CBSE Class 12 Chemistry Question Paper 2017 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) **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. Arrange the following hydrides of Group-16 elements in the decreasing order of their reducing character:

H_2O, H_2S, H_2Se, H_2Te [1 mark]

Solution:

Concept:

- Reducing character is the tendency of a substance to undergo oxidation while reducing another substance.
- For Group-16 hydrides, increasing atomic size down the group weakens the element–hydrogen bond and decreases thermal stability.

Step 1: Compare bond strength From oxygen to tellurium, the central atom becomes larger, so its bond with hydrogen becomes weaker. Thus the hydrides become progressively less stable down Group 16.

Step 2: Apply the reducing-character trend A less stable hydride loses hydrogen or undergoes oxidation more readily and therefore acts as a stronger reducing agent. Consequently reducing character increases on going from water to hydrogen telluride; write the requested decreasing order in the reverse direction.

Step 3: Conclusion

$$\boxed{H_2Te > H_2Se > H_2S > H_2O}$$

Quick Tip to Solve: For Group-16 hydrides, weaker E–H bonds down the group mean stronger reducing character.

2. What is the role of desorption in the process of catalysis? [1 mark]

Solution:

Concept:

- Adsorption brings reactant molecules onto the active sites of a solid catalyst, where the surface reaction occurs.
- Desorption is the release of the adsorbed products from the catalyst surface.

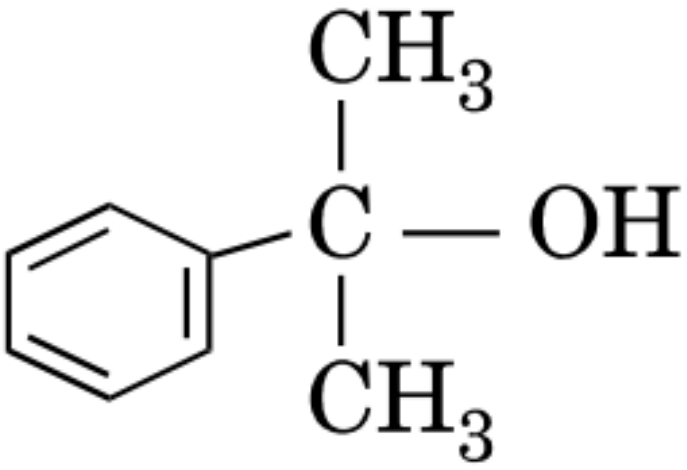
Step 1: Release the products After reactants have reacted at the catalyst surface, the products must leave that surface. Desorption allows these products to enter the surrounding gas or liquid phase.

Step 2: Regenerate active sites If the products remained strongly adsorbed, they would occupy the active sites and prevent fresh reactant molecules from being adsorbed. Their desorption frees these sites, so another set of reactants can react and the catalytic cycle can continue.

Step 3: Conclusion Desorption removes products from the catalyst surface and frees its active sites for further adsorption and catalysis.

Quick Tip to Solve: Remember the final surface-catalysis step: products leave, making active sites available again.

3. Write the IUPAC name of the following compound: [1 mark]



Solution:

Concept:

- Choose the longest carbon chain containing the carbon bearing the hydroxyl group; the alcohol is named using the suffix $-\mathrm{ol}$.
- Number the parent chain to give the hydroxyl group its lowest locant, then identify substituents.

Step 1: Identify the parent alcohol The printed structure is $C_6H_5C(OH)(CH_3)_2$. The chain containing the hydroxyl-bearing carbon is $CH_3 - C(OH) - CH_3$, a three-carbon chain. Its parent name is propan-2-ol.

Step 2: Locate the phenyl substituent The benzene ring is attached directly to carbon 2 of this chain and is named as a phenyl substituent. Both the hydroxyl group and the phenyl substituent are therefore on carbon 2; no additional methyl substituent is needed because both methyl carbons belong to the parent chain.

Step 3: Conclusion The IUPAC name is $\boxed{\text{2-phenylpropan-2-ol}}$.

Quick Tip to Solve: Include both methyl groups in the three-carbon alcohol parent; treat the benzene ring as phenyl.

4. Among the isomers of pentane (C_5H_{12}), write the one which on photochemical chlorination yields a single monochloride. [1 mark]

Solution:

Concept:

- Photochemical chlorination substitutes a hydrogen atom by chlorine through a free-radical reaction.
- A single monochloride results when all replaceable hydrogen atoms are chemically equivalent by symmetry.

Step 1: Choose the symmetric pentane isomer The isomer $C(CH_3)_4$ has a central carbon bonded

Quick Tip to Solve: Test symmetry before counting products: all twelve hydrogens of neopentane are equivalent.

to four identical methyl groups. Its structure is highly symmetric, and the central carbon has no hydrogen atom.

Step 2: Check hydrogen equivalence All twelve hydrogen atoms lie on these equivalent methyl groups. Replacing any one of them by chlorine gives the same compound, $ClCH_2C(CH_3)_3$. The other pentane isomers have more than one hydrogen environment and hence produce several monochlorides.

Step 3: Conclusion The required isomer is $\boxed{\text{2,2-dimethylpropane (neopentane)}}$, $C(CH_3)_4$.

Quick Tip to Solve: Test symmetry before counting products: all twelve hydrogens of neopentane are equivalent.

5. What is the formula of a compound in which the element P forms ccp lattice and atoms of Q occupy 1/3rd of tetrahedral voids? [1 mark]

Solution:

Concept:

- A close-packed lattice containing N atoms has $2N$ tetrahedral voids.
- The empirical formula is obtained by reducing the ratio of the numbers of atoms to the smallest whole numbers.

Step 1: Count occupied tetrahedral voids Let the ccp lattice contain N atoms of P. There are then $2N$ tetrahedral voids. Since Q occupies one-third of these voids, the number of Q atoms is $\frac{1}{3}(2N) = \frac{2N}{3}$.

Step 2: Reduce the atomic ratio The ratio is $P : Q = N : \frac{2N}{3} = 3 : 2$. Equivalently, choosing three P atoms gives six tetrahedral voids, of which two are occupied by Q. These integers directly give the subscripts in the compound formula.

Step 3: Conclusion The formula is $\boxed{P_3Q_2}$.

Quick Tip to Solve: Multiply the tetrahedral-void occupancy fraction by 2 before forming the Q-to-P ratio.

6. In a galvanic cell, the following cell reaction occurs:

Zn (s) + 2 Ag^+ (aq) $\rightarrow$ Zn^{2+} (aq) + 2 Ag (s); $E^\circ_{cell} = +1.56\,V$

(a) Is the direction of flow of electrons from zinc to silver or silver to zinc?

(b) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions? [2 marks]

Solution:

Concept:

- Oxidation occurs at the anode and releases electrons; reduction occurs at the cathode and consumes electrons.
- In a galvanic cell, electrons flow through the external circuit from the anode to the cathode.
- The reaction equation shows which dissolved ions are produced and which are consumed as the cell operates.

Quick Tip to Solve: Use the half-reactions: ions on the product side increase; ions on the reactant side decrease.

Step 1: (a) Identify the electrodes and electron flow The half-reactions are

$$\text{Anode: } \mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}(aq)} + 2\mathrm{e^-},$$
$$\text{Cathode: } 2\mathrm{Ag^+(aq)} + 2\mathrm{e^-} \rightarrow 2\mathrm{Ag(s)}.$$

Zinc undergoes oxidation and supplies electrons, whereas silver ions undergo reduction at the silver electrode. Thus electrons travel through the external wire from the zinc electrode to the silver electrode. The positive standard cell potential is consistent with the forward reaction being spontaneous under standard conditions.

Step 2: (b) Follow the dissolved ions For every mole of zinc oxidised, one mole of $\mathrm{Zn^{2+}}$ enters the zinc half-cell solution. At the same time, two moles of $\mathrm{Ag^+}$ are removed from the silver half-cell solution and deposited as metallic silver. Hence, as the reaction proceeds at essentially fixed solution volumes, the zinc-ion concentration rises while the silver-ion concentration falls.

Step 3: Conclusion (a) Electrons flow from zinc to silver through the external circuit.
(b) $[\mathrm{Zn^{2+}}]$ increases and $[\mathrm{Ag^+}]$ decreases.

Quick Tip to Solve: Use the half-reactions: ions on the product side increase; ions on the reactant side decrease.

7. In the following ions:
$\mathrm{Mn^{3+}}$, $\mathrm{V^{3+}}$, $\mathrm{Cr^{3+}}$, $\mathrm{Ti^{4+}}$
(Atomic no.: Mn = 25, V = 23, Cr = 24, Ti = 22)
(a) Which ion is most stable in an aqueous solution?
(b) Which ion is the strongest oxidizing agent?
(c) Which ion is colourless?
(d) Which ion has the highest number of unpaired electrons? [2 marks]

Solution:

Concept:

- The ionic electronic configuration is obtained by removing the $4s$ electrons before the $3d$ electrons. The number of unpaired d electrons influences magnetic behaviour.
- Aqueous stability depends on the electronic configuration and hydration. An oxidizing agent accepts electrons; formation of a particularly stable product favours this reduction.

Step 1: Write the ionic configurations The configurations are $\mathrm{Mn^{3+}}$: $[Ar]3d^4$, $\mathrm{V^{3+}}$: $[Ar]3d^2$, $\mathrm{Cr^{3+}}$: $[Ar]3d^3$ and $\mathrm{Ti^{4+}}$: $[Ar]3d^0$. In their ordinary aqueous ions, the respective numbers of unpaired electrons are 4, 2, 3 and 0.

Step 2: Identify stability and oxidizing power (a) $\mathrm{Cr^{3+}}$ is the most stable ion in aqueous solution among those given. Its d^3 configuration gives the stable t_{2g}^3 arrangement in an octahedral aqua complex.
(b) $\mathrm{Mn^{3+}}$ is the strongest oxidizing agent: it readily accepts an electron to form $\mathrm{Mn^{2+}}$, which has the stable half-filled $3d^5$ configuration.

Quick Tip to Solve: Remove $4s$ electrons first, then compare the resulting d^0, d^2, d^3, d^4 configurations.

Step 3: Identify colour and unpaired electrons (c) Ti^{4+} is colourless because it has no d electrons and hence cannot undergo a d-d transition.

(d) Mn^{3+}, with $3d^4$, has the highest number of unpaired electrons: four.

Step 4: Conclusion (a) Cr^{3+}; (b) Mn^{3+}; (c) Ti^{4+}; (d) Mn^{3+} (four unpaired electrons).

Quick Tip to Solve: Remove $4s$ electrons first, then compare the resulting d^0, d^2, d^3, d^4 configurations.

8(a). Do the following conversions in not more than two steps:

(a) Propene to Acetone

(b) Propanoic acid to 2-hydroxypropanoic acid [2 marks]

Solution:

Concept:

- Acid-catalysed hydration of propene follows Markovnikov addition and gives propan-2-ol. Oxidation of a secondary alcohol gives a ketone.
- The Hell-Volhard-Zelinsky (HVZ) reaction introduces halogen at the carbon adjacent to $-COOH$. Aqueous alkali then replaces this halogen by $-OH$.

Step 1: Convert propene to acetone First hydrate propene using water in the presence of dilute sulphuric acid; then oxidize the secondary alcohol using acidified potassium dichromate.

$$CH_3CH{=}CH_2 \xrightarrow{H_2O/H^+} CH_3CH(OH)CH_3$$
$$\xrightarrow{K_2Cr_2O_7/H^+} CH_3COCH_3.$$

The intermediate is propan-2-ol, so oxidation gives acetone without changing the three-carbon skeleton.

Step 2: Convert propanoic acid to 2-hydroxypropanoic acid Carry out alpha-bromination with bromine and red phosphorus, followed by hydrolysis with aqueous alkali and acidification.

$$CH_3CH_2COOH \xrightarrow{Br_2/\text{red P}} CH_3CHBrCOOH$$
$$\xrightarrow[\text{then } H^+]{\text{aq. KOH}} CH_3CH(OH)COOH.$$

Bromination occurs at carbon 2, which has an alpha-hydrogen. Hydrolysis replaces the alpha-bromine with hydroxyl; acidification regenerates the carboxylic acid from its salt.

Step 3: Conclusion Propene gives acetone through propan-2-ol. Propanoic acid gives 2-hydroxypropanoic acid through 2-bromopropanoic acid, each in two steps.

Quick Tip to Solve: For an alpha-hydroxy acid, install alpha-bromine by HVZ before replacing it with hydroxyl.

OR

8(b). Write the reaction involved in the following:

(a) Etard reaction

(b) Wolff-Kishner reduction [2 marks]

Solution:

Concept:

- Etard oxidation converts the side-chain methyl group of toluene into an aldehyde using chromyl chloride, followed by hydrolysis.
- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and strong base on heating.

Step 1: Write the Etard reaction Toluene is treated with chromyl chloride, CrO_2Cl_2, in an inert solvent such as CS_2. Hydrolysis of the resulting Etard complex gives benzaldehyde:

$$C_6H_5CH_3 \xrightarrow[\text{then hydrolysis}]{CrO_2Cl_2/CS_2} C_6H_5CHO.$$

Controlled oxidation stops at the aldehyde stage; the methyl side chain becomes $-CHO$.

Step 2: Write the Wolff-Kishner reduction The carbonyl compound first forms a hydrazone with hydrazine. Heating with KOH in a high-boiling solvent such as ethylene glycol reduces it to a hydrocarbon, releasing nitrogen. For acetone:

$$CH_3COCH_3 + H_2NNH_2 \xrightarrow[\text{ethylene glycol}]{KOH,\ \Delta} CH_3CH_2CH_3 + N_2 + H_2O.$$

Thus, the carbonyl oxygen is replaced by two hydrogen atoms, while the carbon skeleton remains intact.

Step 3: Conclusion Etard reaction: toluene $\rightarrow$ benzaldehyde with CrO_2Cl_2, then hydrolysis. Wolff-Kishner reduction: carbonyl compound $\rightarrow$ hydrocarbon with NH_2NH_2/KOH and heat.

Quick Tip to Solve: Remember Etard as side-chain oxidation to an aldehyde, and Wolff-Kishner as carbonyl removal in basic medium.

9. What is meant by elevation in boiling point? Why is it a colligative property? [2 marks]

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure. Dissolving a non-volatile solute lowers the vapour pressure of the solvent.
- For a dilute ideal solution, $\Delta T_b = K_b m$, where K_b is the solvent ebullioscopic constant and m is the solute molality.

Step 1: Define elevation in boiling point Elevation in boiling point is the increase in the boiling

Quick Tip to Solve: Connect lower vapour pressure to higher boiling temperature, then use $\Delta T_b = K_b m$ to explain particle dependence.

temperature of a solvent when a non-volatile solute is dissolved in it, measured at the same external pressure:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{pure solvent}).$$

Because the solution has a lower vapour pressure at a given temperature, it must be heated to a higher temperature before its vapour pressure reaches the external pressure.

Step 2: Explain why it is colligative For dilute solutions, $\Delta T_b = K_b m$. For a fixed solvent, K_b is constant and molality counts moles of solute per kilogram of solvent. Hence the elevation depends on the number of dissolved solute particles relative to the amount of solvent, rather than their chemical nature. If a solute dissociates or associates, the effective particle number changes and the relation becomes $\Delta T_b = iK_b m$, with i the van't Hoff factor.

Step 3: Conclusion Elevation in boiling point is $T_b(\text{solution}) - T_b(\text{solvent})$. It is colligative because it depends on the number of dissolved particles, not their identity.

Quick Tip to Solve: Connect lower vapour pressure to higher boiling temperature, then use $\Delta T_b = K_b m$ to explain particle dependence.

10. (a) Write the IUPAC name of the following complex:

$[Co(NH_3)_4Cl(NO_2)]Cl$

(b) Write the formula for the following:

Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride [2 marks]

Solution:

Concept:

- Name ligands alphabetically, ignoring multiplicative prefixes, and then name the metal with its oxidation state in Roman numerals.
- Ammonia and ethane-1,2-diamine (en) are neutral ligands; chlorido and nitrito ligands each carry charge -1. The ion outside brackets is the counter-ion.

Step 1: (a) Determine the oxidation state and name the complex The outer chloride ion has charge -1, so the coordination entity is a cation of charge $+1$. If cobalt has oxidation state x, then

$$x + 4(0) - 1 - 1 = +1 \quad \Rightarrow \quad x = +3.$$

The four ammonia ligands give tetraammine; the coordinated chloride gives chlorido. The printed NO_2 denotes the nitrogen-bonded nitrito ligand, named nitrito-N (also traditionally called nitro). Their alphabetical order is ammine, chlorido, nitrito. Since the complex is cationic, the metal is named cobalt, followed by (III). Finally name the external chloride counter-ion.

Step 2: (b) Construct the formula from the name Dichlorido means two coordinated Cl^- ligands, and bis(ethane-1,2-diamine) means two neutral en ligands. With cobalt(III), the coordination entity has charge $+3 - 2 = +1$. One chloride ion is therefore required outside the coordination brackets to make the salt electrically neutral. Each en is bidentate, so the two en ligands supply four donor sites and the two chlorido ligands supply two more, giving coordination number six.

Quick Tip to Solve: Use the outer chloride to find the complex charge first; neutral ammine and en ligands do not change the oxidation-state sum.

Step 3: Conclusion (a) Tetraamminechloridonitrito-N-cobalt(III) chloride (tetraamminechloridonitro-cobalt(III) chloride).
(b) $\boxed{[CoCl_2(en)_2]Cl}$, where en is ethane-1,2-diamine.

Quick Tip to Solve: Use the outer chloride to find the complex charge first; neutral ammine and en ligands do not change the oxidation-state sum.

11. Account for the following:

(a) $CuCl_2$ is more stable than Cu_2Cl_2.

(b) Atomic radii of 4d and 5d series elements are nearly same.

(c) Hydrochloric acid is not used in permanganate titrations. [3 marks]

Solution:

Concept:

- Stability of an oxidation state depends on the overall energy balance, including ionisation and hydration energies, rather than electronic configuration alone.
- Lanthanoid contraction is the gradual decrease in size across the lanthanoids due to poor shielding by $4f$ electrons.
- Acidified permanganate is a strong oxidising agent; the acid used in a titration must not itself introduce a species that is oxidised.

Step 1: (a) Compare copper(I) and copper(II) stability In Cu_2Cl_2, copper is in the $+1$ oxidation state, whereas in $CuCl_2$ it is in the $+2$ oxidation state. Although Cu^+ has the filled $3d^{10}$ configuration, Cu^{2+} has a much more negative hydration enthalpy because of its greater charge density. In aqueous solution this extra hydration stabilisation compensates for the energy needed to remove the second electron. Thus copper(II) is more stable under aqueous conditions, and copper(I) tends to disproportionate:

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s).$$

This hydration-energy argument explains the usual comparison in the question; a filled subshell alone does not establish greater aqueous stability.

Step 2: (b) Explain the similar radii of corresponding 4d and 5d elements The lanthanoids occur before the $5d$ transition series. Across the lanthanoids, the added $4f$ electrons shield the increasing nuclear charge poorly. The effective nuclear attraction therefore increases and contracts the electron cloud. This lanthanoid contraction largely offsets the increase in size expected from the extra shell in the $5d$ elements. Consequently, corresponding $4d$ and $5d$ elements, such as zirconium and hafnium, have nearly the same atomic radii.

Step 3: (c) Explain why hydrochloric acid is unsuitable Acidified permanganate oxidises the chloride ions supplied by hydrochloric acid to chlorine gas. The balanced interfering reaction is

$$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 8H_2O + 5Cl_2.$$

This consumes permanganate in addition to that consumed by the substance being titrated, giving an

Quick Tip to Solve: Link each reason to its cause: copper to hydration energy, equal radii to poor 4f shielding, and HCl interference to chloride oxidation.

incorrect titre. Dilute sulphuric acid is used instead, as sulphate does not undergo this interfering oxidation under the titration conditions.

Step 4: Conclusion (a) Greater hydration stabilisation favours Cu^{2+} in aqueous solution. (b) Lanthanoid contraction makes corresponding $4d$ and $5d$ radii nearly equal. (c) HCl is avoided because its chloride ions are oxidised to chlorine by permanganate.

Quick Tip to Solve: Link each reason to its cause: copper to hydration energy, equal radii to poor 4f shielding, and HCl interference to chloride oxidation.

12. Define the following terms:

(a) Analgesic

(b) Anionic detergent

(c) Antacid [3 marks]

Solution:

Concept:

- A drug class is defined by its therapeutic action; a suitable example illustrates the definition but does not replace it.
- A detergent has a hydrophobic hydrocarbon part and a hydrophilic ionic part. Its classification depends on the charge of the cleansing-active part in water.
- Antacids reduce excess gastric acidity by neutralising acid in the stomach.

Step 1: (a) Define an analgesic An analgesic is a drug that reduces or abolishes pain without causing loss of consciousness, mental confusion, incoordination or paralysis, or other disturbances of the nervous system. Analgesics provide relief from the sensation of pain; this is their defining action. Aspirin and paracetamol are examples of non-narcotic analgesics. Aspirin is useful for mild to moderate pain, while stronger pain may require other classes of analgesics under medical supervision.

Step 2: (b) Define an anionic detergent An anionic detergent is a cleansing agent whose active surface-active part is a negatively charged ion in aqueous solution. Common examples are sodium salts of sulphates of long-chain alcohols or sodium salts of long-chain alkylbenzenesulphonic acids. Sodium lauryl sulphate is one example:

$$CH_3(CH_2)_{11}OSO_3^-Na^+.$$

Its long hydrocarbon chain associates with grease, while the negatively charged sulphate-containing end interacts with water. Thus the cleansing-active species is the anion; the sodium cation is the counter-ion.

Step 3: (c) Define an antacid An antacid is a substance used to neutralise excess hydrochloric acid in the stomach and relieve acidity or heartburn. Mild basic substances such as magnesium hydroxide and aluminium hydroxide act as antacids. For example, magnesium hydroxide consumes gastric acid according to

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O.$$

Quick Tip to Solve: For each definition state the distinguishing action first, then give an example: pain relief, anionic cleansing, or acid neutralisation.

This decreases the excess acidity by an acid-base neutralisation reaction. The defining property here is neutralisation of stomach acid, rather than relief of pain or removal of grease.

Step 4: Conclusion Analgesics relieve pain without loss of consciousness; anionic detergents have a negatively charged cleansing-active ion; antacids neutralise excess stomach acid.

Quick Tip to Solve: For each definition state the distinguishing action first, then give an example: pain relief, anionic cleansing, or acid neutralisation.

13. The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is $4.55 \times 10^3\,\Omega$. Calculate its molar conductivity. [3 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$, where R is measured in ohms and G in siemens.
- Conductivity is $\kappa = G(l/A) = l/(RA)$, where l is the length of the solution column and A is its cross-sectional area. With lengths in centimetres, its unit is $\mathrm{S\,cm^{-1}}$.
- Molar conductivity is $\Lambda_m = 1000\kappa/C$, where C is the concentration in $\mathrm{mol\,L^{-1}}$. The factor 1000 converts litres into cubic centimetres.

Step 1: Calculate the cross-sectional area The column is cylindrical. Its diameter is 1 cm, so its radius is $r = 0.5\,\mathrm{cm}$. Hence,

$$A = \pi r^2 = \pi(0.5)^2 = 0.7854\,\mathrm{cm^2}.$$

Use the radius in this expression; substituting the diameter would make the area four times too large.

Step 2: Obtain the conductivity from resistance Using $l = 45.5\,\mathrm{cm}$ and $R = 4.55 \times 10^3\,\Omega$,

$$\begin{aligned}\kappa &= \frac{l}{RA}\\ &= \frac{45.5}{(4.55 \times 10^3)(0.7854)}\\ &= 1.2732 \times 10^{-2}\,\mathrm{S\,cm^{-1}}.\end{aligned}$$

The length-to-area ratio supplies the cell constant, so the measured resistance is converted to a property of the solution.

Step 3: Convert conductivity to molar conductivity The molarity is $C = 0.05\,\mathrm{mol\,L^{-1}}$. Therefore,

$$\Lambda_m = \frac{1000(1.2732 \times 10^{-2})}{0.05} = 254.64\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Step 4: Conclusion The molar conductivity of the KOH solution is $\boxed{\Lambda_m \approx 254.6\,\mathrm{S\,cm^2\,mol^{-1}}}$.

Quick Tip to Solve: First halve the diameter to find the area; then use $\Lambda_m = 1000l/(RAC)$ with all lengths in centimetres.

14(a). Define the following terms with an example in each:

(a) Lyophobic colloids

(b) Homogeneous catalysis

(c) O/W emulsion [3 marks]

Solution:

Concept:

- A colloidal system has a dispersed phase distributed through a dispersion medium. Its affinity for that medium determines whether it is lyophilic or lyophobic.
- In catalysis, a catalyst changes the reaction rate without undergoing a net chemical change. Homogeneous catalysis requires the reactants and catalyst to be in the same phase.
- An emulsion is a colloidal dispersion of one liquid in another immiscible liquid. In O/W, oil is the dispersed phase and water is the dispersion medium.

Step 1: (a) Define lyophobic colloids and give an example Lyophobic colloids are colloidal systems in which the particles of the dispersed phase have little or no affinity for the dispersion medium. They are called solvent-hating colloids and usually require special methods of preparation, rather than forming by simple mixing. For example, a gold sol in water is a lyophobic colloid: gold particles form the dispersed phase and water forms the dispersion medium. Such sols are relatively unstable and can be coagulated by adding a small amount of a suitable electrolyte.

Step 2: (b) Define homogeneous catalysis and give an example Homogeneous catalysis is catalysis in which the catalyst and the reactants are present in the same phase. For example, nitric oxide catalyses the oxidation of sulphur dioxide by oxygen:

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g).$$

Here sulphur dioxide, oxygen and nitric oxide are all gases, so the catalysis is homogeneous. Nitric oxide participates in intermediate reactions and is regenerated overall.

Step 3: (c) Define an O/W emulsion and give an example An oil-in-water (O/W) emulsion is one in which fine droplets of oil are dispersed throughout a continuous aqueous medium. Milk is an example: liquid fat droplets are the dispersed phase and water is the dispersion medium. The notation identifies the dispersed liquid first and the continuous liquid second; thus O/W differs from a water-in-oil emulsion.

Step 4: Conclusion Lyophobic colloids have little affinity for their medium (gold sol); homogeneous catalysis has reactants and catalyst in one phase (NO-catalysed oxidation of SO_2); an O/W emulsion contains oil droplets in water (milk).

Quick Tip to Solve: Pair each definition with a named example; for O/W, read the first letter as the dispersed phase and the second as the medium.

OR

14(b). Write three differences between Physisorption and Chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance at the surface of another substance; the accumulated species is the adsorbate and the surface material is the adsorbent.
- Physisorption involves weak intermolecular attractions, whereas chemisorption involves chemical bond formation between adsorbate and surface.
- The nature of the attractive force determines the specificity and possible number of adsorbed layers. Comparisons should state the same property for both processes.

Step 1: Compare the forces holding the adsorbate In physisorption, adsorbate particles are held on the surface by weak van der Waals forces, without forming chemical bonds with the adsorbent. In chemisorption, strong chemical bonds are formed between the adsorbate and the surface. Thus the attachment in chemisorption is generally much stronger than in physisorption. This difference in the binding force is the fundamental distinction between the two types of adsorption.

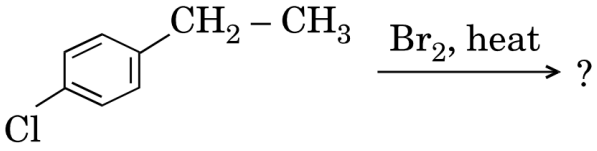
Step 2: Compare their specificity Physisorption is not highly specific: several different gases can be physically adsorbed on the same solid surface because van der Waals attractions act between many kinds of particles. Chemisorption is highly specific: it occurs only when the adsorbate and adsorbent can form appropriate chemical bonds. For example, a surface must have suitable chemical sites to bond to the species being chemisorbed.

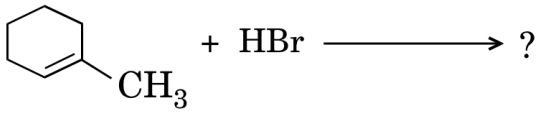
Step 3: Compare the number of layers formed Physisorption can form multimolecular layers. After the first layer attaches to the solid, further adsorbate particles can be attracted to the particles already adsorbed by intermolecular forces. Chemisorption forms a monomolecular layer because chemical bonds require direct contact with available sites on the adsorbent surface. Once these surface sites are occupied, additional layers cannot be bonded to those same sites in the chemisorption process.

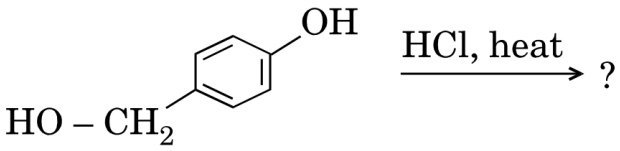
Step 4: Conclusion The three differences are: physisorption uses weak van der Waals forces, is not highly specific and can form multiple layers; chemisorption uses chemical bonds, is highly specific and forms a single molecular layer.

Quick Tip to Solve: Remember forces, specificity and layers: weak/general/multiple for physisorption; bonded/specific/single for chemisorption.

15. Draw the structures of the major monohalo product for each of the following reactions: [3 marks]

(a) 

(b) 

(c) 

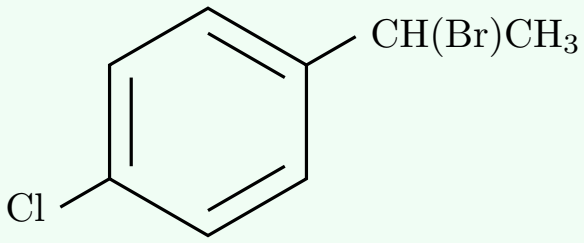
Solution:

Concept:

- Bromine with heat gives free-radical substitution at the benzylic carbon of an alkylbenzene. A benzylic radical is stabilised by resonance with the aromatic ring.
- Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov's rule: hydrogen adds to the carbon already bearing more hydrogen atoms.
- HCl converts a benzylic alcohol group into a chloromethyl group, but does not replace the phenolic hydroxyl group attached directly to the aromatic ring.

Step 1: (a) Brominate the benzylic position The substrate is para-chloroethylbenzene. Under the given conditions, bromination occurs in the side chain, at the carbon next to the ring. Removal of a hydrogen from this carbon produces a resonance-stabilised benzylic radical; bromination at the terminal methyl carbon would require a less stable primary radical. Thus the side chain changes from $-CH_2CH_3$ to $-CH(Br)CH_3$. The ring chlorine is retained:

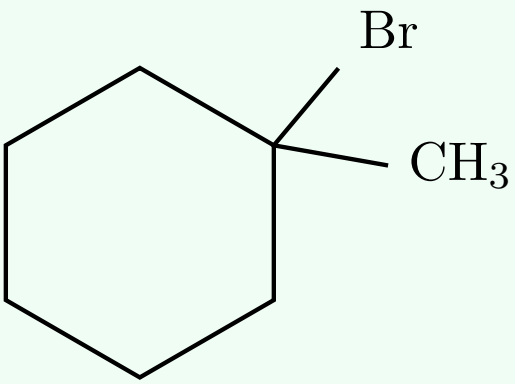
$$p\text{-}ClC_6H_4CH_2CH_3 + Br_2 \xrightarrow{\text{heat}} p\text{-}ClC_6H_4CH(Br)CH_3 + HBr.$$



(a) Benzylic bromination product

Step 2: (b) Add HBr across the double bond In 1-methylcyclohexene, the double-bond carbon bearing methyl has no hydrogen, whereas the other double-bond carbon has one hydrogen. Protonation at the latter carbon gives a tertiary carbocation on the methyl-bearing carbon. The reverse orientation would give a less stable secondary carbocation. Bromide attacks the tertiary carbocation, so Br and methyl occur on the same ring carbon, giving 1-bromo-1-methylcyclohexane.

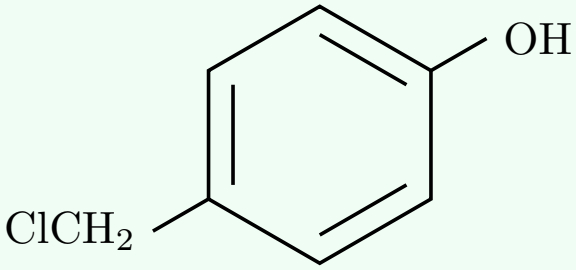
Quick Tip to Solve: First identify the conditions: heat with bromine selects the benzylic side chain; HBr selects the more substituted alkene carbon; HCl replaces benzylic OH while phenolic OH remains.



(b) 1-Bromo-1-methylcyclohexane

Step 3: (c) Replace the benzylic alcohol group The starting compound contains both a phenolic $-\mathrm{OH}$ group and a benzylic $-\mathrm{CH_2OH}$ group, para to each other. HCl protonates the benzylic alcohol, enabling water to leave and chloride to substitute. The phenolic carbon–oxygen bond is strengthened by resonance and is not cleaved by HCl under these conditions. Therefore:

$$p\text{-}\mathrm{HOC_6H_4CH_2OH} + \mathrm{HCl} \xrightarrow{\text{heat}} p\text{-}\mathrm{HOC_6H_4CH_2Cl} + \mathrm{H_2O}.$$



(c) 4-(Chloromethyl)phenol

Step 4: Conclusion The major products are:

(a) $p\text{-}\mathrm{ClC_6H_4CH(Br)CH_3}$;

(b) 1-bromo-1-methylcyclohexane;

(c) $p\text{-}\mathrm{HOC_6H_4CH_2Cl}$. Their structures are shown above; each reaction introduces one halogen atom.

Quick Tip to Solve: First identify the conditions: heat with bromine selects the benzylic side chain; HBr selects the more substituted alkene carbon; HCl replaces benzylic OH while phenolic OH remains.

16. A solution of glucose (Molar mass = 180 g mol^{-1}) in water has a boiling point of 100.20°C. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 K kg mol^{-1} and 0.512 K kg mol^{-1} respectively. [3 marks]

Solution:

Concept:

- For a dilute solution of a nonvolatile solute, the boiling-point elevation is $\Delta T_b = iK_b m$, where m is molality and i is the van't Hoff factor.
- The freezing-point depression of the same solution is $\Delta T_f = iK_f m$. Glucose does not dissociate or associate in water, so $i = 1$.
- Water boils at $100.00\,^\circ\mathrm{C}$ and freezes at $0.00\,^\circ\mathrm{C}$ at the pressure implicit in this question. Temperature differences have the same numerical values in kelvin and degrees Celsius.

Step 1: Calculate the boiling-point elevation Subtract the boiling point of pure water from that of the solution:

$$\Delta T_b = T_b(\text{solution}) - T_b(\text{water}) = 100.20 - 100.00 = 0.20\,\mathrm{K}.$$

The measured boiling point is higher because dissolved glucose lowers the vapour pressure of water.

Step 2: Determine the molality of the solution Since glucose is a nonelectrolyte, use $\Delta T_b = K_b m$:

$$m = \frac{\Delta T_b}{K_b} = \frac{0.20\,\mathrm{K}}{0.512\,\mathrm{K\,kg\,mol^{-1}}} = 0.390625\,\mathrm{mol\,kg^{-1}}.$$

The glucose molar mass is not needed: the boiling-point elevation directly supplies the number of solute particles per kilogram of solvent. Keep this unrounded molality for the next calculation.

Step 3: Calculate the depression and apply its sign The same solution has the same molality in the freezing-point relation:

$$\begin{aligned} \Delta T_f &= K_f m = 1.86 \times 0.390625 \\ &= 0.7265625\,\mathrm{K}, \\ T_f(\text{solution}) &= T_f(\text{water}) - \Delta T_f \\ &= 0.00 - 0.7265625\,^\circ\mathrm{C}. \end{aligned}$$

Depression is a positive difference, but the actual freezing temperature lies below zero. Equivalently, one may use $\Delta T_f / \Delta T_b = K_f / K_b$, since the common molality cancels.

Step 4: Conclusion The freezing point of the glucose solution is $\boxed{-0.727\,^\circ\mathrm{C}}$, approximately $-0.73\,^\circ\mathrm{C}$.

Quick Tip to Solve: For the same nonelectrolyte solution, multiply the boiling-point elevation by K_f/K_b, then subtract the result from the freezing point of pure water.

17. (a) Write the name of the method used for the refining of the following metals:

(i) Titanium

(ii) Germanium

(iii) Copper

(b) Write the name of the method of concentration applied for the following ores:

(i) Zinc blende

(ii) Haematite

(iii) Bauxite [3 marks]

Solution:

Concept:

- Refining purifies the metal after its extraction. The choice depends on properties such as formation of a volatile compound, impurity solubility in the melt, or electrochemical behaviour.
- Concentration removes gangue before metal extraction. It uses a physical property difference or selective dissolution of the desired ore in a suitable reagent.

Step 1: (a) Name the refining methods and their basis (i) Titanium: the van Arkel method, also called iodide refining. Impure titanium forms volatile titanium tetraiodide; its decomposition on a heated tungsten filament deposits pure titanium:

$$\mathrm{Ti} + 2\mathrm{I_2} \longrightarrow \mathrm{TiI_4}, \qquad \mathrm{TiI_4} \xrightarrow{\text{hot filament}} \mathrm{Ti} + 2\mathrm{I_2}.$$

(ii) Germanium: zone refining. Impurities are more soluble in the molten metal than in the solid. A narrow molten zone is moved repeatedly along the rod, carrying impurities to one end, which is then removed. This produces the high purity required for semiconductor use.

(iii) Copper: electrolytic refining. Impure copper is the anode, pure copper is the cathode and acidified copper sulphate solution is the electrolyte. Copper dissolves from the anode and deposits on the cathode; noble-metal impurities collect as anode mud.

Step 2: (b) Name the concentration methods and their basis (i) Zinc blende, ZnS: froth flotation. Sulphide particles are preferentially wetted by oil and rise with the froth, whereas gangue is wetted by water and remains behind.

(ii) Haematite, $\mathrm{Fe_2O_3}$: hydraulic washing, also called gravity separation. The heavier ore particles are separated from lighter gangue by a stream of water.

(iii) Bauxite: leaching, specifically Bayer's process. The alumina component dissolves selectively in hot concentrated sodium hydroxide as aluminate, while insoluble impurities are separated. Thus a chemical solubility difference is used rather than the oil-wetting principle used for zinc blende.

Step 3: Conclusion (a) Titanium: van Arkel (iodide) refining; germanium: zone refining; copper: electrolytic refining.

(b) Zinc blende: froth flotation; haematite: hydraulic washing (gravity separation); bauxite: leaching (Bayer's process).

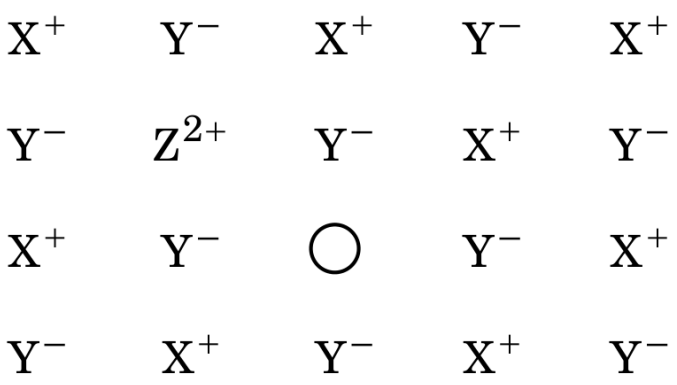
Quick Tip to Solve: Remember the property being used: volatile iodide for Ti, a moving melt for Ge, electrolysis for Cu; sulphide froth for ZnS, density for haematite, and selective alkali dissolution for bauxite.

18. (a) What is the radius of sodium atom if it crystallises in bcc structure with the cell edge of 400 pm?

(b) Examine the given defective crystal:

(i) Write the term used for this type of defect.

(ii) What is the result when XY crystal is doped with divalent (Z^{2+}) impurity? [3 marks]



Solution:

Concept:

- In a body-centred cubic (bcc) unit cell, atoms touch along the body diagonal. If a is the cell edge and r the atomic radius, $\sqrt{3}a = 4r$.
- An impurity defect can produce cation vacancies when a divalent cation replaces a monovalent cation. The crystal must remain electrically neutral.

Step 1: (a) Calculate the sodium atomic radius The body diagonal passes through a corner atom, the central atom and the diagonally opposite corner atom. Their touching radii contribute $r + 2r + r = 4r$, while the geometric length is $\sqrt{3}a$. Thus, for $a = 400\,\text{pm}$,

$$r = \frac{\sqrt{3}a}{4} = \frac{\sqrt{3} \times 400}{4}\,\text{pm} = 100\sqrt{3}\,\text{pm} \approx 173.2\,\text{pm}.$$

The relevant diagonal is the body diagonal, since the corner atoms do not touch along the cell edge in a bcc lattice.

Step 2: (b)(i) Identify the printed defect The figure shows a Z^{2+} ion occupying a site normally occupied by X^{+}, together with an empty cation site indicated by the circle. This is an **impurity defect**, involving a cation vacancy. The foreign ion and vacancy together preserve electrical neutrality; it is not a Frenkel defect because no ion is shown displaced into an interstitial site.

Step 3: (b)(ii) Explain the effect of divalent doping A Z^{2+} ion replacing one X^{+} ion introduces one extra positive charge. To compensate, one additional X^{+} lattice site is left vacant. Therefore one divalent impurity ion effectively replaces two monovalent cations: it occupies one of their sites and leaves the other empty. One cation vacancy is produced for each incorporated Z^{2+} ion, maintaining the charge balance with the Y^{-} anions.

Step 4: Conclusion (a) $r = 100\sqrt{3}\,\text{pm} \approx 173.2\,\text{pm}$. (b)(i) Impurity defect. (ii) Doping creates one X^{+} vacancy per Z^{2+} ion to maintain electrical neutrality.

Quick Tip to Solve: For bcc use the body diagonal, $4r = \sqrt{3}a$; for divalent doping count the extra positive charge to determine the cation vacancies.

19. Give reasons:

(a) Propanone is less reactive than ethanal towards nucleophilic addition reactions.

(b) O_2N - CH_2 - COOH has lower pKa value than CH_3COOH.

(c) $(CH_3)_2CH$ - CHO undergoes aldol condensation whereas $(CH_3)_3C$ - CHO does not. [3 marks]

Solution:

Concept:

- Nucleophilic addition is favoured by a more electrophilic and less sterically hindered carbonyl carbon. Alkyl groups donate electron density through the $+I$ effect.
- A stronger acid has a more stable conjugate base, a larger K_a, and a smaller $pK_a = -\log K_a$.
- Aldol reaction requires at least one α-hydrogen, a hydrogen on the carbon adjacent to the carbonyl group, so that an enolate can form.

Step 1: (a) Compare propanone with ethanal Propanone, CH_3COCH_3, has two electron-donating methyl groups attached to the carbonyl carbon, whereas ethanal, CH_3CHO, has one methyl group and one hydrogen. The stronger combined $+I$ effect in propanone reduces the partial positive charge on the carbonyl carbon, making attack by a nucleophile less favourable. Also, the two methyl groups create greater steric hindrance than the methyl group and small hydrogen of ethanal. Both electronic and steric effects therefore make propanone less reactive towards nucleophilic addition.

Step 2: (b) Explain the lower pKa of nitroacetic acid In O_2N-CH_2-COOH, the nitro group exerts a strong electron-withdrawing $-I$ effect. It withdraws electron density through sigma bonds and stabilises the negative charge of the conjugate base, $O_2N-CH_2-COO^-$. In acetic acid, the methyl group has a $+I$ effect and tends to destabilise the carboxylate ion. Proton loss is therefore more favourable from nitroacetic acid: its K_a is larger and hence its pK_a is lower.

Step 3: (c) Check the alpha-hydrogens In $(CH_3)_2CH-CHO$, the carbon adjacent to $-CHO$ is a CH group and carries one α-hydrogen. A base can remove this hydrogen to form an enolate, which attacks another carbonyl molecule in the aldol reaction. In $(CH_3)_3C-CHO$, the adjacent carbon is bonded to three methyl groups and the aldehyde carbon; it has no hydrogen. It cannot form the required enolate by removal of an α-hydrogen and therefore does not undergo self-aldol condensation. The hydrogens of its methyl groups are not on the alpha carbon.

Step 4: Conclusion (a) Propanone has greater electron donation and steric hindrance. (b) The nitro group's $-I$ effect stabilises the conjugate base and lowers pK_a. (c) $(CH_3)_2CHCHO$ has an α-hydrogen; $(CH_3)_3CCHO$ has none.

Quick Tip to Solve: For aldol eligibility, inspect only the carbon immediately next to the carbonyl carbon; hydrogens farther away do not count as alpha-hydrogens.

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

(a) Neoprene

(b) Buna-N

(c) PHBV [3 marks]

Solution:

Concept:

- Monomers are the small molecules from which a polymer is formed. Addition polymerisation uses unsaturated monomers, while polyester formation links hydroxyl and carboxyl groups.
- Neoprene is a homopolymer of chloroprene; Buna-N and PHBV each contain units derived from two different monomers.

Step 1: (a) Neoprene The monomer is **chloroprene**, whose systematic name is **2-chlorobuta-1,3-diene**. Its condensed structural formula is

$$\mathrm{CH_2 = C(Cl) - CH = CH_2}.$$

The four-carbon conjugated diene chain carries chlorine on carbon 2. Addition polymerisation of this monomer produces neoprene. The chlorine belongs to the monomer itself; neoprene is not obtained by using unsubstituted buta-1,3-diene alone.

Step 2: (b) Buna-N Buna-N is a copolymer of **buta-1,3-diene** and **acrylonitrile** (prop-2-enenitrile). Their structures are

$$\begin{aligned} \text{Buta-1,3-diene:} &\quad \mathrm{CH_2 = CH - CH = CH_2}, \\ \text{Acrylonitrile:} &\quad \mathrm{CH_2 = CH - C \equiv N}. \end{aligned}$$

Both molecules contain carbon-carbon double bonds that participate in addition copolymerisation. The nitrile group of acrylonitrile remains as a substituent in the polymer and distinguishes Buna-N from Buna-S, which uses styrene instead.

Step 3: (c) PHBV PHBV is poly(β-hydroxybutyrate-co-β-hydroxyvalerate). Its monomers are **3-hydroxybutanoic acid** and **3-hydroxypentanoic acid**:

$$\begin{aligned} \text{3-Hydroxybutanoic acid:} &\quad \mathrm{CH_3 - CH(OH) - CH_2 - COOH}, \\ \text{3-Hydroxypentanoic acid:} &\quad \mathrm{CH_3 - CH_2 - CH(OH) - CH_2 - COOH}. \end{aligned}$$

Numbering begins at the carboxyl carbon, so the hydroxyl group is on carbon 3 in both molecules. Each monomer contains both an alcohol group and a carboxylic acid group; their linkage creates the ester bonds of the biodegradable copolyester.

Step 4: Conclusion Neoprene: chloroprene. Buna-N: buta-1,3-diene and acrylonitrile. PHBV: 3-hydroxybutanoic acid and 3-hydroxypentanoic acid, with the structures shown above.

Quick Tip to Solve: Remember N in Buna-N as the nitrile monomer; in PHBV, count four and five carbons from COOH and place OH on carbon 3 in each monomer.

21. (a) Define crystal field splitting energy. On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$.

(b) Write the hybridization and magnetic character of $[CoF_6]^{3-}$. (At. no. of Co = 27) [3 marks]

Solution:

Concept:

- In an octahedral ligand field, the five initially degenerate metal d orbitals split into the lower-energy t_{2g} set and the higher-energy e_g set. Their energy separation is the octahedral crystal field splitting energy, Δ_o.
- The competition between Δ_o and pairing energy P, the energy required to pair electrons in one orbital, determines whether an octahedral complex is low spin or high spin.
- For hybridization and magnetic character, first determine the metal oxidation state and its d-electron count, then count unpaired electrons in the ligand field.

Step 1: (a) Define the splitting and fill the strong-field configuration Crystal field splitting energy is the energy difference between the two sets of d orbitals produced by the surrounding ligands. For an octahedral complex,

$$\Delta_o = E(e_g) - E(t_{2g}).$$

If $\Delta_o > P$, pairing in the lower t_{2g} set costs less energy than promotion to e_g. For a d^4 ion, the first three electrons singly occupy the three t_{2g} orbitals, and the fourth pairs in one of them. Thus the low-spin configuration is $t_{2g}^4 e_g^0$, with occupancies $(2, 1, 1)$ in t_{2g} and two unpaired electrons.

Step 2: (b) Find the configuration of cobalt in the fluoride complex Let the oxidation state of cobalt in $[CoF_6]^{3-}$ be x. Each fluoride ligand has charge -1, so

$$x + 6(-1) = -3 \quad \Rightarrow \quad x = +3.$$

Cobalt has atomic number 27 and configuration $[Ar]3d^7 4s^2$. Removing the two $4s$ electrons and one $3d$ electron gives Co^{3+} : $[Ar]3d^6$.

Step 3: (b) Determine hybridization and magnetic character Fluoride is a weak-field ligand, so this octahedral complex is high spin. Its six d electrons occupy $t_{2g}^4 e_g^2$: the lower orbitals have occupancies $(2, 1, 1)$, and each upper orbital contains one electron. There are therefore four unpaired electrons. In valence-bond terminology, the inner $3d$ orbitals do not supply two vacant orbitals; one $4s$, three $4p$ and two $4d$ orbitals form six sp^3d^2 hybrid orbitals. This is an outer-orbital octahedral complex and is paramagnetic.

Step 4: Conclusion (a) Δ_o is the separation between the octahedral t_{2g} and e_g levels; for d^4 with $\Delta_o > P$, the configuration is $t_{2g}^4 e_g^0$. (b) $[CoF_6]^{3-}$ has sp^3d^2 hybridization and is paramagnetic with four unpaired electrons.

Quick Tip to Solve: Determine the cobalt oxidation state before counting d electrons; weak-field fluoride makes this d6 complex high spin.

22. What happens when

(a) $(CH_3)_3C$ - O - CH_3 is treated with HI,

(b) Anisole is treated with CH_3COCl/anhydrous $AlCl_3$,

(c) Phenol is treated with Br_2/CS_2?

Write chemical equations in support of your answer. [3 marks]

Solution:

Concept:

- Hydrogen iodide cleaves protonated ethers. When one alkyl group is tertiary, cleavage forms the stable tertiary carbocation, which is captured by iodide.
- The methoxy group of anisole activates its aromatic ring and directs electrophilic substitution to the ortho and para positions. Anhydrous $AlCl_3$ enables Friedel–Crafts acylation.
- Phenol undergoes ortho/para-directed bromination. In a nonpolar solvent such as CS_2, controlled bromination gives monobromophenols, with the para product predominating.

Step 1: (a) Cleave tert-butyl methyl ether with HI The ether oxygen is first protonated. The bond between oxygen and the tertiary carbon then breaks, since it can produce a stable tert-butyl carbocation. Iodide captures this carbocation, while the methyl group remains attached to oxygen as methanol:

$$(CH_3)_3C{-}O{-}CH_3 + HI \longrightarrow (CH_3)_3C{-}I + CH_3OH.$$

Thus the products of this ether cleavage are tert-butyl iodide and methanol.

Step 2: (b) Acylate anisole Acetyl chloride and anhydrous aluminium chloride provide the acetyl electrophile. The $-OCH_3$ group directs attack to the ortho and para positions of the ring. The products are 2-methoxyacetophenone and 4-methoxyacetophenone, with the para isomer major because it suffers less steric hindrance:

$$C_6H_5OCH_3 + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} o\text{-}CH_3COC_6H_4OCH_3 + HCl,$$

$$C_6H_5OCH_3 + CH_3COCl \xrightarrow{\text{anhydrous } AlCl_3} p\text{-}CH_3COC_6H_4OCH_3 + HCl.$$

Each equation represents one alternative substitution pathway.

Step 3: (c) Brominate phenol in carbon disulphide Phenol gives 2-bromophenol and 4-bromophenol (major) in the nonpolar solvent CS_2:

$$C_6H_5OH + Br_2 \xrightarrow{CS_2} o\text{-}BrC_6H_4OH + HBr,$$

$$C_6H_5OH + Br_2 \xrightarrow{CS_2} p\text{-}BrC_6H_4OH + HBr.$$

The hydroxyl group activates both ortho and para positions; less crowding favours para substitution. Bromination in this solvent gives monobromo products.

Step 4: Conclusion (a) Tert-butyl iodide and methanol form. (b) Anisole gives ortho- and para-methoxyacetophenone, with para major. (c) Phenol gives ortho- and para-bromophenol in CS_2, with para major.

Quick Tip to Solve: Check the ether's tertiary carbon in (a), and the solvent in (c): HI cleavage and phenol bromination depend on these details.

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, Veena, 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 proteins and vitamins-rich food like fruits, salads, sprouts, etc. The decision was welcomed by the parents and students.

After reading the above passage, answer the following questions:

(a) What are the values (at least two) displayed by Veena?

(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 means using scientific awareness to protect the health of others and taking constructive action through the appropriate authority.
- Starch is the principal storage polysaccharide of plants and is abundant in cereal grains such as wheat, whose flour is used to make bread.
- The secondary structure of a protein describes regular local folding of its polypeptide chain, stabilised mainly by hydrogen bonding between peptide groups.
- Vitamins are classified by their solubility: the B-group vitamins and vitamin C are water soluble, whereas vitamins A, D, E and K are fat soluble.

Step 1: (a) Identify Veena's values from her actions Veena shows concern for the health and welfare of fellow students: after learning about harmful food additives, she wants others to be aware of their adverse effects. She also shows social responsibility and initiative by approaching the principal and requesting a practical change in the canteen menu. Her conduct further reflects scientific awareness, since she applies information learnt from an educational programme to a real-life situation. Concern for others and social responsibility are two clear values supported directly by the passage.

Step 2: (b) Identify the polysaccharide in bread Bread is commonly prepared from wheat flour. Wheat stores carbohydrate mainly as starch, a polysaccharide composed of glucose units. Starch contains amylose and amylopectin. Therefore, the polysaccharide asked for is starch; glucose itself is a monosaccharide, and cellulose is the structural polysaccharide of plant cell walls.

Step 3: (c) Name the secondary structures of proteins The two common secondary structures are the α-helix and the β-pleated sheet. In an α-helix, the polypeptide backbone coils into a helix and is stabilised by hydrogen bonds within the chain. In a β-pleated sheet, extended chain segments lie alongside one another and are held together by hydrogen bonds between peptide groups. These describe local arrangements of the backbone, whereas the primary structure is the amino-acid sequence.

Step 4: (d) Give water-soluble vitamin examples Vitamin B_1 (thiamine) and vitamin C (ascorbic acid) are two examples of water-soluble vitamins. Vitamin B_1 belongs to the water-soluble B group.

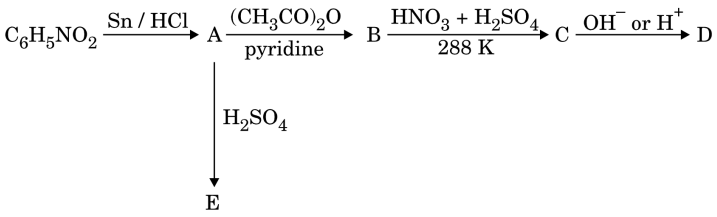
Quick Tip to Solve: For this passage, connect each value to Veena's action; remember bread contains starch, proteins have helix and sheet secondary forms, and B-group vitamins plus C are water soluble.

Vitamin C is also water soluble. Vitamins A, D, E and K would not be suitable examples because they are fat soluble.

Step 5: Conclusion (a) Concern for others' health and social responsibility (also initiative and scientific awareness). (b) Starch. (c) α-helix and β-pleated sheet. (d) Vitamin B_1 (thiamine) and vitamin C (ascorbic acid).

Quick Tip to Solve: For this passage, connect each value to Veena's action; remember bread contains starch, proteins have helix and sheet secondary forms, and B-group vitamins plus C are water soluble.

24(a). Write the structures of A, B, C, D and E in the following reactions: [5 marks]



Solution:

Concept:

- Reduction of an aromatic nitro group gives an amino group without changing the benzene ring: $-NO_2 \rightarrow -NH_2$.
- Acetylation converts $-NH_2$ into $-NHCOCH_3$, protecting the amino group. This group directs electrophilic substitution to the ortho and para positions.
- Hydrolysis removes the acetyl protecting group. Aniline also acts as a base and forms an anilinium salt with a strong acid.

Step 1: Identify A by reduction Tin and hydrochloric acid reduce nitrobenzene to aniline. The carbon skeleton remains unchanged; only the nitro group is reduced. Thus the structure of A is $C_6H_5 - NH_2$.

$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O.$$

Although aniline is protonated in the acidic reaction medium, the organic product used in the next acetylation step is aniline.

Step 2: Identify B by acetylation Aniline reacts with acetic anhydride in pyridine. One hydrogen on nitrogen is replaced by an acetyl group, giving acetanilide, B, with structure $C_6H_5 - NH - C(=O) - CH_3$.

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

Acetylation moderates the strongly activating amino group and protects it during nitration.

Step 3: Identify C by nitration The mixture of nitric acid and sulphuric acid supplies the nitronium electrophile. At 288 K, acetanilide undergoes nitration mainly at the para position relative to $-NHCOCH_3$. Both ortho and para substitution are directed by this group, but the para product

Quick Tip to Solve: Follow the branch from aniline separately: acetylate, nitrate para, and hydrolyse on the main route; sulphuric acid alone gives the anilinium salt.

predominates because steric hindrance is lower.

$$C_6H_5NHCOCH_3 + HNO_3 \longrightarrow \text{p-}NO_2 - C_6H_4 - NHCOCH_3 + H_2O.$$

Hence C is p-nitroacetanilide, with $-NO_2$ and $-NHCOCH_3$ on opposite ring carbons.

Step 4: Identify D by hydrolysis Acidic or alkaline hydrolysis cleaves the amide protecting group of C. The acetyl group is removed, while the nitro group retains its para position on the ring. After the usual work-up, D is p-nitroaniline:

$$\text{p-}NO_2 - C_6H_4 - NHCOCH_3 + H_2O \longrightarrow \text{p-}NO_2 - C_6H_4 - NH_2 + CH_3COOH.$$

In alkaline medium the acid product is acetate; the aromatic product has the same $-NH_2$ structure after isolation.

Step 5: Identify E by salt formation The separate downward arrow starts from A, aniline, and shows only sulphuric acid. Protonation of nitrogen produces anilinium hydrogen sulphate:

$$C_6H_5NH_2 + H_2SO_4 \longrightarrow [C_6H_5NH_3]^+[HSO_4]^-.$$

Thus E is an acid-base salt, with the positive charge on the protonated amino group. Heating, which would be required to obtain sulphanilic acid, is not specified on this arrow.

Step 6: Conclusion $A = C_6H_5 - NH_2$ (aniline); $B = C_6H_5 - NH - C(=O) - CH_3$ (acetanilide); $C = p\text{-}NO_2 - C_6H_4 - NH - C(=O) - CH_3$ (p-nitroacetanilide); $D = p\text{-}NO_2 - C_6H_4 - NH_2$ (p-nitroaniline); $E = [C_6H_5NH_3]^+[HSO_4]^-$ (anilinium hydrogen sulphate).

Quick Tip to Solve: Follow the branch from aniline separately: acetylate, nitrate para, and hydrolyse on the main route; sulphuric acid alone gives the anilinium salt.

OR

24(b). (a) Write the structures of the main products when benzene diazonium chloride reacts with the following reagents:

(i) CuCN

(ii) CH_3CH_2OH

(iii) Cu/HCl

(b) Arrange the following in the increasing order of their basic strength:

CH_3NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$

(c) Write one chemical test to distinguish between Aniline and Ethyl amine. [5 marks]

Solution:

Concept:

- An aryl diazonium group is readily replaced with loss of nitrogen gas. CuCN replaces it by $-CN$, copper and HCl replace it by chlorine, and ethanol reduces it to hydrogen.

Quick Tip to Solve: For diazonium reactions, track the group replacing nitrogen: CuCN gives CN, ethanol gives H, and Cu/HCl gives Cl; keep the nitrous acid test cold.

- Basic strength depends on the availability of the nitrogen lone pair for accepting a proton. Resonance delocalisation in aniline reduces this availability, whereas the electron-releasing effect of methyl groups increases it in methylamines.
- A primary aromatic amine forms a diazonium salt with nitrous acid at 273–278 K. A primary aliphatic amine instead gives an alcohol with evolution of nitrogen because its diazonium intermediate is unstable.

Step 1: (a)(i) Replacement by the cyano group Benzene diazonium chloride undergoes the Sandmeyer reaction with cuprous cyanide. The diazonium group is replaced by a cyano group bonded through carbon, giving benzonitrile:

$$C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5{-}C \equiv N + N_2.$$

The required product structure is therefore $C_6H_5{-}C \equiv N$; it is an aryl nitrile, not an isocyanide.

Step 2: (a)(ii) Reduction by ethanol Ethanol replaces the diazonium group by hydrogen, so the aromatic product is benzene. Ethanol itself is oxidised to ethanal:

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + CH_3CHO + N_2 + HCl.$$

Thus the main organic product derived from the diazonium salt has the benzene structure, $C_6H_5{-}H$. An ethoxy group is not introduced into the ring in this reaction.

Step 3: (a)(iii) Replacement by chlorine Copper powder in hydrochloric acid brings about the Gattermann replacement of the diazonium group by chlorine:

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu/HCl} C_6H_5{-}Cl + N_2.$$

The product structure is $C_6H_5{-}Cl$, chlorobenzene. Nitrogen gas is liberated as the carbon–nitrogen bond is replaced by a carbon–chlorine bond.

Step 4: (b) Compare basic strengths In aniline, the nitrogen lone pair is delocalised directly into the benzene ring, making proton acceptance least favourable. In benzylamine, a $-CH_2-$ group separates nitrogen from the ring, so its lone pair does not participate in the ring's resonance. It is consequently more basic than aniline. Benzylamine is less basic than methylamine because the phenyl group's inductive withdrawal through the methylene group reduces electron density compared with the electron-releasing methyl group. Dimethylamine is still more basic than methylamine in the usual aqueous comparison: two methyl groups donate electron density, and the protonated secondary amine is sufficiently solvated. Hence the increasing order is

$$C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH.$$

Step 5: (c) Distinguish by the nitrous acid test Treat each amine with freshly prepared nitrous acid, generated using sodium nitrite and dilute HCl, while keeping the mixture at 273–278 K. Ethylamine evolves nitrogen gas and forms ethanol:

$$C_2H_5NH_2 + HNO_2 \longrightarrow C_2H_5OH + N_2\uparrow + H_2O.$$

Quick Tip to Solve: For diazonium reactions, track the group replacing nitrogen: CuCN gives CN, ethanol gives H, and Cu/HCl gives Cl; keep the nitrous acid test cold.

Aniline forms benzene diazonium chloride under these cold acidic conditions, without the immediate nitrogen evolution characteristic of ethylamine:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2H_2O.$$

For a positive confirmation, add the cold diazonium solution to alkaline β-naphthol: an orange-red azo dye forms. Ethylamine does not give this azo-dye coupling test. Maintain the low temperature during diazotisation, since warming an aromatic diazonium salt can also release nitrogen and obscure the distinction.

Step 6: Conclusion (a) The products are (i) benzonitrile, $C_6H_5-C\equiv N$; (ii) benzene, C_6H_5-H; and (iii) chlorobenzene, C_6H_5-Cl. (b) $C_6H_5NH_2 < C_6H_5CH_2NH_2 < CH_3NH_2 < (CH_3)_2NH$. (c) Cold nitrous acid gives nitrogen gas with ethylamine, whereas aniline forms a diazonium salt that couples to produce an azo dye.

Quick Tip to Solve: For diazonium reactions, track the group replacing nitrogen: CuCN gives CN, ethanol gives H, and Cu/HCl gives Cl; keep the nitrous acid test cold.

25(a). A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.

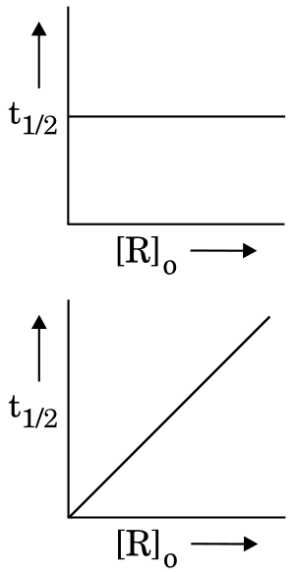
(b) Predict the order of the reaction in the given plots:

(i)

(ii)

where $[R]_0$ is the initial concentration of reactant.

(Given: log 2 = 0.3010, log 4 = 0.6021) [5 marks]



Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[R]_0}{[R]_t}$, where k is the rate constant and $[R]_t$ is the reactant concentration remaining after time t.
- The first-order half-life is $t_{1/2} = \dfrac{0.693}{k} = \dfrac{2.303\log 2}{k}$. It is independent of the initial reactant concentration.
- For a zero-order reaction, $[R]_t = [R]_0 - kt$, so $t_{1/2} = \dfrac{[R]_0}{2k}$. At constant temperature, this half-life is directly proportional to $[R]_0$.

Step 1: (a) Identify the fraction of reactant remaining Completion refers to the reactant consumed. If 75% has reacted in $40\,\text{min}$, the remaining fraction is $25\% = 1/4$. Thus $[R]_{40} = [R]_0/4$, and the concentration ratio to insert into the first-order equation is $[R]_0/[R]_{40} = 4$. Using the consumed fraction instead of the remaining fraction would give an incorrect rate constant.

Step 2: Calculate the rate constant and half-life Substituting the given time and logarithm,

$$k = \frac{2.303}{40}\log 4 = \frac{2.303 \times 0.6021}{40} = 0.034666\,\text{min}^{-1}.$$

Therefore,

$$t_{1/2} = \frac{2.303 \times 0.3010}{0.034666} = 40\frac{0.3010}{0.6021} \simeq 20.0\,\text{min}.$$

The slight numerical difference from exactly 20 comes from rounding the supplied logarithms. An independent check is that the reactant decreases from $[R]_0$ to $[R]_0/2$, then to $[R]_0/4$, in two equal first-order half-lives. The given 40 minutes therefore represents two half-lives.

Step 3: (b)(i) Interpret the horizontal half-life plot The vertical axis is $t_{1/2}$ and the horizontal axis is $[R]_0$. The horizontal line means that changing the initial concentration does not change the half-life. This matches $t_{1/2} = 0.693/k$, which contains no concentration term. Hence plot (i) represents a first-order reaction. The plot is a half-life versus initial-concentration plot, so it must not be confused with a concentration versus time graph.

Step 4: (b)(ii) Interpret the straight line through the origin In plot (ii), $t_{1/2}$ increases linearly with $[R]_0$, and the line passes through the origin. Setting $[R]_t = [R]_0/2$ in the zero-order integrated equation gives

$$\frac{[R]_0}{2} = [R]_0 - kt_{1/2}, \qquad t_{1/2} = \frac{[R]_0}{2k}.$$

Thus its slope is $1/(2k)$, and doubling the initial concentration doubles the half-life. This is the characteristic dependence of a zero-order reaction. A first-order reaction would instead give the horizontal line seen in (i).

Step 5: Conclusion (a) $\boxed{t_{1/2} = 20\,\text{min}}$. (b) Plot (i): $\boxed{\text{first order}}$; plot (ii): $\boxed{\text{zero order}}$.

Quick Tip to Solve: For first order, 75 percent completion leaves one quarter of the reactant, which is exactly two half-lives. For the plots, read the axes first: constant half-life means first order, while half-life proportional to initial concentration means zero order.

OR

25(b). The following data were obtained for the reaction:

$2\,NO + O_2 \rightarrow 2\,NO_2$

Experiment	[NO]/M	$[O_2]$/M	Initial rate of formation of NO_2 / M min^{-1}
1	0.3	0.2	7.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

(a) Find the order of reaction with respect to NO and O_2.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k). [5 marks]

Solution:

Concept:

- In the initial-rate method, write $r = k[\mathrm{NO}]^m[\mathrm{O_2}]^n$, where r is the given initial rate of formation of $\mathrm{NO_2}$, k is the rate constant, and m, n are the experimentally determined partial orders.
- Comparing two experiments in which one reactant concentration is constant eliminates that reactant and the rate constant. The overall order is the sum $m + n$; stoichiometric coefficients do not determine these experimental orders.
- For overall order p, the units of k are concentration raised to $1 - p$, divided by time. Here concentration is in M and time is in minutes.

Step 1: (a) Determine the order with respect to NO Use experiments 2 and 4, since $[\mathrm{O_2}] = 0.1\,\mathrm{M}$ in both. The NO concentration increases from 0.1 to $0.4\,\mathrm{M}$, while the rate increases from 6.0×10^{-3} to $2.40 \times 10^{-2}\,\mathrm{M\,min^{-1}}$. Therefore,

$$\frac{r_4}{r_2} = \left(\frac{[\mathrm{NO}]_4}{[\mathrm{NO}]_2}\right)^m, \qquad 4 = 4^m.$$

Thus $m = 1$: the rate is directly proportional to the NO concentration when the oxygen concentration is held fixed.

Step 2: (a) Determine the order with respect to oxygen Compare experiments 1 and 3, where $[\mathrm{NO}] = 0.3\,\mathrm{M}$ is unchanged. Doubling oxygen from 0.2 to $0.4\,\mathrm{M}$ multiplies the rate by four:

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \left(\frac{0.4}{0.2}\right)^n, \qquad 4 = 2^n.$$

Hence $n = 2$. The rate depends on the square of the oxygen concentration. This conclusion follows from the table even though oxygen has coefficient one in the balanced reaction.

Step 3: (b) Form the rate law and add the partial orders Substituting the independently established exponents gives

$$r = \frac{d[\mathrm{NO_2}]}{dt} = k[\mathrm{NO}][\mathrm{O_2}]^2.$$

Quick Tip to Solve: Compare experiments 2 and 4 for NO, then 1 and 3 for oxygen: a fourfold rate change means first order for a fourfold concentration change, but second order for a twofold change.

The overall order is $1 + 2 = 3$. Here r denotes precisely the product-formation rate tabulated in the question. Using the stoichiometrically normalised reaction rate $\frac{1}{2}d[\mathrm{NO_2}]/dt$ would change the numerical rate constant, so the supplied rate convention must be retained in the calculation.

Step 4: (c) Calculate and check the rate constant From experiment 2,

$$k = \frac{r_2}{[\mathrm{NO}]_2[\mathrm{O_2}]_2^2} = \frac{6.0 \times 10^{-3}}{(0.1)(0.1)^2} = 6.0\,\mathrm{M^{-2}\,min^{-1}}.$$

The units follow from $(\mathrm{M\,min^{-1}})/\mathrm{M^3}$. As a consistency check, this value predicts the rates in experiments 1, 3 and 4 as, respectively,

$$6.0(0.3)(0.2)^2 = 0.072,$$
$$6.0(0.3)(0.4)^2 = 0.288,$$
$$6.0(0.4)(0.1)^2 = 0.024,$$

all in $\mathrm{M\,min^{-1}}$, agreeing with every entry in the printed table.

Step 5: Conclusion (a) Order in NO: 1; order in $\mathrm{O_2}$: 2. (b) $r = k[\mathrm{NO}][\mathrm{O_2}]^2$, with overall order 3. (c) $k = 6.0\,\mathrm{M^{-2}\,min^{-1}}$, equivalently $6.0\,\mathrm{L^2\,mol^{-2}\,min^{-1}}$, for the given rate of formation of $\mathrm{NO_2}$.

Quick Tip to Solve: Compare experiments 2 and 4 for NO, then 1 and 3 for oxygen: a fourfold rate change means first order for a fourfold concentration change, but second order for a twofold change.

26(a). Account for the following:

(i) BiH_3 is the strongest reducing agent in Group 15 elements hydrides.

(ii) Cl_2 acts as a bleaching agent.

(iii) Noble gases have very low boiling points.

(b) Draw the structures of the following:

(i) $H_4P_2O_7$

(ii) $XeOF_4$ [5 marks]

Solution:

Concept:

- The reducing power of Group 15 hydrides increases as the element-hydrogen bond weakens down the group; their thermal stability decreases.
- Moist chlorine bleaches by oxidation. Noble gas atoms attract one another only through weak London dispersion forces.
- Pyrophosphoric acid contains two tetrahedral phosphorus centres joined by an oxygen bridge. In VSEPR theory, $\mathrm{XeOF_4}$ has six electron domains: five bonding domains and one lone pair.

Step 1: (a)(i) Reducing power of bismuth hydride Down Group 15, the central atom becomes larger and overlap with the hydrogen orbital becomes poorer. Consequently the element-hydrogen bond strength and hydride stability decrease in the order

$$\mathrm{NH_3} > \mathrm{PH_3} > \mathrm{AsH_3} > \mathrm{SbH_3} > \mathrm{BiH_3}.$$

Quick Tip to Solve: Count a multiple bond as one VSEPR domain: XeOF4 has five bonded atoms plus one lone pair, giving a square pyramid.

The weak Bi-H bonds make BiH_3 the least stable hydride and the most readily oxidised. It therefore donates reducing equivalents most readily and has the greatest reducing power among these hydrides.

Step 2: (a)(ii) Bleaching action of chlorine Chlorine reacts with water to produce hydrochloric acid and hypochlorous acid:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

Hypochlorous acid oxidises coloured substances into colourless products. The usual school-level representation is

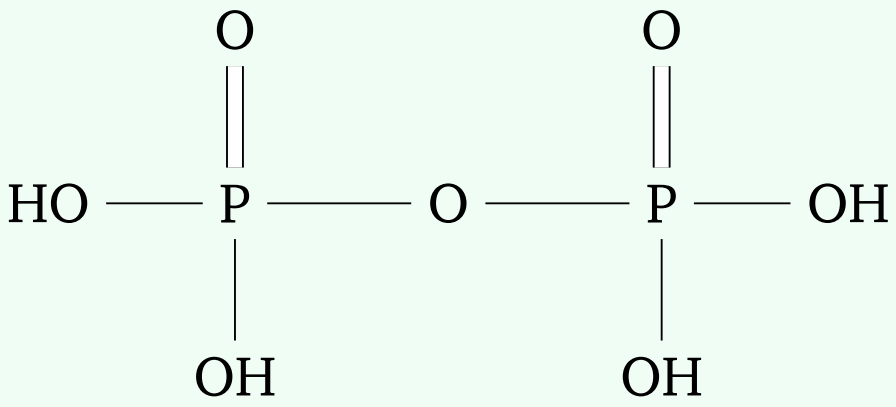
$$HOCl \longrightarrow HCl + [O],$$

$$\text{coloured substance} + [O] \longrightarrow \text{colourless substance}.$$

Here $[O]$ represents oxidising oxygen in this shorthand description. Moisture is necessary, so dry chlorine does not bleach dry coloured material. The oxidation causes permanent bleaching.

Step 3: (a)(iii) Low boiling points of noble gases Noble gases are monatomic and have closed valence shells. Their atoms have no permanent dipole moments; the only interatomic attractions are weak London dispersion forces caused by temporary dipoles. Little energy is needed to separate the atoms into the gaseous state, giving very low boiling points. These forces strengthen as atomic size and polarisability increase down the group, so boiling points increase down the group while remaining low.

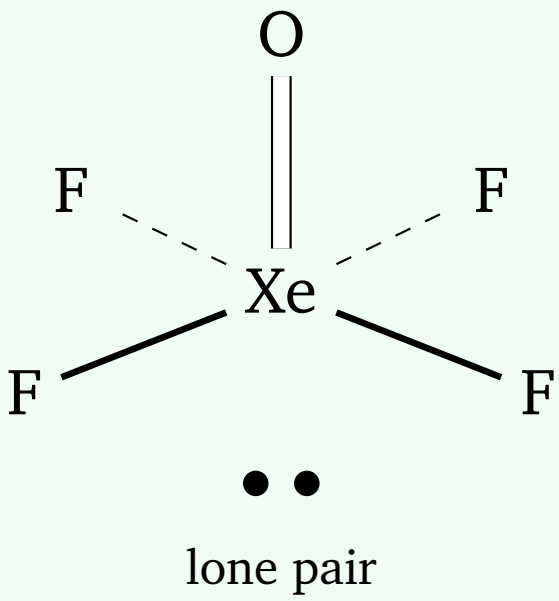
Step 4: (b)(i) Structure of pyrophosphoric acid In $H_4P_2O_7$, the two phosphorus atoms are linked by a P-O-P bridge. Each phosphorus is bonded to one terminal oxygen through a double bond, two hydroxyl groups and the bridging oxygen. Thus the four hydrogen atoms occur in four O-H groups, with no P-H bond. The connectivity is $(HO)_2P(=O)-O-P(=O)(OH)_2$; the arrangement around each phosphorus is approximately tetrahedral.



Connectivity of pyrophosphoric acid; each phosphorus centre is tetrahedral.

Step 5: (b)(ii) Structure of xenon oxytetrafluoride Xenon has four Xe-F bonds, one Xe=O bond and one lone pair. A double bond counts as a single electron domain, so the six domains have an octahedral arrangement. The four fluorine atoms form the square base, with oxygen at one axial position and the lone pair at the opposite axial position. The molecular shape, considering only atoms, is square pyramidal. The drawing places the lone pair opposite the oxygen to make the geometry explicit.

Quick Tip to Solve: Count a multiple bond as one VSEPR domain: XeOF4 has five bonded atoms plus one lone pair, giving a square pyramid.



Square-pyramidal XeOF4; the lone pair lies opposite the axial oxygen.

Step 6: Conclusion BiH_3 has the weakest element-hydrogen bonds and strongest reducing power; moist chlorine bleaches by oxidation; noble gases have weak dispersion forces and hence low boiling points. The structures are the oxygen-bridged $H_4P_2O_7$ and square-pyramidal $XeOF_4$ shown above.

Quick Tip to Solve: Count a multiple bond as one VSEPR domain: XeOF4 has five bonded atoms plus one lone pair, giving a square pyramid.

OR

26(b). (a) Although nitrogen and chlorine have nearly same electronegativity yet nitrogen forms hydrogen bonding while chlorine does not. Why?

(b) What happens when F_2 reacts with water?

(c) Write the name of the gas evolved when Ca_3P_2 is dissolved in water.

(d) Write the formula of a noble gas species which is isostructural with IBr_2^-.

(e) Complete the equation: $[Fe(H_2O)_6]^{2+}$ + NO $\rightarrow$? [5 marks]

Solution:

Concept:

- Hydrogen bonding requires both high electronegativity and a small atomic size: a compact lone pair attracts hydrogen strongly in a neighbouring molecule.
- Fluorine is a very strong oxidising agent and oxidises water to oxygen while itself forming fluoride in hydrogen fluoride.
- Hydrolysis of a metal phosphide produces phosphine, PH_3. Molecular shapes follow the number of bonding domains and lone pairs on the central atom.

Quick Tip to Solve: For isostructural species, count bond domains and lone pairs; for the brown-ring complex, replace exactly one water ligand by NO.

- Nitric oxide forms a nitrosyl complex with aqueous iron(II) ions by replacing one coordinated water molecule.

Step 1: (a) Compare the sizes of nitrogen and chlorine Nitrogen is much smaller than chlorine. Its lone pair is concentrated in a small volume, so its electron density is high and it can attract the hydrogen atom of a neighbouring polar molecule strongly. Chlorine has a larger, more diffuse electron cloud; despite its nearly similar electronegativity, its lone pairs do not provide the sufficiently concentrated attraction needed for appreciable conventional hydrogen bonding. Thus small size, as well as electronegativity, explains the difference.

Step 2: (b) Write the reaction of fluorine with water Fluorine oxidises water, liberating oxygen and producing hydrogen fluoride:

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2.$$

Oxygen changes from oxidation state -2 in water to 0, while fluorine changes from 0 to -1. These oxidation-state changes identify water as the substance oxidised and fluorine as the oxidising agent.

Step 3: (c) Identify the gas from calcium phosphide Calcium phosphide undergoes hydrolysis. The phosphide component forms phosphine, while calcium forms calcium hydroxide:

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3 \uparrow.$$

The gaseous product is therefore phosphine. The equation balances three calcium atoms, two phosphorus atoms and the hydrogen and oxygen supplied by water.

Step 4: (d) Determine the isostructural noble-gas species In IBr_2^-, iodine has two bond pairs and three lone pairs, giving five electron-pair domains. Their trigonal-bipyramidal arrangement places the three lone pairs in equatorial positions and the two bonds in axial positions, producing a linear molecular shape. XeF_2 likewise has two bonding domains and three lone pairs on xenon; it is linear and isostructural with IBr_2^-.

Step 5: (e) Complete formation of the nitrosyl complex Nitric oxide replaces one water ligand of the hexaaquairon(II) ion to form the brown-ring nitrosyl complex:

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O.$$

Five water ligands remain coordinated and one nitric oxide ligand is added; the displaced water appears as a product. The total charge remains $+2$ on both sides of the equation.

Step 6: Conclusion (a) Nitrogen's smaller size and concentrated lone pair favour hydrogen bonding. (b) Fluorine forms HF and liberates oxygen from water. (c) The gas is phosphine, PH_3. (d) The species is XeF_2. (e) The products are $[Fe(H_2O)_5(NO)]^{2+} + H_2O$.

Quick Tip to Solve: For isostructural species, count bond domains and lone pairs; for the brown-ring complex, replace exactly one water ligand by NO.