CBSE Class 12 Chemistry Question Paper 2010 with Solution PDF-Set 56/1 (Outside Delhi)

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) Marks for each question are indicated against it.
(iii) Questions number **1** to **8** are very short-answer questions and carry **1** mark each.
(iv) Questions number **9** to **18** are short-answer questions and carry **2** marks each.
(v) Questions number **19** to **27** are also short-answer questions and carry **3** marks each.
(vi) Questions number **28** to **30** are long-answer questions and carry **5** marks each.
(vii) Use Log Tables, if necessary. Use of calculators is not allowed.

1. What type of interactions hold the molecules together in a polar molecular solid? [1 mark]

Solution:

Concept:

- Polar molecules possess permanent electric dipoles, with partial positive and partial negative ends.
- Dipole–dipole attraction acts between oppositely charged ends of neighbouring polar molecules.

Step 1: Identify the molecular property A polar molecule has an unsymmetrical charge distribution and therefore a permanent dipole moment. Its partial charges persist even without an external electric field.

Step 2: Identify the cohesive interaction In the solid, neighbouring molecules tend to orient so that the partially positive end of one attracts the partially negative end of another. These intermolecular dipole–dipole attractions provide the characteristic cohesion of polar molecular solids.

Step 3: Conclusion The molecules are held together mainly by dipole–dipole interactions.

Quick Tip to Solve: For a molecular solid made of polar molecules, identify permanent dipoles and name dipole–dipole attraction.

2. What is meant by 'limiting molar conductivity'? [1 mark]

Solution:

Concept:

- Molar conductivity, Λ_m, is the conductivity contribution associated with one mole of electrolyte.
- The limiting value is obtained as concentration c approaches zero, that is, at infinite dilution.

Step 1: Describe dilution As an electrolyte solution is diluted, the ions become increasingly separated and the effect of interionic attraction on their movement decreases. The molar conductivity approaches a limiting value.

Step 2: State the mathematical definition This limiting molar conductivity is denoted by Λ_m°:

$$\Lambda_m^\circ = \lim_{c \to 0} \Lambda_m.$$

At this limit each ion contributes independently to the total molar conductivity.

Step 3: Conclusion Limiting molar conductivity is the molar conductivity of an electrolyte at infinite dilution (concentration approaching zero).

Quick Tip to Solve: The word limiting refers to concentration tending to zero, not to the conductivity of pure water.

3. Fluorine does not exhibit any positive oxidation state. Why? [1 mark]

Solution:

Concept:

- Oxidation states are assigned by attributing bonding electrons to the more electronegative atom.
- Fluorine is the most electronegative element.

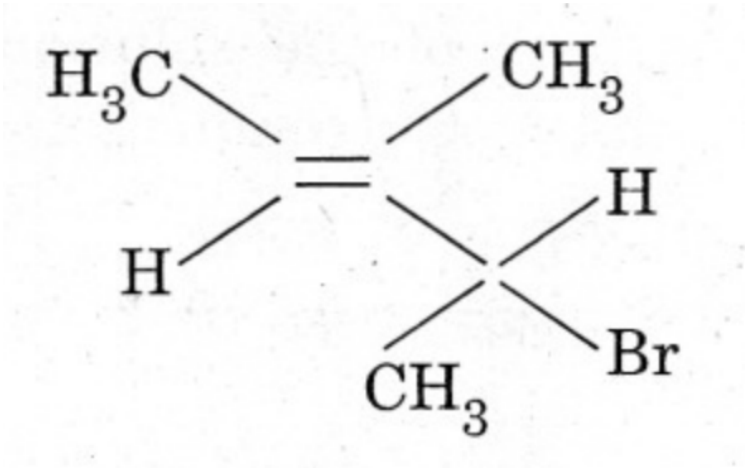
Step 1: Apply the electronegativity rule In a bond between fluorine and any different element, fluorine attracts the shared electron pair more strongly. The bonding electrons are therefore assigned to fluorine in the oxidation-state calculation.

Step 2: Infer the possible oxidation states Consequently, fluorine has oxidation state -1 in its compounds and cannot be assigned a positive oxidation state. In elemental F_2, the atoms are identical and each has oxidation state zero.

Step 3: Conclusion Fluorine does not exhibit a positive oxidation state because it is the most electronegative element.

Quick Tip to Solve: Use highest electronegativity as the decisive reason; remember that elemental fluorine has oxidation state zero.

4. Give the IUPAC name of the following compound: [1 mark]



Solution:

Concept:

- Choose the longest carbon chain containing the double bond and number it to give the double bond its lowest locant.
- For an E/Z descriptor, compare the higher-priority substituent on each double-bonded carbon using atomic numbers.

Step 1: Choose and number the parent The longest chain through the double bond contains five carbon atoms. Numbering from the end nearer the double bond gives pent-2-ene. The methyl group is at carbon 3 and the bromo substituent is at carbon 4.

Step 2: Check substituent order and geometry List bromo before methyl alphabetically. In the printed structure, CH_3 has priority over H at carbon 2, while $CHBrCH_3$ has priority over CH_3 at carbon 3. These higher-priority groups lie on opposite sides of the double bond, giving the $2E$ configuration.

Step 3: Conclusion The IUPAC name is $(2E)$-4-bromo-3-methylpent-2-ene (constitutional name: 4-bromo-3-methylpent-2-ene).

Quick Tip to Solve: Give the double bond the lower number before considering substituent locants; then list bromo before methyl.

5. Write the structure of the molecule of a compound whose IUPAC name is 1-phenylpropan-2-ol.

[1 mark]

Solution:

Concept:

- The parent name propan-2-ol specifies a three-carbon chain bearing an $-OH$ group on carbon 2.
- A phenyl group, C_6H_5-, is a benzene ring attached through one ring carbon; the locant 1 places it on carbon 1 of the parent chain.

Step 1: Construct the parent alcohol Start with propan-2-ol, $CH_3 - CH(OH) - CH_3$. Its central carbon is carbon 2 and carries the hydroxyl group.

Step 2: Attach phenyl at carbon 1 Replace one hydrogen on carbon 1 by C_6H_5-. That terminal carbon becomes $-CH_2-$, giving $C_6H_5 - CH_2 - CH(OH) - CH_3$. The phenyl group is attached to carbon 1, while the hydroxyl group remains on carbon 2, as required by both locants.

Step 3: Conclusion The required condensed structural formula is $\boxed{C_6H_5 - CH_2 - CH(OH) - CH_3}$.

Quick Tip to Solve: Build propan-2-ol first, then replace a terminal hydrogen at carbon 1 by a phenyl group.

6. What is Tollen's reagent? Write one use of this reagent. [1 mark]

Solution:

Concept:

- Tollens' reagent is an ammoniacal solution of silver nitrate containing $[Ag(NH_3)_2]^+$.
- Aldehydes reduce silver(I) ions to metallic silver while being oxidised to carboxylate ions in alkaline medium.

Step 1: Identify the reagent The active species in Tollens' reagent is the diamminesilver(I) complex, $[Ag(NH_3)_2]^+$, in alkaline ammoniacal solution. Thus it is commonly described as ammoniacal silver nitrate.

Step 2: State one use It is used to detect an aldehyde group by the silver-mirror test. On warming an aldehyde with the reagent, silver(I) is reduced to metallic silver, which deposits as a shining mirror on the inner wall of a clean test tube. Ordinary ketones do not give this test.

Step 3: Conclusion Tollens' reagent is ammoniacal silver nitrate; one use is the detection of aldehydes by the silver-mirror test.

Quick Tip to Solve: Associate Tollens' reagent with diamminesilver(I) and the silver mirror produced by an aldehyde.

7. What is meant by 'reducing sugars'? [1 mark]

Solution:

Concept:

- Reducing sugars reduce mild oxidising reagents such as Tollens' reagent or Fehling's solution.
- A free anomeric group allows a sugar to form an open-chain carbonyl form in solution.

Step 1: Describe the chemical behaviour A reducing sugar reduces Tollens' reagent to metallic silver or Fehling's solution to red Cu_2O, while the sugar itself is oxidised. This reducing behaviour is the basis of its name.

Step 2: Relate behaviour to structure Such sugars have a free anomeric group and can give a reactive open-chain form. Examples are glucose and maltose. Fructose also behaves as a reducing sugar because in the alkaline test medium it rearranges to aldoses; sucrose is non-reducing because both anomeric centres are involved in its glycosidic bond.

Step 3: Conclusion Reducing sugars are sugars that reduce Tollens' reagent or Fehling's solution, for example glucose.

Quick Tip to Solve: Check whether an anomeric centre is free; a ketose such as fructose can still give alkaline reducing-sugar tests.

8. What does the designation '6, 6' mean in the name nylon-6,6? [1 mark]

Solution:

Concept:

- In a nylon made from a diamine and a dicarboxylic acid, the two numbers give the carbon atoms in the diamine and acid molecules, respectively.
- Nylon-6,6 is a condensation polyamide formed from hexamethylenediamine and adipic acid.

Step 1: Count the carbons in the diamine The diamine is hexamethylenediamine, $H_2N(CH_2)_6NH_2$. Its chain contains six carbon atoms; this gives the first 6.

Step 2: Count the carbons in the acid Adipic acid is $HOOC(CH_2)_4COOH$. It contains four methylene carbons and two carboxyl carbons, giving six carbons in all and hence the second 6.

Step 3: Conclusion The designation 6,6 means that both the diamine and the dicarboxylic acid used to prepare nylon-6,6 contain six carbon atoms each.

Quick Tip to Solve: Count the two carboxyl carbon atoms as well as the four methylene carbons in adipic acid.

9. Define the terms 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions? [2 marks]

Solution:

Concept:

- Osmosis requires a semipermeable membrane that permits passage of solvent but blocks solute.
- For a dilute solution, osmotic pressure obeys $\pi V = nRT$, so $M = wRT/(\pi V)$, where w is solute mass and M is its molar mass.

Step 1: Define osmosis and osmotic pressure Osmosis is the spontaneous passage of solvent through a semipermeable membrane from pure solvent or a more dilute solution into a more concentrated solution. Osmotic pressure, π, is the minimum excess external pressure applied on the solution side that just prevents this net flow of solvent.

Step 2: Explain the advantage for molar-mass determination Osmotic pressure is appreciable and can be measured accurately even for very dilute solutions, whereas changes in boiling point, freezing point and vapour pressure may be too small to measure reliably. It can also be measured at room temperature. Thus it is especially useful for determining molar masses of large molecules such as proteins and polymers without heating or cooling them enough to cause decomposition or denaturation.

Step 3: Conclusion Osmosis is solvent flow across a semipermeable membrane toward the more concentrated solution; osmotic pressure stops that flow. Its measurable magnitude in dilute solutions and measurement at room temperature make it advantageous for molar-mass determination.

Quick Tip to Solve: For a high-molar-mass solute, choose osmotic pressure: dilute solutions still give an appreciable pressure at room temperature.

10. Express the relation among the cell constant, the resistance of the solution in the cell, and the conductivity of the solution. How is the conductivity of a solution related to its molar conductivity? [2 marks]

Solution:

Concept:

- The cell constant is l/A, where l is the electrode separation and A is the effective electrode area.
- Resistance obeys $R = \rho l/A$, with resistivity $\rho = 1/\kappa$, where κ is conductivity.

Step 1: Relate conductivity to cell constant and resistance Substituting $\rho = 1/\kappa$ into the resistance expression gives

$$R = \frac{l}{\kappa A}, \qquad \kappa = \frac{l/A}{R}.$$

Thus cell constant $= \kappa R$. With the cell constant in cm^{-1} and resistance in Ω, conductivity has units S cm^{-1}.

Step 2: Relate molar conductivity to conductivity Molar conductivity Λ_m is the conductivity multiplied

by the volume containing one mole of solute. If concentration c is in mol L^{-1}, that volume is $1000/c\,cm^3$. Hence

$$\Lambda_m = \frac{1000\kappa}{c},$$

with κ in S cm^{-1} and Λ_m in S cm^2 mol^{-1}. In consistent SI units, $\Lambda_m = \kappa/c$ for c in mol m^{-3}.

Step 3: Conclusion $\kappa = (\text{cell constant})/R$, and $\Lambda_m = 1000\kappa/c$ when c is in mol L^{-1} and κ in S cm^{-1}.

Quick Tip to Solve: Use the factor 1000 only when converting molarity in litres to the cubic-centimetre volume used with conductivity in S per cm.

11(a). Given that the standard electrode potentials (E°) of metals are:

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Cu^{2+}/Cu = 0.34$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V, $Fe^{2+}/Fe = -0.44$ V.

Arrange these metals in an increasing order of their reducing power. [2 marks]

Solution:

Concept:

- A metal acts as a reducing agent by losing electrons: $M \rightarrow M^{n+} + ne^-$.
- A more negative standard reduction potential for M^{n+}/M corresponds to a stronger tendency of the metal to oxidise and hence greater reducing power.

Step 1: Order the standard reduction potentials The given values, arranged from most positive to most negative, are

$$\begin{aligned} \text{Ag}: +0.80\,\text{V}, \quad \text{Cu}: +0.34\,\text{V}, \\ \text{Fe}: -0.44\,\text{V}, \quad \text{Cr}: -0.74\,\text{V}, \\ \text{Mg}: -2.37\,\text{V}, \quad \text{K}: -2.93\,\text{V}. \end{aligned}$$

These are reduction potentials of the metal-ion/metal couples, not oxidation potentials.

Step 2: Convert this ordering into reducing strength Silver, with the most positive reduction potential, has the least tendency among these metals to give up electrons. Moving toward potassium makes the reduction potential increasingly negative, so oxidation of the metal and donation of electrons become more favourable. Thus reducing power increases along the same sequence as this descending list of reduction potentials.

Step 3: Conclusion The increasing order of reducing power is

$$\boxed{\text{Ag} < \text{Cu} < \text{Fe} < \text{Cr} < \text{Mg} < \text{K}}.$$

Quick Tip to Solve: For reducing power of metals, place the most positive reduction potential first and the most negative last.

OR

11(b). Two half-reactions of an electrochemical cell are given below:

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$, $E^\circ = +1.51$ V

$Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$, $E^\circ = +0.15$ V

Construct the redox reaction equation from the two half-reactions and calculate the cell potential from the standard potentials, and predict if the reaction is reactant or product favoured. [2 marks]

Solution:

Concept:

- Combine a reduction half-reaction with an oxidation half-reaction after equalising the electrons transferred.
- Add the electrode potentials when both half-reactions are used in their printed directions; do not multiply potentials when multiplying equations. Positive E°_{cell} gives $\Delta G^\circ = -nFE^\circ_{\text{cell}} < 0$.

Step 1: Balance electron transfer and add the half-reactions Permanganate consumes five electrons, while each tin(II) ion supplies two. Multiply the first equation by 2 and the second by 5:

$$2\text{MnO}_4^- + 16\text{H}^+ + 10e^- \longrightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O},$$
$$5\text{Sn}^{2+} \longrightarrow 5\text{Sn}^{4+} + 10e^-.$$

Cancel the ten electrons. The resulting equation has charge $+24$ on each side and conserves all atoms.

Step 2: Calculate the cell potential and favourability The printed tin half-reaction is an oxidation and its stated potential is $+0.15\,\text{V}$ for that direction. Therefore

$$E^\circ_{\text{cell}} = E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}} = 1.51 + 0.15 = 1.66\,\text{V}.$$

The multipliers 2 and 5 balance electrons but do not multiply electrode potentials. Since $n = 10$ and the cell potential is positive, $\Delta G^\circ = -10F(1.66) < 0$; the forward reaction is thermodynamically product favoured under standard conditions.

Step 3: Conclusion

$$2\text{MnO}_4^-(aq) + 16\text{H}^+(aq) + 5\text{Sn}^{2+}(aq) \longrightarrow 2\text{Mn}^{2+}(aq) + 8\text{H}_2\text{O}(l) + 5\text{Sn}^{4+}(aq).$$

The standard cell potential is $\boxed{+1.66\,\text{V}}$, and the reaction is product favoured.

Quick Tip to Solve: Check the direction attached to each stated potential: the tin equation is already an oxidation, so add its printed potential.

12. Describe the following:

(i) Tyndall effect

(ii) Shape-selective catalysis [2 marks]

Solution:

Concept:

- Colloidal particles scatter light because the dispersed phase and dispersion medium have different refractive indices.
- A porous catalyst can select molecules according to their size and shape.

Step 1: Describe the Tyndall effect The scattering of a beam of light by colloidal particles is called the Tyndall effect. When a strong beam passes through a sol, its path becomes visible as a bright cone when viewed from the side. This illuminated region is called the Tyndall cone. A true solution does not show an appreciable Tyndall effect under ordinary conditions because its solute particles are too small.

Step 2: Describe shape-selective catalysis Shape-selective catalysis is catalysis in which the reaction depends on the size and shape of the reactant and product molecules and on the pore structure of the catalyst. Only molecules that can enter the pores and react at the internal active sites undergo the selected reaction; products must also be able to leave. Zeolites are shape-selective catalysts. For example, ZSM-5 is used in converting alcohols into gasoline-range hydrocarbons.

Step 3: Conclusion Tyndall effect is the scattering of light by colloidal particles; shape-selective catalysis is molecular selection by the size and shape of a catalyst's pores.

Quick Tip to Solve: For Tyndall effect name scattering; for shape selectivity connect molecular dimensions with catalyst pores.

13. What is meant by coagulation of a colloidal solution? Name any method by which coagulation of lyophobic sols can be carried out. [2 marks]

Solution:

Concept:

- Lyophobic sol particles normally carry similar electric charges, whose mutual repulsion helps keep them dispersed.
- Coagulation occurs when this stabilising charge is removed or sufficiently reduced.

Step 1: Define coagulation Coagulation is the process in which colloidal particles aggregate into larger particles and separate from the dispersion medium as a precipitate. The process is also called flocculation. In a stable lyophobic sol, particles repel one another because they carry like charges. When this repulsion is reduced, the particles can approach closely enough to stick together.

Step 2: Give a method for a lyophobic sol Add a suitable electrolyte in sufficient quantity. The ions carrying charge opposite to that of the colloidal particles are adsorbed on the particles and neutralise their charge. The particles then aggregate and precipitate. For example, adding sodium chloride to a negatively charged arsenious sulphide sol supplies Na^+ ions, which bring about coagulation when a sufficient concentration is reached.

Step 3: Conclusion Coagulation is aggregation and precipitation of colloidal particles. A lyophobic sol can be coagulated by adding a suitable electrolyte.

Quick Tip to Solve: For an electrolyte method, identify the ion opposite in charge to the sol particles.

14. Complete the following chemical reaction equations:

(i) I_2 + HNO_3 (conc.) $\rightarrow$

(ii) $HgCl_2$ + PH_3 $\rightarrow$ [2 marks]

Solution:

Concept:

- Concentrated nitric acid oxidises iodine to iodic acid and is itself reduced to nitrogen dioxide.
- Phosphine reacts with mercuric chloride to form mercuric phosphide and hydrogen chloride.

Step 1: Complete and balance the iodine reaction Iodine is oxidised from oxidation state 0 in I_2 to $+5$ in HIO_3. Nitrogen is reduced from $+5$ to $+4$, so the two iodine atoms release ten electrons in all and require ten nitric acid molecules. The balanced equation is

$$I_2 + 10HNO_3\ (\text{conc.}) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O.$$

Both sides contain two iodine atoms, ten nitrogen atoms, ten hydrogen atoms and thirty oxygen atoms.

Step 2: Complete and balance the phosphine reaction The product is mercuric phosphide, Hg_3P_2, which separates as a black precipitate. Matching three mercury atoms and two phosphorus atoms fixes the reactant coefficients; the remaining hydrogen and chlorine form hydrogen chloride:

$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2\downarrow + 6HCl.$$

The equation has three mercury atoms, two phosphorus atoms, six chlorine atoms and six hydrogen atoms on each side.

Step 3: Conclusion The balanced reactions are

$$I_2 + 10HNO_3\ (\text{conc.}) \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O,$$
$$3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2\downarrow + 6HCl.$$

Quick Tip to Solve: Balance iodine oxidation with ten nitric acid molecules; use the formula Hg3P2 to fix the second equation.

15. Draw the structural formulae of the following compounds:

(i) $H_4P_2O_5$

(ii) XeF_4 [2 marks]

Solution:

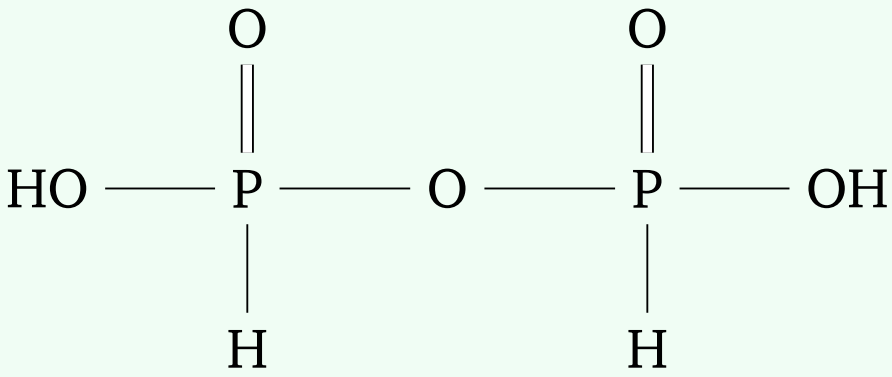
Concept:

- Pyrophosphorous acid, $H_4P_2O_5$, contains two phosphorus centres linked through a bridging oxygen atom.
- In XeF_4, four bonding pairs and two lone pairs surround xenon; the lone pairs occupy opposite positions.

Step 1: Draw pyrophosphorous acid Each phosphorus atom has one $P{=}O$ bond, one $P{-}H$ bond, one $P{-}OH$ bond and one bond to the bridging oxygen. The connectivity is

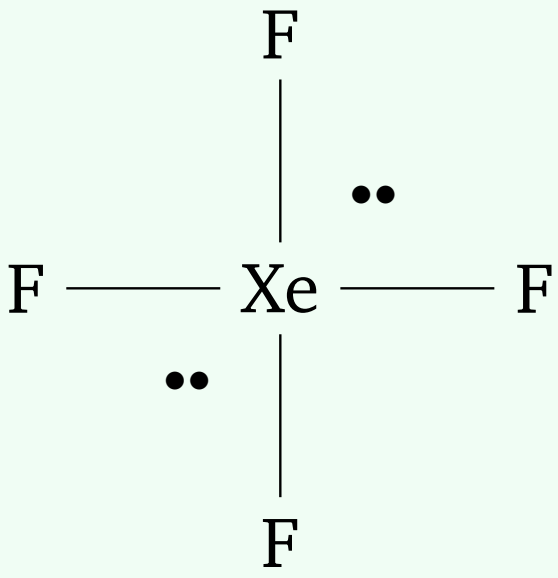
$$HO{-}P(=O)(H){-}O{-}P(=O)(H){-}OH.$$

Thus there are two terminal hydroxyl groups, two directly bonded hydrogen atoms and five oxygen atoms in total. The two hydroxyl hydrogens are ionisable; the hydrogens directly bonded to phosphorus are not.



Structural formula of pyrophosphorous acid

Step 2: Draw xenon tetrafluoride Xenon has eight valence electrons. Four are used in forming four single bonds to fluorine, leaving two lone pairs on xenon. The six electron pairs adopt an octahedral arrangement, with the two lone pairs opposite each other to minimise repulsion. The four fluorine atoms therefore lie at the corners of a square with xenon at its centre. Adjacent $F{-}Xe{-}F$ angles are 90°, and opposite fluorines subtend 180°.



Square-planar xenon tetrafluoride; the lone pairs lie above and below the molecular plane

Step 3: Conclusion $H_4P_2O_5$ has a $P-O-P$ bridge; XeF_4 is square planar with two opposite lone pairs on xenon.

Quick Tip to Solve: In H4P2O5 retain one P-H bond on each phosphorus; in XeF4 put the two lone pairs opposite each other.

16. Give the chemical tests to distinguish between the following pairs of compounds:

(i) Ethylamine and Aniline

(ii) Aniline and Benzylamine [2 marks]

Solution:

Concept:

- Primary aromatic amines form stable diazonium salts with nitrous acid at 273–278 K; primary aliphatic amines release nitrogen under the same conditions.
- A diazonium salt couples with alkaline β-naphthol to form a strongly coloured azo dye. This provides a positive test for aniline.

Step 1: (i) Ethylamine and aniline Treat separate cold solutions with sodium nitrite and dilute hydrochloric acid, then add alkaline β-naphthol. Ethylamine evolves nitrogen and gives no azo dye:

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

Aniline first forms benzenediazonium chloride and then gives an orange-red azo dye on coupling. The dye distinguishes aniline from ethylamine.

Step 2: (ii) Aniline and benzylamine Apply the same cold diazotisation and coupling test. Aniline

gives the orange-red azo dye. Benzylamine, $C_6H_5CH_2NH_2$, has its amino group on the side chain and behaves as a primary aliphatic amine. It evolves nitrogen and forms benzyl alcohol, giving no azo dye:

$$C_6H_5CH_2NH_2 + HNO_2 \longrightarrow C_6H_5CH_2OH + N_2 \uparrow + H_2O.$$

Step 3: Conclusion In both pairs, aniline gives an azo dye after cold diazotisation and coupling; ethylamine and benzylamine evolve nitrogen and do not give this dye.

Quick Tip to Solve: Check whether the amino nitrogen is directly attached to the benzene ring before predicting the diazotisation test.

17. Identify A and B in each of the following processes:

(i) $\mathbf{CH_3CH_2Cl} \xrightarrow{NaCN} \mathbf{A} \xrightarrow[Ni/H_2]{reduction} \mathbf{B}$

(ii) $\mathbf{C_6H_5NH_2} \xrightarrow{NaNO_2/HCl} \mathbf{A} \xrightarrow[OH^-]{C_6H_5NH_2} \mathbf{B}$ [2 marks]

Solution:

Concept:

- Cyanide substitutes chloride through its carbon atom, producing a nitrile with one extra carbon atom.
- Catalytic hydrogenation converts $-C \equiv N$ into $-CH_2NH_2$. Diazotisation followed by azo coupling joins two aromatic rings through $-N = N-$.

Step 1: (i) Identify the nitrile and its reduction product In sodium cyanide, the carbon end of cyanide attacks ethyl chloride. Thus A is propanenitrile, not ethanenitrile:

$$CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN + NaCl.$$

Hydrogen in the presence of nickel reduces the nitrile group without losing its carbon atom:

$$CH_3CH_2CN + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_2NH_2.$$

Hence B is propan-1-amine.

Step 2: (ii) Identify the diazonium salt and coupling product Sodium nitrite and hydrochloric acid generate nitrous acid. At 273–278 K, aniline forms benzenediazonium chloride, $A = C_6H_5N_2^+Cl^-$. The diazonium ion couples with aniline mainly at its free para position, giving the azo compound $B = C_6H_5-N=N-C_6H_4-NH_2$, with NH_2 para to the azo linkage. This product is p-aminoazobenzene (aniline yellow).

Step 3: Conclusion (i) $A = CH_3CH_2CN$, $B = CH_3CH_2CH_2NH_2$. (ii) $A = C_6H_5N_2^+Cl^-$, $B = p$-aminoazobenzene.

Quick Tip to Solve: Count the carbon in cyanide as part of the product chain; locate the azo group para to the amino group in the coupling product.

18. Draw the molecular structures of the monomers of

(i) PVC

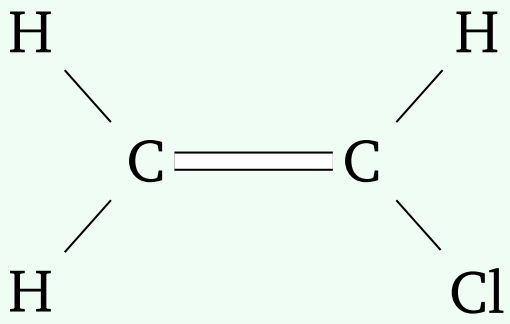
(ii) Teflon [2 marks]

Solution:

Concept:

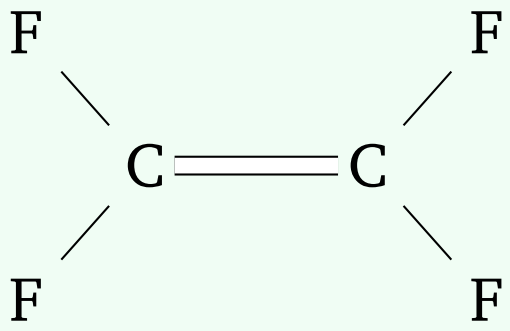
- An addition-polymer monomer contains a carbon–carbon double bond. Polymerisation opens its π bond to form the polymer backbone.
- To recover a vinyl monomer from a repeat unit, restore the double bond between its two backbone carbon atoms while keeping their substituents unchanged.

Step 1: (i) Monomer of PVC PVC is polyvinyl chloride. Its monomer is vinyl chloride, also called chloroethene, $CH_2 = CHCl$. One carbon of the double bond bears two hydrogen atoms; the other bears one hydrogen and one chlorine atom, as drawn below. Addition polymerisation produces the repeat unit $[-CH_2 - CHCl-]_n$. The chlorine is a substituent on the carbon backbone and is retained during polymerisation.



Vinyl chloride (chloroethene)

Step 2: (ii) Monomer of Teflon Teflon is polytetrafluoroethene (PTFE). Its monomer is tetrafluoroethene, $CF_2 = CF_2$. Each carbon of the double bond bears two fluorine atoms, so the molecule contains four fluorine atoms and no hydrogen atoms. Addition polymerisation gives $[-CF_2 - CF_2-]_n$. The double bond in each monomer becomes a single backbone bond; no small molecule is eliminated.



Tetrafluoroethene

Step 3: Conclusion The monomers are (i) vinyl chloride, $CH_2 = CHCl$, and (ii) tetrafluoroethene, $CF_2 = CF_2$.

Quick Tip to Solve: Restore a C=C bond in each two-carbon repeat unit, retaining Cl for PVC and all four F atoms for Teflon.

19. The density of copper metal is 8.95 g cm^{-3}. The radius of copper is 127.8 pm. Is the copper unit cell simple cubic, body-centred cubic, or face-centred cubic?
(Given: atomic mass of Cu = 63.54 g mol^{-1} and N_A = 6.02 $\times$ 10^{23} mol^{-1}) [3 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = ZM/(N_A a^3)$, where Z is the number of atoms per cell, M the molar mass and a the edge length.
- Atoms touch along an edge in simple cubic, along the body diagonal in body-centred cubic, and along the face diagonal in face-centred cubic. Hence their radius-edge relations differ.

Step 1: Convert the radius and state the candidate structures The atomic radius is $r = 127.8\,\text{pm} = 1.278 \times 10^{-8}\,\text{cm}$. The three possibilities have $(Z, a) = (1, 2r)$, $(2, 4r/\sqrt{3})$, and $(4, 2\sqrt{2}r)$, respectively. We calculate the density predicted by each packing and compare it with the measured value.

Step 2: Test simple cubic and body-centred cubic For simple cubic, $a = 2.556 \times 10^{-8}\,\text{cm}$, giving

$$\rho_{\text{sc}} = \frac{63.54}{6.02 \times 10^{23}(2.556 \times 10^{-8})^3} = 6.32\,\text{g cm}^{-3}.$$

For body-centred cubic, $a = 2.9514 \times 10^{-8}\,\text{cm}$, so

$$\rho_{\text{bcc}} = \frac{2(63.54)}{6.02 \times 10^{23}(2.9514 \times 10^{-8})^3} = 8.21\,\text{g cm}^{-3}.$$

Neither agrees with the stated density.

Step 3: Test face-centred cubic For face-centred cubic, $a = 2\sqrt{2}r = 3.6147 \times 10^{-8}\,\text{cm}$. Therefore

$$\rho_{\text{fcc}} = \frac{4(63.54)}{6.02 \times 10^{23}(3.6147 \times 10^{-8})^3} = 8.94\,\text{g cm}^{-3}.$$

This agrees with $8.95\,\text{g cm}^{-3}$ within the rounding of the given data.

Step 4: Conclusion Copper has a face-centred cubic (fcc) unit cell, containing four atoms per unit cell.

Quick Tip to Solve: Convert pm to cm before using a density in g cm^{-3}, and compare densities using the correct radius-edge relation for each lattice.

20. What mass of NaCl (molar mass = 58.5 g mol^{-1}) should be dissolved in 65 g of water to lower the freezing point by 7.5°C? The freezing point depression constant, K_f, for water is 1.86 K kg mol^{-1}. Assume the van't Hoff factor for NaCl is 1.87. [3 marks]

Solution:

Concept:

- Freezing-point depression for an electrolyte is $\Delta T_f = iK_f m$, where i is the vant́ Hoff factor and m is molality.
- Molality is moles of solute per kilogram of solvent: $m = (w/M)/W$, with solute mass w, molar mass M, and solvent mass W in kilograms.

Step 1: Identify the solvent mass and temperature depression The water mass is $65\,\text{g} = 0.065\,\text{kg}$. A decrease of $7.5\,^\circ\text{C}$ is a temperature difference of $7.5\,\text{K}$. Use the given effective factor $i = 1.87$; it already accounts for the increase in the number of solute particles produced by NaCl in this solution.

Step 2: Calculate the required molality and number of moles Using $K_f = 1.86\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_f}{iK_f} = \frac{7.5}{1.87 \times 1.86} = 2.1576\,\text{mol kg}^{-1}.$$

Thus the number of moles to dissolve in the specified mass of water is

$$n = mW = 2.1576 \times 0.065 = 0.14016\,\text{mol}.$$

The denominator in molality is the solvent mass, so the mass of dissolved salt is not added to the water mass here.

Step 3: Convert the amount to a mass For $M_{\text{NaCl}} = 58.5\,\text{g mol}^{-1}$,

$$w = nM = 0.14016 \times 58.5 = 8.199\,\text{g}.$$

Equivalently, $w = \Delta T_f MW/(iK_f)$. Substituting this amount back gives

$$1.87 \times 1.86 \times \frac{8.199/58.5}{0.065} = 7.50\,\text{K}.$$

This agrees with the required depression.

Step 4: Conclusion The required mass of NaCl is approximately $8.20\,\text{g}$.

Quick Tip to Solve: Use the supplied vant́ Hoff factor 1.87 rather than replacing it with the ideal value 2; use kilograms of water in molality.

21(a). Describe the role of the following:

(i) NaCN in the extraction of silver from a silver ore

(ii) Iodine in the refining of titanium

(iii) Cryolite in the metallurgy of aluminium [3 marks]

Solution:

Concept:

- Complex formation can selectively dissolve a metal from its ore, while formation and decomposition of a volatile compound can purify a metal.
- In electrolytic extraction, additives can lower the operating temperature and improve the conductivity of the molten electrolyte.

Step 1: (i) Role of NaCN in silver extraction Sodium cyanide is a leaching agent. It converts silver into the soluble dicyanidoargentate(I) complex, $[Ag(CN)_2]^-$, allowing it to be separated from insoluble gangue. For a silver sulphide ore, the complex formation can be represented as

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S.$$

Silver is subsequently recovered from the cyanide solution by displacement with zinc. Thus NaCN enables selective extraction through formation of a soluble complex.

Step 2: (ii) Role of iodine in titanium refining Iodine is used in the van Arkel process. Impure titanium reacts with iodine to form volatile titanium tetraiodide; nonvolatile impurities remain behind:

$$Ti + 2I_2 \longrightarrow TiI_4.$$

The vapour reaches a hot tungsten filament, where the iodide decomposes:

$$TiI_4 \longrightarrow Ti + 2I_2.$$

Pure titanium deposits on the filament and iodine is regenerated. The purification depends on the volatility and thermal decomposition of the iodide.

Step 3: (iii) Role of cryolite in aluminium metallurgy Cryolite, Na_3AlF_6, is mixed with alumina in the Hall-Heroult process. It dissolves alumina and lowers the melting temperature of the electrolyte from that of pure alumina to a practical operating temperature. It also increases electrical conductivity, making electrolysis easier and reducing the energy needed for extraction.

Step 4: Conclusion NaCN leaches silver as a soluble cyanide complex; iodine purifies titanium through volatile TiI_4; cryolite lowers the electrolyte melting temperature and improves its conductivity in aluminium extraction.

Quick Tip to Solve: Link each reagent to its process: cyanide to soluble complex formation, iodine to volatile iodide purification, and cryolite to the molten electrolyte.

OR

21(b). Describe the principle involved in each of the following processes of metallurgy:

(i) Froth floatation method

(ii) Electrolytic refining of metals

(iii) Zone refining of metals [3 marks]

Solution:

Concept:

- Froth floatation separates sulphide ore from gangue by their different wetting behaviour towards oil and water.
- Electrolytic refining uses selective anodic dissolution and cathodic deposition of the required metal.
- Zone refining relies on impurities being more soluble in molten metal than in solid metal.

Step 1: Explain froth floatation (i) Finely powdered sulphide ore is mixed with water and a collector such as pine oil. Sulphide particles are preferentially wetted by oil, whereas gangue is wetted by water. On blowing air through the mixture, the oil-wetted ore particles attach to air bubbles and rise as froth. The gangue remains in water. The ore-rich froth is skimmed off, giving a concentrated ore.

Step 2: Explain electrolytic refining (ii) The impure metal is the anode and a thin sheet of pure metal is the cathode. A soluble salt of the same metal is used as electrolyte. On passing current, metal dissolves from the anode and an equivalent amount of pure metal deposits on the cathode. For copper, the electrode reactions are

$$\mathrm{Cu} \longrightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-} \qquad \text{(anode)}$$

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^{-} \longrightarrow \mathrm{Cu} \qquad \text{(cathode)}.$$

Less reactive insoluble impurities collect as anode mud; more reactive impurities can remain in solution rather than depositing under the operating conditions.

Step 3: Explain zone refining (iii) A moving heater melts a narrow zone of an impure metal rod. As the heater moves, pure metal crystallises behind it, while impurities preferentially remain in the molten zone. Repeated movement of the molten zone carries the impurities to one end. That impurity-rich end is cut off. This method produces highly pure semiconductors such as silicon and germanium.

Step 4: Conclusion Froth floatation uses selective wetting; electrolytic refining uses selective electrode reactions; zone refining uses the greater solubility of impurities in the molten phase.

Quick Tip to Solve: For each process, identify its separating property first: wetting, electrode deposition, or impurity solubility in the melt.

22. Explain the following cases giving appropriate reasons:

(i) Nickel does not form low spin octahedral complexes.

(ii) The π-complexes are known for the transition metals only.

(iii) Co^{2+} is easily oxidized to Co^{3+} in the presence of a strong ligand. [3 marks]

Solution:

Concept:

- In an octahedral field the five d orbitals split into lower t_{2g} and higher e_g levels.
- Strong ligands can produce a large splitting Δ_o, stabilising low-spin configurations when an alternative electron arrangement exists.
- Metal-ligand π bonding can involve ligand-to-metal donation and metal-to-ligand back donation.

Step 1: Examine the octahedral nickel configuration (i) In the usual nickel(II) complexes, Ni^{2+} has a $3d^8$ configuration. Its octahedral arrangement is $t_{2g}^6 e_g^2$. The two electrons in the degenerate e_g orbitals occupy different orbitals with parallel spins, leaving two unpaired electrons. Increasing ligand-field strength cannot move these electrons into the already filled t_{2g} set. Thus octahedral nickel(II) has no distinct high-spin/low-spin choice. Strong ligands may instead favour square-planar nickel(II), which is a different geometry.

Step 2: Explain the formation of pi complexes (ii) Transition metals possess suitable vacant orbitals that accept electron density from a ligand and occupied d orbitals that can donate electron density into suitable vacant ligand orbitals. With ligands such as carbon monoxide or alkenes, donation and π back donation reinforce one another. The availability of d orbitals of appropriate symmetry and energy accounts for the characteristic formation and stability of transition-metal π-complexes in the present context.

Step 3: Compare cobalt in the two oxidation states (iii) Co^{2+} is $3d^7$, whereas Co^{3+} is $3d^6$. A strong ligand gives a large octahedral splitting and strongly stabilises the low-spin t_{2g}^6 configuration of cobalt(III). This enhanced complex stability favours oxidation of coordinated cobalt(II) to cobalt(III), even though the free aqueous cobalt(III) ion is strongly oxidising. The ligand therefore changes the relative stability of the two oxidation states.

Step 4: Conclusion Octahedral nickel(II) retains two unpaired electrons; suitable transition-metal d orbitals support π bonding; strong ligands stabilise low-spin cobalt(III), facilitating oxidation of cobalt(II).

Quick Tip to Solve: Write the d-electron counts first: nickel(II) is d^8, cobalt(II) is d^7, and cobalt(III) is d^6. Then fill the octahedral levels.

23. How would you differentiate between S_N1 and S_N2 mechanisms of substitution reactions? Give one example of each. [3 marks]

Solution:

Concept:

- S_N1 denotes substitution with a unimolecular rate-determining step; S_N2 has a bimolecular rate-determining step.
- The mechanism determines the rate law, intermediate or transition state, substrate preference and stereochemical outcome.

Step 1: Describe the unimolecular mechanism In S_N1, slow cleavage of the carbon-halogen bond first forms a carbocation; rapid nucleophilic attack follows. Hence the rate is $k[\mathrm{RX}]$, independent of nucleophile concentration. Stable carbocations favour the reaction, so tertiary substrates are generally more suitable than primary substrates. For an example, hydrolysis of tert-butyl bromide proceeds by

$$(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$$

followed by water attack and loss of a proton:

$$(CH_3)_3C^+ + H_2O \longrightarrow (CH_3)_3COH_2{}^+$$

$$(CH_3)_3COH_2{}^+ + H_2O \longrightarrow (CH_3)_3COH + H_3O^+.$$

A planar carbocation permits attack from either face, so a chiral substrate generally shows racemisation, often with some excess inversion.

Step 2: Describe the bimolecular mechanism In S_N2, the nucleophile attacks from the back of the carbon-leaving-group bond while the leaving group departs. Bond formation and cleavage occur together in one concerted step, through a transition state and without a carbocation intermediate. The rate is $k[\mathrm{RX}][\mathrm{Nu}^-]$. Steric crowding hinders attack, so methyl and primary substrates are favoured over tertiary substrates. One example is

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-.$$

Backside attack causes inversion of configuration when the reacting carbon is stereogenic. Rearrangement is absent because no carbocation forms.

Step 3: Contrast the diagnostic features S_N1 is stepwise and first order overall, can undergo carbocation rearrangement, and is favoured by conditions that stabilise ions. S_N2 is concerted and second order overall, is favoured by an accessible carbon and a strong nucleophile, and gives inversion rather than racemisation at a stereogenic reaction centre.

Step 4: Conclusion S_N1: carbocation pathway, rate $k[\mathrm{RX}]$, exemplified by tert-butyl bromide hydrolysis. S_N2: concerted backside attack, rate $k[\mathrm{RX}][\mathrm{Nu}^-]$, exemplified by methyl bromide reacting with hydroxide.

Quick Tip to Solve: Compare molecularity using the rate law, then check for a carbocation: its presence predicts rearrangement and loss of stereochemical purity.

24. How would you convert the following:

(i) Phenol to benzoquinone

(ii) Propanone to 2-Methylpropan-2-ol

(iii) Propene to Propan-2-ol [3 marks]

Solution:

Concept:

- Oxidation converts phenol into the conjugated diketone benzoquinone. Acidified dichromate provides the oxidising agent.
- A Grignard reagent adds an alkyl group to a carbonyl carbon; acidic hydrolysis then converts the magnesium alkoxide into an alcohol.
- Acid-catalysed hydration of an unsymmetrical alkene follows Markovnikov addition: the hydroxyl group reaches the more substituted carbon.

Step 1: (i) Oxidise phenol Treat phenol with sodium dichromate and dilute sulphuric acid. Oxidation gives para-benzoquinone (1,4-benzoquinone):

$$C_6H_5OH + 2[O] \xrightarrow{Na_2Cr_2O_7/H_2SO_4} C_6H_4O_2 + H_2O.$$

The two carbonyl groups in the product occupy positions 1 and 4 of the ring.

Step 2: (ii) Add a methyl group to propanone React propanone with methylmagnesium bromide in dry ether, then hydrolyse the addition product with dilute acid:

$$(CH_3)_2CO + CH_3MgBr \xrightarrow{\text{dry ether}} (CH_3)_3COMgBr,$$
$$(CH_3)_3COMgBr + H_2O \xrightarrow{H^+} (CH_3)_3COH + Mg(OH)Br.$$

The carbonyl carbon receives a third methyl group and becomes the tertiary alcohol carbon. Dry ether prevents premature destruction of the Grignard reagent by moisture.

Step 3: (iii) Hydrate propene Heat propene with water in the presence of dilute sulphuric acid:

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

Proton addition generates the more stable secondary carbocation, followed by attack of water and loss of a proton. Thus hydroxyl attaches at carbon 2.

Step 4: Conclusion The required conversions use, respectively, acidified dichromate; CH_3MgBr in dry ether followed by acidic hydrolysis; and acid-catalysed hydration of propene.

Quick Tip to Solve: For the extra carbon in the tertiary alcohol, count methyl groups: propanone has two, so add one with methylmagnesium bromide.

25. How would you account for the following:

(i) NCl_3 is an endothermic compound while NF_3 is an exothermic one.

(ii) XeF_2 is a linear molecule without a bend.

(iii) The electron gain enthalpy with negative sign for fluorine is less than that for chlorine; still fluorine is a stronger oxidizing agent than chlorine. [3 marks]

Solution:

Concept:

- The enthalpy of formation reflects energy absorbed in breaking reactant bonds and energy released in forming product bonds.
- VSEPR theory arranges electron pairs to minimise repulsions; lone pairs determine electron-pair geometry but are excluded when naming molecular shape.
- Oxidising strength of a halogen in water depends on dissociation, electron gain and hydration together, rather than electron gain enthalpy alone.

Step 1: (i) Compare formation energetics Formation from the elements requires breaking the very strong nitrogen triple bond and the halogen bonds. The N–F bonds formed are very strong because the small nitrogen and fluorine atoms have effective orbital overlap. Their formation releases enough energy to outweigh bond breaking, making formation of NF_3 exothermic. N–Cl bonds are much weaker, owing to less effective overlap between the differently sized atoms. Their formation does not compensate for the energy required to break the reactant bonds; hence formation of NCl_3 is endothermic.

Step 2: (ii) Apply VSEPR to xenon difluoride Xenon has eight valence electrons. Two Xe–F bonds leave three lone pairs on xenon, giving five electron-pair domains: AX_2E_3. They adopt a trigonal-bipyramidal arrangement. All three lone pairs occupy equatorial positions, where each has fewer 90-degree interactions. The two bond pairs therefore occupy opposite axial positions. The F–Xe–F bond angle is 180°, so the molecular shape is linear.

Step 3: (iii) Compare oxidation in aqueous solution The reduction process is $X_2(g) + 2e^- \rightarrow 2X^-(aq)$. Its energetics include breaking X–X, adding electrons to gaseous atoms, and hydrating the resulting ions. Fluorine has a less negative electron gain enthalpy than chlorine because its compact 2p shell produces greater electron repulsion. Nevertheless, the F–F bond is weak and the very small fluoride ion has a much more negative hydration enthalpy. These favourable contributions outweigh the electron-gain disadvantage, making fluorine the stronger oxidising agent.

Step 4: Conclusion NF_3 is stabilised by strong N–F bonds; XeF_2 is linear because its three lone pairs are equatorial; fluorine is the stronger aqueous oxidant because of favourable bond dissociation and hydration energetics.

Quick Tip to Solve: For halogen oxidising strength in water, always consider all three energy terms: bond breaking, electron gain and ion hydration.

26. Amino acids may be acidic, alkaline, or neutral. How does this happen? What are essential and non-essential amino acids? Name one of each type. [3 marks]

Solution:

Concept:

- Amino acids contain acidic carboxyl groups, $-COOH$, and basic amino groups, $-NH_2$; additional groups in the side chain determine their classification.
- Essential and non-essential refer to whether the human body can synthesise enough of an amino acid to meet its requirements, not to its importance.

Step 1: Explain acidic, alkaline and neutral amino acids An amino acid is acidic when it contains more carboxyl groups than amino groups; the excess carboxyl group gives acidic character. Glutamic acid, with two carboxyl groups and one amino group, is an example. It is alkaline or basic when amino groups outnumber carboxyl groups; lysine, with two amino groups and one carboxyl group, is an example. When their numbers are equal, it is classified as neutral; glycine, H_2NCH_2COOH, is an example. In water, amino acids commonly exist as zwitterions, containing both $-NH_3^+$ and $-COO^-$. This internal proton transfer accounts for their amphoteric behaviour; the classification above concerns the relative acidic and basic groups.

Step 2: Define essential amino acids Essential amino acids cannot be synthesised by the human body in sufficient quantities. They must therefore be supplied through the diet. Valine is one example of an essential amino acid.

Step 3: Define non-essential amino acids Non-essential amino acids can be synthesised by the human body, so a separate dietary supply is not normally essential. Glycine is one example. The word non-essential does not mean that these compounds are unnecessary: both classes are needed for protein synthesis and normal body function.

Step 4: Conclusion Excess carboxyl groups give acidic character, excess amino groups give basic character, and equal numbers give neutral amino acids. Valine is essential; glycine is non-essential.

Quick Tip to Solve: Count carboxyl and amino groups for acid-base classification, but ask whether the body can synthesise the amino acid for dietary classification.

27. Explain the following terms with one example in each case:

(i) Food preservatives

(ii) Enzymes

(iii) Detergents [3 marks]

Solution:

Concept:

- Food preservation slows spoilage, enzymes catalyse biochemical reactions, and detergents remove grease by surface action.
- An example must belong to the stated class: a preservative is a food additive, an enzyme is a biological catalyst, and a detergent is a cleansing agent.

Step 1: (i) Food preservatives Food preservatives are substances added to food to prevent or retard spoilage caused by microorganisms, thereby increasing its storage life. For example, sodium benzoate, C_6H_5COONa, is used to preserve acidic foods such as fruit juices and squashes. It inhibits the growth of microorganisms responsible for deterioration.

Step 2: (ii) Enzymes Enzymes are biological catalysts, generally proteins, which accelerate biochemical reactions in living organisms without being consumed. They act specifically on their substrates under suitable conditions of temperature and pH. For example, invertase catalyses the hydrolysis of sucrose into glucose and fructose.

Step 3: (iii) Detergents Detergents are cleansing agents whose molecules have a water-attracting hydrophilic part and a grease-attracting hydrophobic part. They help disperse oily dirt in water so that it can be washed away. For example, sodium dodecyl sulphate, $CH_3(CH_2)_{11}OSO_3Na$, is an anionic synthetic detergent. Unlike ordinary soaps, such synthetic detergents can cleanse in hard water.

Step 4: Conclusion Suitable examples are sodium benzoate for food preservatives, invertase for enzymes, and sodium dodecyl sulphate for detergents.

Quick Tip to Solve: Pair each definition immediately with its example: sodium benzoate preserves, invertase catalyses, and sodium dodecyl sulphate cleanses.

28(a). Explain the following terms:

(i) Rate of a reaction

(ii) Activation energy of a reaction

(b) The decomposition of phosphine, PH_3, proceeds according to the following equation:

$4PH_3(g) \rightarrow P_4(g) + 6H_2(g)$

It is found that the reaction follows the rate equation: Rate = $k[PH_3]$

The half-life of PH_3 is 37.9 s at 120°C.

(i) How much time is required for 3/4th of PH_3 to decompose?

(ii) What fraction of the original sample of PH_3 remains behind after 1 minute? [5 marks]

Solution:

Concept:

- The rate measures concentration change per unit time; activation energy is the energy barrier between reactants and the activated complex.
- For first-order disappearance, $[A]_t/[A]_0 = e^{-kt}$ and $t_{1/2} = \ln 2/k$, where k is the rate constant and t is elapsed time.

Step 1: (a)(i) Rate of a reaction The rate of a reaction is the decrease in concentration of a reactant, or increase in concentration of a product, per unit time. An average disappearance rate is $-\Delta[A]/\Delta t$; the minus sign makes the rate positive as reactant concentration falls. For a balanced reaction, the concentration changes are divided by their stoichiometric coefficients to define one common reaction

rate. For the given equation,

$$r = -\frac{1}{4}\frac{d[\mathrm{PH_3}]}{dt} = \frac{d[\mathrm{P_4}]}{dt} = \frac{1}{6}\frac{d[\mathrm{H_2}]}{dt}.$$

Concentration-based rates usually have units $\mathrm{mol\,L^{-1}\,s^{-1}}$.

Step 2: (a)(ii) Activation energy Activation energy, E_a, is the minimum additional energy that reacting species must acquire to reach the activated complex and undergo reaction. On an energy profile it is the difference between the energy of the activated complex and that of the reactants. Collisions below this energy barrier cannot produce the required chemical change; suitable molecular orientation is also necessary. Activation energy is expressed per mole, usually in $\mathrm{kJ\,mol^{-1}}$.

Step 3: (b)(i) Time for three-fourths decomposition The given rate law is first order in phosphine, so successive half-lives reduce its amount by the same factor of two. When three-fourths has decomposed, one-fourth remains:

$$\frac{[\mathrm{PH_3}]_t}{[\mathrm{PH_3}]_0} = 1 - \frac{3}{4} = \frac{1}{4} = \left(\frac{1}{2}\right)^2.$$

Thus two half-lives have elapsed, giving

$$t = 2t_{1/2} = 2(37.9) = 75.8\,\mathrm{s}.$$

The coefficient 4 in the balanced equation does not change the number of half-lives needed for this fractional decrease.

Step 4: (b)(ii) Fraction remaining after one minute Convert one minute to $60\,\mathrm{s}$, consistent with the given half-life. Combining the integrated first-order equation with the half-life relation avoids any dependence on the initial amount:

$$f = \frac{[\mathrm{PH_3}]_{60}}{[\mathrm{PH_3}]_0} = \left(\frac{1}{2}\right)^{60/37.9}$$
$$= e^{-(\ln 2)(60/37.9)} \approx 0.334.$$

The elapsed time lies between one and two half-lives, so a remaining fraction between $1/2$ and $1/4$ is consistent with the calculation.

Step 5: Conclusion The required time is $75.8\,\mathrm{s}$; after one minute the fraction of the original phosphine remaining is approximately 0.334, or 33.4%.

Quick Tip to Solve: Three-fourths decomposed means one-fourth remains: count two half-lives directly, then use $f = 2^{-t/t_{1/2}}$ for 60 seconds.

OR

28(b). (a) Explain the following terms:

(i) Order of a reaction

(ii) Molecularity of a reaction

(b) The rate of a reaction increases four times when the temperature changes from 300 K to 320 K. Calculate the energy of activation of the reaction, assuming that it does not change with temperature. (R = 8.314 J K^{-1} mol^{-1}) [5 marks]

Solution:

Concept:

- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law. It describes how the measured rate depends on concentration.
- Molecularity counts the reacting species participating in a single elementary step. It is determined from the mechanism of that elementary step.
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy and R the gas constant.

Step 1: (a)(i) Define order of a reaction If the experimentally established rate law is

$$r = k[A]^m[B]^n,$$

the overall order is $m + n$. The individual orders with respect to A and B are m and n, respectively. These exponents must be obtained experimentally and cannot generally be read from the balanced overall chemical equation. Order may be zero, an integer or a fraction. For example, a rate law $r = k[A]^2[B]$ has overall order $2 + 1 = 3$.

Step 2: (a)(ii) Define molecularity of a reaction Molecularity is the number of reacting species (atoms, ions or molecules) that take part together in one elementary reaction step. A step involving one reacting species is unimolecular; a step involving two is bimolecular. Thus molecularity is always a positive integer and is neither zero nor fractional. It applies to an elementary step, rather than to an overall complex reaction. For an elementary step its molecularity equals the sum of the reactant stoichiometric coefficients in that step; this rule must not be applied to a multistep overall equation.

Step 3: (b) Relate the fourfold increase to the rate constants At the same reactant concentrations, the temperature dependence of the reaction rate is represented by the rate constant. Hence the stated increase gives

$$T_1 = 300\,\text{K}, \qquad T_2 = 320\,\text{K}, \qquad \frac{k_2}{k_1} = 4.$$

Taking the ratio of the Arrhenius expressions at these two temperatures, with constant activation energy and the usual temperature-independent frequency-factor approximation over this interval, gives

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right).$$

The reciprocal-temperature difference is positive because the second temperature is higher.

Step 4: Substitute the numerical values Rearranging before substitution,

$$\begin{aligned} E_a &= \frac{R\ln(k_2/k_1)}{1/T_1 - 1/T_2} \\ &= 8.314 \times \ln 4 \times \frac{300 \times 320}{320 - 300} \\ &= 8.314 \times 1.38629 \times 4800 \\ &= 5.5324 \times 10^4\ \text{J mol}^{-1}. \end{aligned}$$

Here the reciprocal-temperature difference is $1/4800\,\text{K}^{-1}$. Dividing the result in joules per mole by 1000 gives the activation energy in kilojoules per mole. Its positive sign agrees with the observed increase in rate on heating.

Step 5: Conclusion Order is the sum of the concentration exponents in the experimental rate law; molecularity is the number of reacting species in an elementary step. The activation energy is $\boxed{E_a \approx 55.3\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: For two temperatures, use $1/T_1 - 1/T_2 = (T_2 - T_1)/(T_1T_2)$ and take the logarithm of the rate ratio, not of the temperature ratio.

29(a). Complete the following chemical equations:

(i) $Cr_2O_7^{2-}(aq) + H_2S(g) + H^+(aq) \rightarrow$

(ii) $Cu^{2+}(aq) + I^-(aq) \rightarrow$

(b) How would you account for the following:

(i) The oxidising power of oxoanions are in the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.

(ii) The third ionization enthalpy of manganese (Z = 25) is exceptionally high.

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. [5 marks]

Solution:

Concept:

- Redox equations conserve both atoms and charge. In acid, balance oxygen with H_2O, hydrogen with H^+, and charge with electrons.
- A larger positive standard reduction potential means a stronger oxidising agent. Stable electronic configurations and hydration affect the ease of oxidation or reduction.

Step 1: (a)(i) Dichromate oxidises hydrogen sulphide Chromium changes from $+6$ to $+3$, while sulphur changes from -2 to 0. The half-reactions are

$$\begin{aligned} \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- &\rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}, \\ \text{H}_2\text{S} &\rightarrow \text{S} + 2\text{H}^+ + 2\text{e}^-. \end{aligned}$$

Multiply the second equation by three, add and cancel electrons and six hydrogen ions:

$$\boxed{\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 3\text{H}_2\text{S}(\text{g}) + 8\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{S}(\text{s}) + 7\text{H}_2\text{O}(\text{l})}.$$

The charge on each side is $+6$; sulphur is deposited as a solid.

Step 2: (a)(ii) Copper(II) reacts with iodide Copper(II) is reduced to copper(I), and iodide is oxidised to iodine:

$$2\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow 2\mathrm{Cu}^+, \qquad 2\mathrm{I}^- \rightarrow \mathrm{I}_2 + 2\mathrm{e}^-.$$

Two additional iodide ions precipitate the copper(I) as insoluble CuI. Thus the overall reaction is

$$\boxed{2\mathrm{Cu}^{2+}(\mathrm{aq}) + 4\mathrm{I}^-(\mathrm{aq}) \rightarrow 2\mathrm{CuI}(\mathrm{s}) + \mathrm{I}_2}.$$

Precipitation of copper(I) iodide drives this reaction; the product is not copper(II) iodide.

Step 3: (b)(i) Compare the oxidising powers In acidic solution, the relevant reductions are $\mathrm{VO}_2^+ \rightarrow \mathrm{VO}^{2+}$, $\mathrm{Cr_2O_7^{2-}} \rightarrow \mathrm{Cr}^{3+}$ and $\mathrm{MnO_4^-} \rightarrow \mathrm{Mn}^{2+}$. Their standard reduction potentials are approximately $+1.00$, $+1.33$ and $+1.51\,\mathrm{V}$, respectively. A more positive reduction potential indicates a greater tendency to accept electrons and oxidise another substance. Therefore

$$\boxed{\mathrm{VO}_2^+ < \mathrm{Cr_2O_7^{2-}} < \mathrm{MnO_4^-}}$$

is the increasing order of oxidising strength. The order follows the reduction potentials, rather than oxidation state alone.

Step 4: (b)(ii) Explain the high third ionisation enthalpy of manganese Manganese has configuration $[\mathrm{Ar}]3d^5 4s^2$. Its first two ionisations remove the two $4s$ electrons, giving $\mathrm{Mn}^{2+} = [\mathrm{Ar}]3d^5$. This half-filled $3d$ subshell has extra stability due to its symmetrical distribution and exchange energy. The third ionisation removes a $3d$ electron, producing $\mathrm{Mn}^{3+} = [\mathrm{Ar}]3d^4$, and destroys that half-filled arrangement. Consequently, an exceptionally large energy is needed.

Step 5: (b)(iii) Compare the reducing powers of chromium(II) and iron(II) Cr^{2+} has a $3d^4$ configuration and readily loses an electron to form Cr^{3+}, with its relatively stable $3d^3$ configuration. In an octahedral field the latter has a stable t_{2g}^3 arrangement. Although oxidation of Fe^{2+} also gives stable half-filled $3d^5$ Fe^{3+}, the aqueous reduction potentials establish the relative tendencies:

$$E^\circ_{\mathrm{Cr}^{3+}/\mathrm{Cr}^{2+}} = -0.41\,\mathrm{V}, \qquad E^\circ_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = +0.77\,\mathrm{V}.$$

The more negative chromium reduction potential means the reverse oxidation of Cr^{2+} is much easier. Hence Cr^{2+} donates electrons more readily and is the stronger reducing agent.

Step 6: Conclusion Dichromate gives Cr^{3+} and sulphur with $\mathrm{H_2S}$; copper(II) gives CuI and iodine with iodide. Increasing reduction potentials explain the oxoanion order, the half-filled $3d^5$ configuration explains manganese's third ionisation enthalpy, and the easier oxidation of Cr^{2+} explains its stronger reducing power.

Quick Tip to Solve: For copper(II) with iodide, count iodide twice: two ions supply electrons and two more precipitate the two copper(I) ions as CuI.

OR

29(b). (a) Complete the following chemical equations:

(i) $MnO_4^-(aq) + S_2O_3^{2-}(aq) + H_2O(l) \rightarrow$

(ii) $Cr_2O_7^{2-}(aq) + Fe^{2+}(aq) + H^+(aq) \rightarrow$

(b) Explain the following observations giving appropriate reasons:

(i) La^{3+} **(**$Z = 57$**) and** Lu^{3+} **(**$Z = 71$**) do not show any colour in solutions.**

(ii) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.

(iii) Cu^+ **ion is not known in aqueous solutions.** [5 marks]

Solution:

Concept:

- Balance redox equations by equating electrons lost and gained, then balance oxygen with H_2O and hydrogen with H^+ or OH^-, according to the medium.
- Colour in lanthanoid ions generally arises from transitions within a partially occupied $4f$ subshell. Empty and completely filled subshells do not permit these transitions.
- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\text{BM}$, where n is the number of unpaired electrons. Hydration can stabilise one oxidation state relative to another in aqueous solution.

Step 1: (a)(i) Permanganate and thiosulphate In the aqueous neutral or alkaline reaction, permanganate is reduced to manganese dioxide and thiosulphate is oxidised to sulphate. The balanced half-reactions are

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-,$$
$$S_2O_3^{2-} + 10OH^- \longrightarrow 2SO_4^{2-} + 5H_2O + 8e^-.$$

Multiply the first by 8 and the second by 3; cancel 24 electrons and the common water and hydroxide terms. Thus

$$8MnO_4^-(aq) + 3S_2O_3^{2-}(aq) + H_2O(l)$$
$$\longrightarrow 8MnO_2(s) + 6SO_4^{2-}(aq) + 2OH^-(aq).$$

Both sides have 8 manganese, 6 sulphur, 42 oxygen and 2 hydrogen atoms, and total charge -14.

Step 2: (a)(ii) Acidified dichromate and iron(II) Dichromate gains six electrons on conversion to chromium(III), whereas each iron(II) ion loses one electron:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O,$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-.$$

Multiplying the iron half-reaction by six and adding gives

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq)$$
$$\longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l).$$

The charge is $+24$ on each side, confirming charge balance.

Step 3: (b)(i) Colourless lanthanum(III) and lutetium(III) The configurations are $La^{3+} : [Xe]4f^0$ and

Lu^{3+} : $[Xe]4f^{14}$. Lanthanum(III) has no $4f$ electrons to excite, while lutetium(III) has a completely filled $4f$ subshell. Consequently neither ion can undergo the characteristic visible-light f-f transitions responsible for the colours of many lanthanoid ions; their solutions are colourless.

Step 4: (b)(ii) Maximum paramagnetism of manganese(II) Neutral manganese has configuration $[Ar]3d^5 4s^2$. Loss of its two $4s$ electrons gives Mn^{2+} : $[Ar]3d^5$, with one electron in each of the five d orbitals. It therefore has five unpaired electrons, the maximum for the divalent ions of the first transition series in the usual free-ion comparison. Hence its paramagnetism is greatest, with $\mu = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92\,\text{BM}$.

Step 5: (b)(iii) Instability of copper(I) in water Although Cu^+ has a filled $3d^{10}$ configuration, aqueous stability also depends on hydration. The much more negative hydration enthalpy of Cu^{2+} compensates for the energy needed to form it. Consequently uncomplexed copper(I) disproportionates spontaneously in water:

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

One copper(I) ion is oxidised and the other reduced. Thus simple aqueous copper(I) solutions are unstable; a filled subshell alone does not ensure aqueous stability.

Step 6: Conclusion The completed equations produce MnO_2, sulphate and hydroxide in (a)(i), and Cr^{3+}, Fe^{3+} and water in (a)(ii), with coefficients as above. The observations follow respectively from $4f^0/4f^{14}$ configurations, five unpaired $3d$ electrons in Mn^{2+}, and disproportionation of aqueous Cu^+.

Quick Tip to Solve: Check both charge and atoms in each redox equation; for ionic properties, write the ion's electron configuration before counting unpaired electrons or discussing colour.

30(a). Illustrate the following name reactions, giving a chemical equation in each case:

(i) Clemmensen reaction

(ii) Cannizzaro's reaction

(b) Describe how the following conversion can be brought about:

(i) Cyclohexanol to Cyclohexan-1-one

(ii) Ethylbenzene to Benzoic acid

(iii) Bromobenzene to Benzoic acid [5 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- Aldehydes without an alpha hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised to carboxylate while another is reduced to alcohol.
- Secondary alcohols oxidise to ketones. Alkylbenzene side chains with a benzylic hydrogen oxidise to benzoic acid; a Grignard reagent reacts with carbon dioxide to give a carboxylic acid after hydrolysis.

Step 1: (a)(i) Clemmensen reaction Treat an aldehyde or ketone with zinc amalgam, $Zn(Hg)$, and

concentrated HCl. Oxygen is removed from the carbonyl group and replaced by two hydrogen atoms. For example, acetophenone gives ethylbenzene:

$$C_6H_5COCH_3 + 4[H] \xrightarrow{Zn(Hg)/\text{conc. HCl}} C_6H_5CH_2CH_3 + H_2O.$$

The carbon skeleton is retained and the carbonyl carbon becomes the methylene carbon of the product.

Step 2: (a)(ii) Cannizzaro reaction Heat benzaldehyde, which has no alpha hydrogen, with concentrated sodium hydroxide. Two aldehyde molecules undergo disproportionation: one forms sodium benzoate and the other forms benzyl alcohol:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{conc.}} C_6H_5COONa + C_6H_5CH_2OH.$$

The immediate oxidation product in the alkaline medium is the sodium salt, not free benzoic acid. Acidifying that salt would yield benzoic acid.

Step 3: (b)(i) Cyclohexanol to cyclohexan-1-one Oxidise the secondary alcohol with acidified potassium dichromate. The carbon bearing the hydroxyl group becomes the carbonyl carbon while the six-membered ring remains intact:

$$\underset{\text{cyclohexanol}}{C_6H_{11}OH} + [O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{cyclohexanone}}{C_6H_{10}O} + H_2O.$$

A secondary alcohol has one hydrogen on its hydroxyl-bearing carbon, allowing oxidation to a ketone.

Step 4: (b)(ii) Ethylbenzene to benzoic acid Heat ethylbenzene with alkaline potassium permanganate, then acidify the resulting potassium benzoate. Ethylbenzene has benzylic hydrogen atoms, so its side chain is oxidised to a carboxyl group regardless of its initial length:

$$C_6H_5CH_2CH_3 \xrightarrow[\text{heat}]{KMnO_4/OH^-} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.$$

The carbon directly attached to the benzene ring is retained as the carboxyl carbon; the extra side-chain carbon is removed by oxidation.

Step 5: (b)(iii) Bromobenzene to benzoic acid First prepare phenylmagnesium bromide by reacting bromobenzene with magnesium in absolutely dry ether. Add carbon dioxide and then hydrolyse with dilute acid:

$$C_6H_5Br + Mg \xrightarrow{\text{dry ether}} C_6H_5MgBr,$$
$$C_6H_5MgBr + CO_2 \longrightarrow C_6H_5COOMgBr,$$
$$C_6H_5COOMgBr + HCl \longrightarrow C_6H_5COOH + MgBrCl.$$

Carbon dioxide supplies the additional carbon of the carboxyl group. Moisture must be excluded during Grignard formation because it would destroy the reagent, producing benzene instead.

Step 6: Conclusion Clemmensen reduction uses $Zn(Hg)/HCl$; Cannizzaro disproportionation uses concentrated alkali. The conversions require, respectively, acidified dichromate, hot alkaline permanganate followed by acidification, and Grignard formation followed by CO_2 and acidic hydrolysis.

Quick Tip to Solve: For bromobenzene to benzoic acid, introduce the extra carbon with carbon dioxide after forming the Grignard reagent in dry ether.

OR

30(b). (a) Illustrate the following name reactions:

(i) Hell-Volhard-Zelinsky reaction

(ii) Wolff-Kishner reduction reaction

(b) How are the following conversions carried out:

(i) Ethylcyanide to ethanoic acid

(ii) Butan-1-ol to butanoic acid

(iii) Methylbenzene to benzoic acid

Write chemical equations for the involved reactions. [5 marks]

Solution:

Concept:

- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen using halogen and red phosphorus.
- Wolff-Kishner reduction converts a carbonyl group into a methylene group through its hydrazone, using hydrazine followed by strong base and heat.
- Hydrolysis retains the nitrile carbon. Hunsdiecker decarboxylation of a silver carboxylate removes that carbon as carbon dioxide, shortening the chain by one carbon.
- Primary alcohols and alkylbenzene side chains are oxidised to the corresponding carboxylic acids under suitable vigorous conditions.

Step 1: (a)(i) Hell-Volhard-Zelinsky reaction A carboxylic acid containing at least one alpha hydrogen reacts with bromine in the presence of red phosphorus, followed by hydrolysis, to form an alpha-bromo acid. For example, propanoic acid gives 2-bromopropanoic acid:

$$\mathrm{CH_3CH_2COOH + Br_2} \xrightarrow[\text{then water}]{\text{red P}} \mathrm{CH_3CHBrCOOH + HBr.}$$

Bromination occurs on the carbon next to the carboxyl group; the carboxyl group is retained.

Step 2: (a)(ii) Wolff-Kishner reduction The aldehyde or ketone first forms a hydrazone with hydrazine. Heating it with potassium hydroxide in ethylene glycol eliminates nitrogen and reduces the carbonyl group. Propanone provides an example:

$$\mathrm{CH_3COCH_3 + H_2NNH_2 \longrightarrow CH_3C(=NNH_2)CH_3 + H_2O,}$$

$$\mathrm{CH_3C(=NNH_2)CH_3} \xrightarrow[\Delta]{\text{KOH, ethylene glycol}} \mathrm{CH_3CH_2CH_3 + N_2.}$$

Thus propanone is reduced to propane without changing the carbon skeleton.

Step 3: (b)(i) Ethylcyanide to ethanoic acid Ethylcyanide is propanenitrile, $\mathrm{CH_3CH_2CN}$, so direct hydrolysis gives propanoic acid, not ethanoic acid. First hydrolyse it by heating with dilute hydrochloric acid:

$$\mathrm{CH_3CH_2CN + 2H_2O + HCl \longrightarrow CH_3CH_2COOH + NH_4Cl.}$$

Prepare its silver salt, then use bromine in carbon tetrachloride to remove one carbon by the Huns-

diecker reaction:

$$2CH_3CH_2COOH + Ag_2O \longrightarrow 2CH_3CH_2COOAg + H_2O,$$

$$CH_3CH_2COOAg + Br_2 \xrightarrow[\Delta]{CCl_4} CH_3CH_2Br + CO_2 + AgBr.$$

Hydrolyse bromoethane with aqueous potassium hydroxide and oxidise the resulting ethanol under reflux:

$$CH_3CH_2Br + KOH(aq) \longrightarrow CH_3CH_2OH + KBr,$$

$$CH_3CH_2OH + 2[O] \xrightarrow[\text{reflux}]{K_2Cr_2O_7/H_2SO_4} CH_3COOH + H_2O.$$

Step 4: (b)(ii) Butan-1-ol to butanoic acid Heat the primary alcohol under reflux with excess acidified potassium dichromate. Reflux permits complete oxidation through the aldehyde to the acid:

$$CH_3CH_2CH_2CH_2OH + 2[O] \xrightarrow[\text{reflux}]{K_2Cr_2O_7/H_2SO_4} CH_3CH_2CH_2COOH + H_2O.$$

All four carbon atoms remain in the product.

Step 5: (b)(iii) Methylbenzene to benzoic acid Heat methylbenzene with alkaline potassium permanganate, then acidify the potassium benzoate produced:

$$C_6H_5CH_3 + 2KMnO_4 \xrightarrow{\Delta} C_6H_5COOK + 2MnO_2 + KOH + H_2O,$$

$$C_6H_5COOK + HCl \longrightarrow C_6H_5COOH + KCl.$$

The benzylic methyl group is oxidised to a carboxyl group while the aromatic ring remains intact.

Step 6: Conclusion HVZ gives alpha-halogenation of carboxylic acids; Wolff-Kishner reduces carbonyl compounds to hydrocarbons. The conversions give ethanoic acid after one-carbon shortening, butanoic acid by primary-alcohol oxidation, and benzoic acid by side-chain oxidation followed by acidification.

Quick Tip to Solve: Count the nitrile carbon: ethylcyanide has three carbons, so its conversion to two-carbon ethanoic acid must include a chain-shortening step.