefore, reduction of Cr^{3+} is much less favourable than reduction of Mn^{3+} .

Step 4: (b) State one similarity and one difference **Similarity:** Both lanthanoids and actinoids commonly exhibit the +3 oxidation state. Their trivalent ions also generally form ionic compounds.

Difference: Actinoids display a much wider range of oxidation states than lanthanoids. In actinoids,

Quick Tip to Solve: Write the d -electron configurations on both sides of each reduction: Mn gains half-filled d^5 stability, while Cr loses its stable d^3 configuration.

the energies of $5f$, $6d$ and $7s$ orbitals are sufficiently close for their electrons to participate in bonding. Lanthanoids are predominantly trivalent because their $4f$ electrons are more deeply buried and less available for bonding; only some lanthanoids additionally show +2 or +4 states.

Step 5: Conclusion Variable oxidation states arise from comparable ns and $(n-1)d$ energies; Zn, Cd and Hg are soft because their filled d^{10} subshells give weak metallic bonding. The high $\text{Mn}^{3+}/\text{Mn}^{2+}$ reduction potential reflects formation of stable $3d^5$ Mn^{2+} , whereas Cr^{3+} is already stable as $3d^3$. Both inner-transition series commonly show +3, but actinoids show a wider range of oxidation states.

Quick Tip to Solve: Write the d-electron configurations on both sides of each reduction: Mn gains half-filled d^5 stability, while Cr loses its stable d^3 configuration.

OR

26(b). (a) Following are the transition metal ions of 3d series:

Ti^{4+} , V^{2+} , Mn^{3+} , Cr^{3+}

(Atomic numbers: Ti = 22, V = 23, Mn = 25, Cr = 24)

Answer the following:

(i) Which ion is most stable in an aqueous solution and why?

(ii) Which ion is a strong oxidising agent and why?

(iii) Which ion is colourless and why?

(b) Complete the following equations:

(i) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{S}^{2-} \rightarrow$

(ii) $\text{KMnO}_4 \xrightarrow{\text{heat}}$

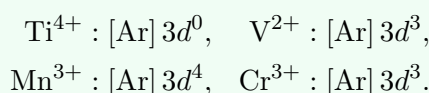
[5 marks]

Solution:

Concept:

- Remove the $4s$ electrons before the $3d$ electrons when writing the electronic configurations of transition-metal ions. A particularly stable electronic configuration can favour formation of an ion or its reduction product.
- In an octahedral aqueous complex, d orbitals split into lower-energy t_{2g} and higher-energy e_g orbitals. The d^3 configuration has three singly occupied t_{2g} orbitals and substantial crystal-field stabilisation.
- A $d-d$ transition requires occupied and available d levels; a d^0 ion cannot undergo such a transition. In redox equations, both atoms and total charge must balance.

Step 1: (a)(i) Identify the most stable aqueous ion The ionic configurations are

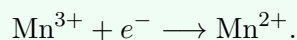


Among these ions, Cr^{3+} is the most stable in aqueous solution. Its $3d^3$ configuration gives the stable t_{2g}^3

Quick Tip to Solve: For these ions, write the d-electron counts first: d^0 signals no d-d colour and reduction of Mn^{3+} to d^5 explains its oxidising power. Balance acidic permanganate using its five-electron reduction to Mn^{2+} .

arrangement in its octahedral hydrated complex: all three lower-energy orbitals are singly occupied. Although V^{2+} also has d^3 , it readily oxidises to V^{3+} and is a reducing agent. Thus, the electron count alone does not make the two ions equally stable in aqueous redox chemistry.

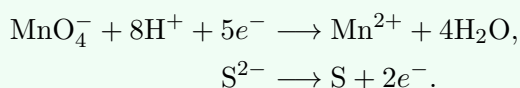
Step 2: (a)(ii) Identify the strong oxidising agent Mn^{3+} readily accepts an electron and is reduced to Mn^{2+} :



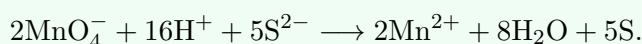
This changes $3d^4$ into the especially stable half-filled $3d^5$ configuration. The strong tendency to undergo this reduction makes Mn^{3+} a strong oxidising agent: it accepts an electron while oxidising the other reactant.

Step 3: (a)(iii) Identify the colourless ion Ti^{4+} is colourless because it has the $3d^0$ configuration. There is no d electron available for excitation between split d levels, so no $d-d$ absorption produces colour. The other listed ions have partially filled d orbitals and their aqueous ions are coloured.

Step 4: (b)(i) Complete the acidic permanganate reaction Acidified permanganate is reduced to Mn^{2+} , while sulphide is oxidised to elemental sulphur. The half-reactions are



Multiply the first half-reaction by two and the second by five, then cancel ten electrons:



There are two Mn atoms, eight O atoms, sixteen H atoms and five S atoms on each side. The total charge on each side is +4, confirming the balance.

Step 5: (b)(ii) Complete the thermal decomposition On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen:



The balanced equation contains two potassium atoms, two manganese atoms and eight oxygen atoms on each side. Manganese changes from +7 to +6 and +4, while part of the oxygen is released as O_2 .

Step 6: Conclusion (a) (i) Cr^{3+} : stable $3d^3$, t_{2g}^3 configuration; (ii) Mn^{3+} : reduced readily to half-filled $3d^5$ Mn^{2+} ; (iii) Ti^{4+} : $3d^0$, hence no $d-d$ transition.

(b) (i) The products are $2Mn^{2+} + 8H_2O + 5S$. (ii) $2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$.

Quick Tip to Solve: For these ions, write the d-electron counts first: d^0 signals no d-d colour and reduction of Mn^{3+} to d^5 explains its oxidising power. Balance acidic permanganate using its five-electron reduction to Mn^{2+} .