CBSE Class 12 Chemistry Question Paper 2014 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) Questions number **1** to **8** are very short-answer questions and carry **1** mark each.
(iii) Questions number **9** to **18** are short-answer questions and carry **2** marks each.
(iv) Questions number **19** to **27** are also short-answer questions and carry **3** marks each.
(v) Questions number **28** to **30** are long-answer questions and carry **5** marks each.
(vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. What is the effect of temperature on chemisorption? [1 mark]

Solution:

Concept:

- Chemisorption involves formation of chemical bonds between adsorbate molecules and the adsorbent surface.
- Bond formation often requires activation energy; adsorption itself is generally exothermic.

Step 1: At initially low temperature At low temperature, few molecules possess the activation energy needed for chemisorption. Increasing the temperature allows more molecules to cross this energy barrier, so chemisorption initially increases.

Step 2: At higher temperature Once the activation barrier is overcome, the exothermic nature of adsorption becomes important. A further rise in temperature favours desorption and decreases the extent of chemisorption.

Step 3: Conclusion Chemisorption first increases with rise in temperature and, after reaching a maximum, decreases at higher temperature.

Quick Tip to Solve: Remember the two effects: activation energy explains the initial rise; exothermic adsorption explains the later fall.

2. What is the role of zinc metal in the extraction of silver? [1 mark]

Solution:

Concept:

- Zinc is more electropositive than silver and acts as a reducing agent in the cyanide process.
- Silver present as the soluble dicyanidoargentate(I) complex is reduced to metallic silver.

Step 1: Identify the dissolved silver species On cyanide leaching, silver passes into solution as the complex ion $[Ag(CN)_2]^-$. Zinc dust is then added to recover silver from this solution.

Step 2: Write the displacement reaction Zinc is oxidised while silver(I) is reduced:

$$2[Ag(CN)_2]^- + Zn \longrightarrow [Zn(CN)_4]^{2-} + 2Ag.$$

Thus zinc precipitates silver by displacement from its cyanide complex.

Step 3: Conclusion Zinc acts as a reducing agent and displaces (precipitates) metallic silver from its cyanide-complex solution.

Quick Tip to Solve: In cyanide extraction, identify zinc as the metal that reduces dissolved silver(I) to silver metal.

3. What is the basicity of H_3PO_3? [1 mark]

Solution:

Concept:

- The basicity of an oxyacid is the number of ionisable hydrogen atoms per molecule.
- In phosphorus oxyacids, hydrogen bonded to oxygen can ionise; hydrogen bonded directly to phosphorus does not.

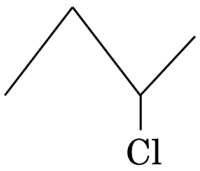
Step 1: Use the structure of phosphorous acid Phosphorous acid, H_3PO_3, has the structure $HP(=O)(OH)_2$. It contains two $O-H$ bonds and one $P-H$ bond.

Step 2: Count the replaceable protons Only the two hydrogen atoms of the hydroxyl groups can be released as H^+. The directly phosphorus-bonded hydrogen is not ionisable in the normal acid dissociation, so three total hydrogens do not mean three replaceable protons.

Step 3: Conclusion The basicity of H_3PO_3 is $\boxed{2}$; it is a dibasic acid.

Quick Tip to Solve: Write HP(=O)(OH)2 first, then count only the two OH groups when determining basicity.

4. Identify the chiral molecule in the following pair: [1 mark]





Solution:

Concept:

- A tetrahedral carbon is an asymmetric (chiral) centre when it is attached to four different groups.
- Compare the complete groups attached to a carbon, rather than just their first atoms.

Step 1: Examine the first molecule The first structure is 2-chlorobutane, $CH_3CH_2CH(Cl)CH_3$. Its chlorine-bearing carbon is bonded to Cl, H, CH_3 and CH_2CH_3. These four groups are all different, giving one chiral centre.

Step 2: Examine the second molecule The second structure is 1-chlorobutane, $ClCH_2CH_2CH_2CH_3$. Its chlorine-bearing carbon has two identical hydrogen atoms; the other carbons also lack four different substituents. It therefore has no chiral centre.

Step 3: Conclusion The first (left-hand) molecule, $\boxed{\text{2-chlorobutane}}$, is chiral.

Quick Tip to Solve: At the chlorine-bearing carbon, distinguish methyl from ethyl: these make the first molecule chiral.

5. Which of the following is a natural polymer?

Buna-S, Proteins, PVC [1 mark]

Solution:

Concept:

- Natural polymers are macromolecules formed by living organisms and found in nature.
- Proteins are polypeptides: their amino-acid units are joined by peptide linkages.

Step 1: Identify the biological polymer Proteins are synthesised by living cells from amino acids. Their repeating peptide backbone and natural biological origin make them natural polymers.

Step 2: Check the other choices Buna-S is a synthetic copolymer of 1,3-butadiene and styrene, used as synthetic rubber. PVC, poly(vinyl chloride), is a synthetic addition polymer of vinyl chloride. Neither belongs to the natural-polymer category.

Step 3: Conclusion Proteins are the natural polymers among the given substances.

Quick Tip to Solve: Associate proteins with amino acids and living cells; Buna-S and PVC are manufactured synthetic polymers.

6. The conversion of primary aromatic amines into diazonium salts is known as ____. [1 mark]

Solution:

Concept:

- Diazotisation converts a primary aromatic amine, $ArNH_2$, into an arenediazonium salt.
- Nitrous acid is generated in situ from sodium nitrite and a mineral acid at 273–278 K.

Step 1: Identify the reaction A primary aromatic amine reacts with nitrous acid in cold acidic solution. The amino group is converted into the diazonium group, $-N_2^+$, giving a diazonium salt.

Step 2: Illustrate with aniline For aniline, the conversion is

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

The mixture is kept cold because arenediazonium salts are unstable at higher temperatures.

Step 3: Conclusion The conversion is known as diazotisation.

Quick Tip to Solve: Recognise ArNH2 becoming ArN2+ in cold nitrous acid as diazotisation, rather than azo coupling.

7. What are the products of hydrolysis of sucrose? [1 mark]

Solution:

Concept:

- Sucrose is a disaccharide: hydrolysis breaks its glycosidic linkage by adding water.
- The two constituent monosaccharides are glucose and fructose.

Quick Tip to Solve: Remember sucrose as glucose plus fructose; maltose instead gives two glucose units.

Step 1: Identify the constituent sugars Sucrose contains one glucose unit and one fructose unit joined through their anomeric carbon atoms. Cleavage of this linkage releases the two sugars; hydrolysis does not give two glucose molecules.

Step 2: Write the hydrolysis reaction In dilute acid or in the presence of invertase, the reaction is

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6\ (\text{glucose}) + C_6H_{12}O_6\ (\text{fructose}).$$

One mole of sucrose therefore gives one mole each of D-glucose and D-fructose.

Step 3: Conclusion The products are an equimolar mixture of D-glucose and D-fructose.

Quick Tip to Solve: Remember sucrose as glucose plus fructose; maltose instead gives two glucose units.

8. Write the structure of p-methylbenzaldehyde. [1 mark]

Solution:

Concept:

- Benzaldehyde has a formyl group, $-CHO$, directly attached to a benzene ring.
- The prefix para (p) specifies the 1,4 relationship of two substituents on benzene.

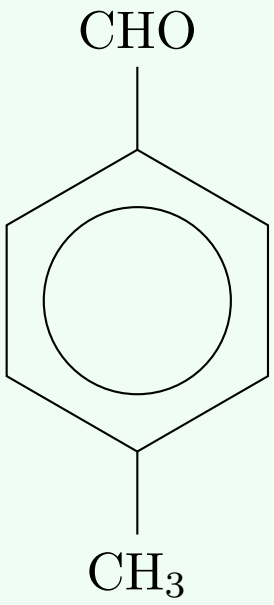
Step 1: Place the aldehyde group Take benzaldehyde as the parent compound. The ring carbon bonded to $-CHO$ is numbered 1; the aldehydic carbon is outside the six-membered aromatic ring.

Step 2: Place the para methyl substituent Attach $-CH_3$ at ring position 4, opposite the carbon bearing $-CHO$. The condensed structural formula is

$$\boxed{p\text{-}CH_3 - C_6H_4 - CHO}.$$

Thus the two substituents occupy opposite positions of the benzene ring, and the compound is also called 4-methylbenzaldehyde.

Quick Tip to Solve: For a para-disubstituted benzene, fix one group at carbon 1 and the second at carbon 4.



Structure of 4-methylbenzaldehyde

Step 3: Conclusion The structure is $\boxed{4\text{-}CH_3 - C_6H_4 - CHO}$, with methyl and formyl groups in the para positions.

Quick Tip to Solve: For a para-disubstituted benzene, fix one group at carbon 1 and the second at carbon 4.

9. An element with density 2.8 g cm^{-3} forms a f.c.c. unit cell with edge length 4 x 10^{-8} cm. Calculate the molar mass of the element.

(Given: N_A = 6.022 x 10^{23} mol^{-1}) [2 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = \dfrac{ZM}{N_A a^3}$, where ρ is density, Z the number of atoms per cell, M molar mass and a edge length.
- An f.c.c. cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms.

Step 1: Calculate the volume of one cell The edge length is $a = 4 \times 10^{-8}$ cm. Hence

$$a^3 = (4 \times 10^{-8})^3 = 64 \times 10^{-24} = 6.4 \times 10^{-23}\ \text{cm}^3.$$

Its mass is density times volume:

$$m_{\text{cell}} = 2.8 \times 6.4 \times 10^{-23} = 1.792 \times 10^{-22}\ \text{g}.$$

Step 2: Convert cell mass into molar mass Four atoms are present in each f.c.c. cell, so the mass of

Quick Tip to Solve: Count the f.c.c. atoms first: use Z = 4, and cube both the numerical edge and its power of ten.

one atom is $m_{\text{cell}}/4$. Multiplication by Avogadro's constant gives

$$\begin{aligned} M &= \frac{\rho a^3 N_{\text{A}}}{4} \\ &= \frac{(2.8)(6.4 \times 10^{-23})(6.022 \times 10^{23})}{4} \\ &= 26.97856\ \text{g mol}^{-1}. \end{aligned}$$

The powers of ten cancel because the cell volume and Avogadro constant have opposite exponents.

Step 3: Conclusion The molar mass of the element is approximately $\boxed{27\ \text{g mol}^{-1}}$.

Quick Tip to Solve: Count the f.c.c. atoms first: use Z = 4, and cube both the numerical edge and its power of ten.

10(a). (i) What type of non-stoichiometric point defect is responsible for the pink colour of LiCl? (ii) What type of stoichiometric defect is shown by NaCl? [2 marks]

Solution:

Concept:

- An F-centre is an anion vacancy occupied by an electron; it produces a metal-excess non-stoichiometric defect.
- A Schottky defect consists of vacancies of equal numbers of cations and anions, preserving electrical neutrality and stoichiometry.

Step 1: Identify the defect responsible for pink LiCl The pink colour is due to a metal-excess defect caused by anion vacancies. Some Cl^- lattice sites are vacant and electrons occupy these sites to maintain charge balance. These electron-containing vacancies are called F-centres. Their electrons absorb energy from visible light and become excited; the associated selective absorption gives the crystal its colour.

Step 2: Identify the stoichiometric defect in NaCl NaCl exhibits the Schottky defect: equal numbers of Na^+ and Cl^- ions are missing from their normal lattice sites. The ratio of the ions remains $1:1$, so the composition and electrical neutrality are maintained. Since ions are missing, the mass and hence density of the crystal decrease.

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

Quick Tip to Solve: Associate coloured alkali halides with electron-filled anion vacancies, and NaCl with paired ionic vacancies.

OR

10(b). How will you distinguish between the following pairs of terms:

(i) Tetrahedral and octahedral voids

(ii) Crystal lattice and unit cell [2 marks]

Solution:

Concept:

- A void is an unoccupied space between closely packed particles; its coordination is the number of nearest surrounding particles.
- A crystal lattice describes the periodic arrangement of points, while a unit cell is a repeating portion that generates it.

Step 1: Distinguish tetrahedral and octahedral voids A tetrahedral void is surrounded by four particles whose centres occupy the corners of a tetrahedron; its coordination number is 4. An octahedral void is surrounded by six particles whose centres form an octahedron; its coordination number is 6. In close packing of N particles there are $2N$ tetrahedral voids and N octahedral voids, and the octahedral void is the larger of the two.

Step 2: Distinguish crystal lattice and unit cell A crystal lattice is a regular, repeating three-dimensional array of points representing equivalent positions in a crystal. A unit cell is the smallest repeating geometrical portion of that lattice which, by translation along the three lattice directions, reproduces the entire lattice. Thus the lattice is the extended periodic array, whereas the unit cell is the finite repeating building block specified by its edge lengths and interaxial angles.

Step 3: Conclusion (i) Tetrahedral and octahedral voids have four and six nearest surrounding particles respectively. (ii) A lattice is the extended periodic array; a unit cell is its repeating building block.

Quick Tip to Solve: Use the prefixes tetra = four and octa = eight faces; an octahedral void has six surrounding particles.

11. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? [2 marks]

Solution:

Concept:

- At infinite dilution, each ion contributes independently to the limiting molar conductivity, irrespective of the nature of the other ion present.
- Conductivity κ depends on the number of mobile ions per unit volume and their mobility.

Step 1: State Kohlrausch's law The limiting molar conductivity of an electrolyte is the sum of the individual ionic contributions, each multiplied by its stoichiometric number:

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ.$$

Quick Tip to Solve: For dilution questions, distinguish conductivity (ions per unit volume) from molar conductivity (the contribution of one mole).

Here ν_+ and ν_- are the numbers of cations and anions in one formula unit, while λ°_+ and λ°_- are their limiting ionic molar conductivities. Interionic interactions become negligible at infinite dilution, so these contributions are independent.

Step 2: Explain dilution's effect on conductivity Adding solvent increases the solution volume and reduces the number of ions per unit volume. Fewer charge carriers are therefore present in a given volume, so conductivity decreases. Dilution may increase ionic mobility and the ionisation of a weak electrolyte, but the decrease in charge-carrier concentration dominates. Distinguish this from molar conductivity, which generally increases on dilution because it refers to the conductance associated with one mole of electrolyte.

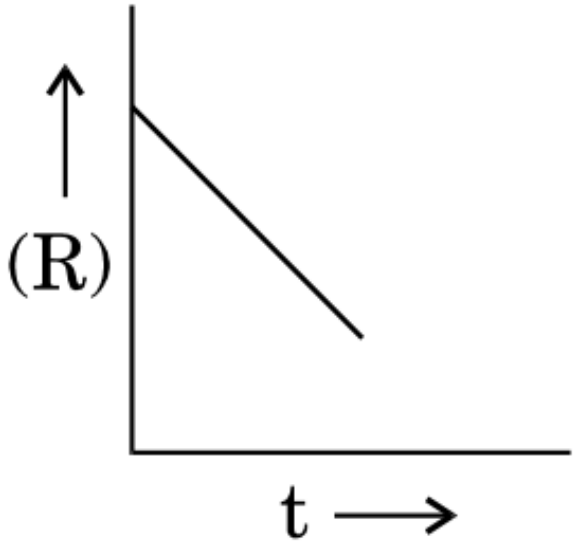
Step 3: Conclusion Kohlrausch's law gives $\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$. Conductivity decreases on dilution because the number of mobile ions per unit volume decreases.

Quick Tip to Solve: For dilution questions, distinguish conductivity (ions per unit volume) from molar conductivity (the contribution of one mole).

12. For a chemical reaction R $\rightarrow$ P, the variation in the concentration (R) vs. time (t) plot is given as

(i) Predict the order of the reaction.

(ii) What is the slope of the curve? [2 marks]



Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$, where k is the rate constant.
- Its integrated rate law is $[R]_t = [R]_0 - kt$. Thus a plot of concentration against time is a straight line with a negative slope.

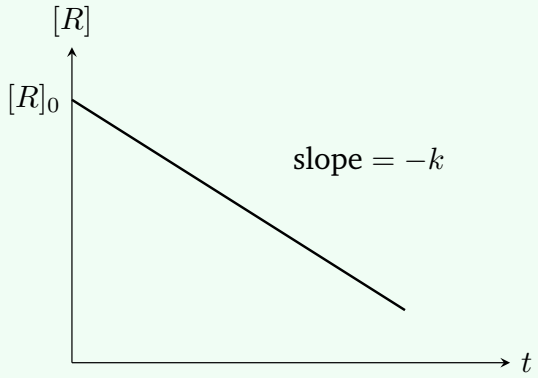
Step 1: Identify the reaction order The graph shows that the concentration of reactant R decreases

Quick Tip to Solve: Identify which quantity is on the vertical axis: a straight descending $[R]$-versus-time line indicates zero order and slope $-k$.

linearly with time. A straight line in a plot of $[R]$ versus t means equal amounts of reactant are consumed in equal time intervals. Hence the rate remains constant as the reactant concentration changes. Comparing the observed graph with the integrated rate equation

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

identifies the reaction as zero order. A first-order reaction instead gives a straight line when $\ln[R]$, rather than $[R]$, is plotted against time.



Linear decrease of reactant concentration for a zero-order reaction.

Step 2: Read the slope from the rate equation Compare $[R]_t = [R]_0 - kt$ with $y = c + mx$. The vertical intercept is $[R]_0$, and the coefficient of time is $-k$. Therefore,

$$\text{slope} = \frac{\Delta[R]}{\Delta t} = -k.$$

The sign is negative because concentration decreases as time increases. No numerical value can be calculated without numerical scales on the axes; the required slope is expressed in terms of the rate constant.

Step 3: Conclusion (i) The reaction is zero order. (ii) The slope of the concentration-time line is $-k$, where k is the zero-order rate constant.

Quick Tip to Solve: Identify which quantity is on the vertical axis: a straight descending $[R]$-versus-time line indicates zero order and slope $-k$.

13. Explain the principle of the method of electrolytic refining of metals. Give one example. [2 marks]

Solution:

Concept:

- Electrolytic refining uses electrolysis to transfer a metal from an impure anode to a pure cathode through a solution containing ions of that metal.
- Oxidation dissolves the anode metal, while reduction deposits pure metal on the cathode. Impurities are separated because their electrode behaviour differs.

Quick Tip to Solve: Remember the direction of purification: impure anode dissolves; pure metal grows on the cathode. Write the two half-reactions to verify this.

Step 1: Explain the refining principle Make the impure metal the anode and a thin sheet of pure metal the cathode. Use a suitable soluble salt of the same metal as the electrolyte. On passing direct current under suitable conditions, the metal dissolves from the anode as ions and an equivalent quantity is deposited on the cathode. Less reactive insoluble impurities collect below the anode as anode mud, while more reactive impurities may enter the solution but do not deposit along with the desired metal.

Step 2: Give copper as an example In copper refining, impure copper is the anode, pure copper is the cathode, and acidified copper(II) sulphate solution is the electrolyte. The electrode reactions are

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

Thus the anode becomes thinner and pure copper accumulates on the cathode. Precious-metal impurities such as silver and gold remain in the anode mud.

Step 3: Conclusion Electrolytic refining purifies a metal by anodic dissolution followed by cathodic deposition. Copper is refined using impure copper, a pure copper cathode and acidified $\mathrm{CuSO_4}$ electrolyte.

Quick Tip to Solve: Remember the direction of purification: impure anode dissolves; pure metal grows on the cathode. Write the two half-reactions to verify this.

14. Complete the following equations:

(i) $\mathbf{P_4 + H_2O \rightarrow}$

(ii) $\mathbf{XeF_4 + O_2F_2 \rightarrow}$ [2 marks]

Solution:

Concept:

- In a disproportionation reaction, atoms of the same element undergo both oxidation and reduction.
- Dioxygen difluoride, $\mathrm{O_2F_2}$, is a strong fluorinating agent; it converts xenon tetrafluoride into xenon hexafluoride.

Step 1: (i) Reaction of phosphorus with water The completed, balanced equation is

$$\mathrm{P_4 + 6H_2O \longrightarrow PH_3 + 3H_3PO_2}.$$

The products are phosphine and hypophosphorous acid. Phosphorus initially has oxidation state zero; it becomes -3 in $\mathrm{PH_3}$ and $+1$ in $\mathrm{H_3PO_2}$. Thus one phosphorus atom is reduced while three are oxidised. There are four P atoms, twelve H atoms and six O atoms on each side.

Step 2: (ii) Fluorination of xenon tetrafluoride The completed, balanced equation is

$$\mathrm{XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2}.$$

Xenon tetrafluoride gains two fluorine atoms to form xenon hexafluoride, and oxygen gas is released. The coefficients are all unity: each side contains one Xe atom, six F atoms and two O atoms.

Quick Tip to Solve: For the phosphorus equation, use one phosphine and three hypophosphorous acid molecules before balancing water.

Step 3: Conclusion $\boxed{P_4 + 6H_2O \rightarrow PH_3 + 3H_3PO_2}$ and $\boxed{XeF_4 + O_2F_2 \rightarrow XeF_6 + O_2}$.

Quick Tip to Solve: For the phosphorus equation, use one phosphine and three hypophosphorous acid molecules before balancing water.

15. Draw the structures of the following:

(i) XeF_2

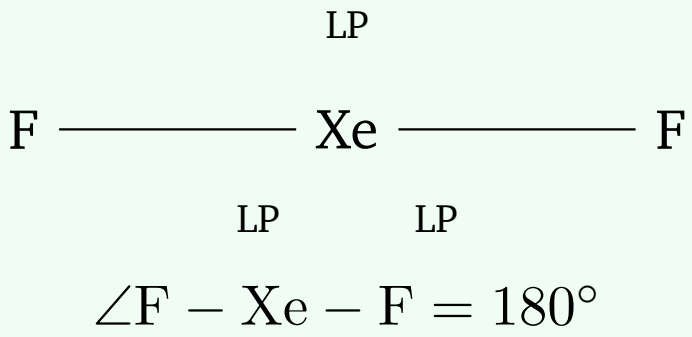
(ii) BrF_3 [2 marks]

Solution:

Concept:

- VSEPR theory predicts geometry by minimising repulsions between electron pairs around the central atom; lone pairs repel more strongly than bonding pairs.
- Five electron domains give a trigonal-bipyramidal electron-pair arrangement. Lone pairs preferentially occupy equatorial sites, which have fewer 90° interactions.

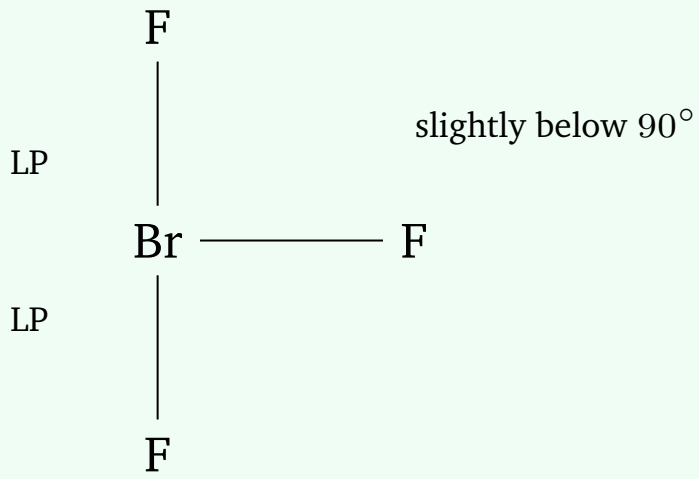
Step 1: (i) Structure of xenon difluoride Xenon has eight valence electrons. Two Xe–F bonds leave three lone pairs on Xe, so the VSEPR type is AX_2E_3. All three lone pairs occupy equatorial positions in the trigonal-bipyramidal electron-pair arrangement. The two F atoms occupy opposite axial positions. Hence the molecular shape is linear, with $\angle \mathrm{F} - \mathrm{Xe} - \mathrm{F} = 180^\circ$; the conventional hybridisation description is sp^3d.



Linear xenon difluoride; the three lone pairs lie in the equatorial plane.

Step 2: (ii) Structure of bromine trifluoride Bromine has seven valence electrons. Three Br–F bonds leave two lone pairs on Br, giving type AX_3E_2. The two lone pairs occupy equatorial sites. Two fluorine atoms are axial and one is equatorial, producing a T-shaped molecule. Lone-pair repulsions distort the ideal arrangement, so the adjacent F–Br–F angles are slightly less than 90°. Its conventional hybridisation description is also sp^3d.

Quick Tip to Solve: Count lone pairs on the central atom first: three equatorial lone pairs leave a line, while two leave a T.



T-shaped bromine trifluoride; LP denotes a lone pair.

Step 3: Conclusion XeF_2 is linear; BrF_3 is T-shaped. The central atoms have three and two lone pairs, respectively.

Quick Tip to Solve: Count lone pairs on the central atom first: three equatorial lone pairs leave a line, while two leave a T.

16. Write the equations involved in the following reactions:

(i) Reimer - Tiemann reaction

(ii) Williamson synthesis [2 marks]

Solution:

Concept:

- The Reimer–Tiemann reaction introduces a formyl group, $-CHO$, mainly ortho to the hydroxyl group of phenol.
- Williamson synthesis forms an ether by nucleophilic substitution between an alkoxide ion and an alkyl halide.

Step 1: (i) Reimer–Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, followed by acidification. The major product is 2-hydroxybenzaldehyde (salicylaldehyde). The overall equation, after work-up, is

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{\Delta} o\text{–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

Acidification liberates the free hydroxy aldehyde from the alkaline reaction mixture. A small amount of the para isomer may also form; the ortho product is the standard major product.

Step 2: (ii) Williamson ether synthesis A sodium alkoxide reacts with an alkyl halide to give an ether:

$$RONa + R'X \longrightarrow ROR' + NaX.$$

Quick Tip to Solve: For Williamson synthesis, place the less hindered alkyl group in the halide so that substitution is favoured.

Here R and R' are alkyl groups and X is a halogen. For example,

$$C_2H_5ONa + CH_3I \longrightarrow C_2H_5OCH_3 + NaI.$$

Sodium ethoxide and methyl iodide give methoxyethane. A methyl or primary alkyl halide is preferred because it undergoes the required S_N2 substitution readily.

Step 3: Conclusion Reimer–Tiemann reaction gives mainly salicylaldehyde from phenol; Williamson synthesis gives an ether from a sodium alkoxide and an alkyl halide.

Quick Tip to Solve: For Williamson synthesis, place the less hindered alkyl group in the halide so that substitution is favoured.

17. Write the mechanism of the following reaction:

$$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$$

[2 marks]

Solution:

Concept:

- The alcohol oxygen accepts a proton from HBr. This converts the poor leaving group $-OH$ into the good leaving group water, H_2O.
- Ethanol is a primary alcohol; bromide displaces water by a concerted S_N2 substitution without forming a free primary carbocation.

Step 1: Protonation of ethanol A lone pair on oxygen attacks the proton of HBr, while the H–Br bond breaks towards bromine:

$$CH_3CH_2OH + HBr \rightleftharpoons CH_3CH_2OH_2^+ + Br^-.$$

The resulting ethyloxonium ion has a positively charged oxygen and a water group that can leave readily.

Step 2: Nucleophilic displacement by bromide The bromide ion attacks the primary carbon bonded to oxygen from the back side. At the same time, the C–O bond breaks and its electron pair goes to oxygen:

$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

Bond formation to bromine and loss of water occur in one step. A separate ethyl carbocation is therefore unnecessary, and the primary carbon favours this substitution pathway.

Step 3: Conclusion Ethanol forms bromoethane by protonation followed by S_N2 displacement of water by Br^-.

Quick Tip to Solve: First protonate an alcohol's OH group; show water, not hydroxide, as the leaving group in acid.

18. Write the name of monomers used for getting the following polymers:

(i) Bakelite

(ii) Neoprene [2 marks]

Solution:

Concept:

- A monomer is a small molecule that supplies structural units to a polymer. Condensation polymers can involve two different monomers, while an addition polymer can be formed from a single unsaturated monomer.
- Bakelite is a phenol-formaldehyde condensation polymer. Neoprene is an addition polymer of a substituted conjugated diene.

Step 1: Monomers of Bakelite Bakelite is prepared from phenol, C_6H_5OH, and formaldehyde (methanal), $HCHO$. Condensation introduces links between phenol rings, and further heating produces a cross-linked network. Thus both phenol and formaldehyde must be named; phenol alone does not give Bakelite.

Step 2: Monomer of neoprene Neoprene is obtained by polymerising chloroprene, whose systematic name is 2-chlorobuta-1,3-diene:

$$CH_2 = C(Cl) - CH = CH_2.$$

It is the chlorine-substituted conjugated diene, not isoprene. Addition across the conjugated system produces the polymer chain without the elimination of a small molecule.

Step 3: Conclusion (i) Bakelite: phenol and formaldehyde (methanal). (ii) Neoprene: chloroprene (2-chlorobuta-1,3-diene).

Quick Tip to Solve: Remember neoprene by its chlorine substituent: its monomer is chloroprene, whereas isoprene forms natural rubber.

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19. (a) Calculate $\Delta_r G^\circ$ for the reaction

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

Given: $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}

(b) Name the type of cell which was used in Apollo space programme for providing electrical power.

[3 marks]

Solution:

Concept:

- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{cell}$, where n is the number of electrons transferred per balanced reaction and F is the Faraday constant.
- A fuel cell continuously converts the chemical energy of externally supplied reactants into electrical energy. Hydrogen and oxygen can react to give water in such a cell.

Quick Tip to Solve: Count the electrons from the balanced half-reactions, and retain the minus sign in the Gibbs energy formula.

Step 1: Determine the electron transfer in part (a) The oxidation and reduction half-reactions are

$$\mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2e^-,$$
$$\mathrm{Cu^{2+}(aq)} + 2e^- \longrightarrow \mathrm{Cu(s)}.$$

Hence two electrons are transferred for the reaction as written, so $n = 2$. The charge of either ion alone must be related to the balanced half-reactions before applying the energy formula.

Step 2: Calculate the standard Gibbs energy change Substituting the supplied positive cell potential gives

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(2.71)\\ &= -523030\,\mathrm{J\ mol^{-1}}\\ &= -523.03\,\mathrm{kJ\ mol^{-1}}.\end{aligned}$$

Since coulomb times volt is joule, these are energy units per mole of the reaction as written. The negative sign agrees with the positive standard cell potential and indicates that the forward reaction is thermodynamically favourable under standard conditions.

Step 3: Identify the cell in part (b) The Apollo space programme used a hydrogen-oxygen fuel cell for electrical power. Hydrogen is the fuel and oxygen is the oxidising reactant. Its overall reaction is $2\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\mathrm{H_2O}$; the resulting water was also useful aboard the spacecraft.

Step 4: Conclusion (a) $\boxed{\Delta_r G^\circ = -523.03\,\mathrm{kJ\ mol^{-1}}}$. (b) A hydrogen-oxygen fuel cell.

Quick Tip to Solve: Count the electrons from the balanced half-reactions, and retain the minus sign in the Gibbs energy formula.

20. The following data were obtained during the first order thermal decomposition of $\mathrm{SO_2Cl_2}$ at a constant volume:

$$\mathrm{SO_2Cl_2(g)} \longrightarrow \mathrm{SO_2(g)} + \mathrm{Cl_2(g)}$$

Experiment	Time/$\mathrm{s^{-1}}$	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant. (Given: $\log 4 = 0.6021,\ \log 2 = 0.3010$**)** [3 marks]

Solution:

Concept:

- For a first-order decomposition, $k = \dfrac{2.303}{t}\log\dfrac{p_0}{p_A}$, where p_0 and p_A are the initial and remaining partial pressures of the reactant.
- At constant volume and temperature, gas pressure is proportional to the amount present. For $A(g) \rightarrow B(g) + C(g)$, the total pressure increases by the pressure equivalent of the amount decomposed.

Step 1: Relate the pressure increase to decomposition Initially only $\mathrm{SO_2Cl_2}$ is present, at $p_0 = 0.4$ atm. Let x atm be the pressure equivalent of the reactant decomposed after 100 s. The partial pressures are

Quick Tip to Solve: For this one-to-two gas decomposition, first calculate the reactant pressure as $p_A = 2p_0 - P_t$.

then $0.4 - x$, x and x for SO_2Cl_2, SO_2 and Cl_2, respectively. Hence

$$P_t = (0.4 - x) + x + x = 0.4 + x.$$

With $P_t = 0.7$ atm, $x = 0.3$ atm, so the remaining reactant pressure is $p_A = 0.1$ atm.

Step 2: Apply the integrated first-order rate equation The pressure ratio replaces the concentration ratio because both pressures refer to the same volume and temperature. Therefore

$$\begin{aligned} k &= \frac{2.303}{100} \log \frac{0.4}{0.1} \\ &= \frac{2.303}{100} \log 4 \\ &= \frac{2.303 \times 0.6021}{100} \\ &= 0.013866\,\text{s}^{-1}. \end{aligned}$$

The total pressure must not be used as the remaining reactant pressure: it includes both gaseous products. The time interval is 100 s.

Step 3: Conclusion The rate constant is $\boxed{k = 1.3866 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For this one-to-two gas decomposition, first calculate the reactant pressure as $p_A = 2p_0 - P_t$.

21. What are emulsions? What are their different types? Give one example of each type. [3 marks]

Solution:

Concept:

- An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids that are essentially immiscible.
- Emulsions are classified by the continuous dispersion medium: water gives oil-in-water, whereas oil gives water-in-oil.

Step 1: Define an emulsion When one of two immiscible liquids is distributed as very fine droplets throughout the other, the resulting colloidal dispersion is called an emulsion. The droplets constitute the dispersed phase, while the surrounding continuous liquid is the dispersion medium. Oil and water are the usual examples of the two liquids. The word oil here includes a liquid organic or fatty phase that does not mix with water.

Step 2: Oil-in-water emulsion In an oil-in-water (O/W) emulsion, oil forms the dispersed droplets and water is the continuous dispersion medium. Milk is an example: liquid fat droplets are dispersed in an aqueous medium. Thus, although fat is present, the surrounding phase in this emulsion is water.

Step 3: Water-in-oil emulsion In a water-in-oil (W/O) emulsion, water forms the dispersed droplets and oil is the continuous dispersion medium. Butter is a standard example, with fine water droplets dispersed in the continuous fat phase. This reverses the roles of the two liquids compared with milk; the classification depends on which liquid surrounds the droplets.

Quick Tip to Solve: Name the dispersed liquid first: O/W means oil droplets in water; W/O means water droplets in oil.

Step 4: Conclusion Emulsions are liquid-in-liquid colloids. Their two types are oil-in-water, exemplified by milk, and water-in-oil, exemplified by butter.

Quick Tip to Solve: Name the dispersed liquid first: O/W means oil droplets in water; W/O means water droplets in oil.

22. Give reasons for the following:

(i) $(CH_3)_3P = O$ exists but $(CH_3)_3N = O$ does not.

(ii) Oxygen has less electron gain enthalpy with negative sign than sulphur.

(iii) H_3PO_2 is a stronger reducing agent than H_3PO_3. [3 marks]

Solution:

Concept:

- A second-period atom such as nitrogen cannot exceed an octet in its ordinary covalent structures; phosphorus can have higher coordination and valence.
- Electron gain enthalpy depends on both nuclear attraction and electron repulsion in the orbital receiving the added electron.
- The reducing action of phosphorus oxyacids is associated with their $P-H$ bonds; $P-OH$ hydrogens determine basicity instead.

Step 1: (i) Compare the bonding capacity of nitrogen and phosphorus In the written structure $(CH_3)_3P=O$, phosphorus has three single bonds and one formal double bond, corresponding to an expanded valence shell. Phosphorus, a third-period element, can support this bonding arrangement. Nitrogen has only the compact second-shell valence orbitals and cannot accommodate ten electrons around it. Consequently, the analogous neutral structure with three $N-C$ bonds and an $N=O$ double bond is not possible. Amine oxides can exist with a charge-separated N^+-O^- bond; that is different from the written $N=O$ structure.

Step 2: (ii) Compare electron addition to oxygen and sulphur The added electron enters the compact $2p$ orbital in oxygen but the larger $3p$ orbital in sulphur. Electron-electron repulsion is greater in the small oxygen orbital. Therefore electron addition to oxygen releases less energy than addition to sulphur, and oxygen has a less negative electron gain enthalpy despite its smaller size.

Step 3: (iii) Count the reducing P-H bonds Hypophosphorous acid has the structure $H_2P(=O)(OH)$, containing two $P-H$ bonds. Phosphorous acid has the structure $HP(=O)(OH)_2$, containing only one $P-H$ bond. The greater number of these reducing bonds makes H_3PO_2 the stronger reducing agent. Counting all hydrogens would be misleading because the $O-H$ bonds do not cause this reducing behaviour.

Step 4: Conclusion (i) Phosphorus can support the expanded-valence structure, but nitrogen cannot. (ii) Greater repulsion in oxygeńs compact $2p$ orbital makes electron gain less exothermic. (iii) H_3PO_2 has two reducing $P-H$ bonds, compared with one in H_3PO_3.

Quick Tip to Solve: For phosphorus oxyacids, write the structure before counting: P-H bonds indicate reducing action; O-H bonds indicate basicity.

23. (i) Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]Cl$.
(ii) What type of isomerism is exhibited by the complex $[Co(en)_3]^{3+}$? (en = ethane-1,2-diamine)
(iii) Why is $[NiCl_4]^{2-}$ paramagnetic but $[Ni(CO)_4]$ is diamagnetic? (At. nos.: Cr = 24, Co = 27, Ni = 28) [3 marks]

Solution:

Concept:

- In naming a complex, ligand names precede the metal name; the metal oxidation state is written as a Roman numeral. Ammine is neutral and chlorido has charge -1.
- Optical isomers are non-superimposable mirror images. Paramagnetism requires unpaired electrons, whereas a complex with all electrons paired is diamagnetic.

Step 1: (i) Name the chromium complex The chloride outside the coordination sphere has charge -1, so the complex ion has charge $+1$. If chromium has oxidation state x, then $x + 4(0) + 2(-1) = +1$, giving $x = +3$. There are four ammine ligands and two chlorido ligands; their names are arranged alphabetically, ignoring multiplicative prefixes. The name is tetraamminedichloridochromium(III) chloride.

Step 2: (ii) Identify the isomerism Each ethane-1,2-diamine ligand binds through two nitrogen atoms. Three such bidentate ligands fill six coordination positions around cobalt, giving an octahedral chelate complex. The two possible arrangements are non-superimposable mirror images, conventionally called Δ and Λ. Thus $[Co(en)_3]^{3+}$ exhibits optical isomerism.

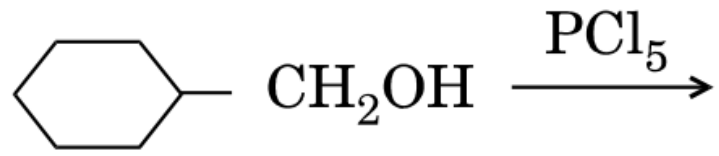
Step 3: (iii) Compare the nickel electron configurations In $[NiCl_4]^{2-}$, nickel is $+2$, with configuration $3d^8$. Chloride is a weak-field ligand and the tetrahedral, sp^3-hybridised complex retains two unpaired electrons, so it is paramagnetic. In $[Ni(CO)_4]$, neutral CO ligands give nickel oxidation state zero. Formation of the complex gives a filled $3d^{10}$ arrangement; the four CO ligands occupy tetrahedrally directed sp^3 orbitals. All electrons are paired, making this complex diamagnetic. The key distinction is that nickel has different oxidation states and electron counts in the two compounds.

Step 4: Conclusion (i) Tetraamminedichloridochromium(III) chloride; (ii) optical isomerism; (iii) $[NiCl_4]^{2-}$ has two unpaired electrons, whereas $[Ni(CO)_4]$ has none.

Quick Tip to Solve: Calculate nickel's oxidation state before counting its d electrons: neutral CO and anionic chloride give different metal electron counts.

24. (a) Draw the structures of major monohalo products in each of the following reactions: (i) cyclohexylmethanol with PCl_5; (ii) $C_6H_5CH_2CH{=}CH_2 + HBr$, as shown below.

(b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction: (i) CH_3Br or CH_3I; (ii) $(CH_3)_3CCl$ or CH_3Cl? [3 marks]



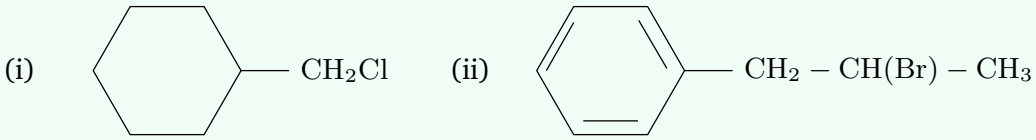
Solution:

Concept:

- PCl_5 replaces the hydroxyl group of an alcohol by chlorine. Without peroxide, HBr adds across an unsymmetrical alkene according to Markovnikov's rule.
- The S_N2 mechanism involves a single concerted backside attack. A better leaving group and less steric hindrance increase its rate under comparable conditions.

Step 1: (a)(i) Replace the alcohol group by chlorine The substrate is cyclohexylmethanol: the CH_2OH group is outside a saturated six-membered ring. Replacement of OH by Cl therefore gives $C_6H_{11}CH_2Cl$, chloromethylcyclohexane. The ring remains saturated and chlorine is attached to the side-chain carbon.

Step 2: (a)(ii) Add hydrogen bromide across the double bond No peroxide is shown. Apply the usual Markovnikov addition: hydrogen adds to the terminal CH_2 carbon, which already carries more hydrogen atoms, and bromine adds to the adjacent carbon. The monohalo product is $C_6H_5CH_2CH(Br)CH_3$, 2-bromo-1-phenylpropane. The product structures for both reactions are drawn below.



Structures of the two monohalo products

Step 3: (b) Compare the two pairs for backside substitution (i) CH_3I reacts faster than CH_3Br. Both have the same methyl carbon and similar accessibility, but the C–I bond is weaker and iodide is a better leaving group than bromide.

(ii) CH_3Cl reacts faster than $(CH_3)_3CCl$. Both have chloride as the leaving group, so steric accessibility decides the comparison. A methyl carbon permits easy backside attack, whereas three methyl groups shield the tertiary carbon of tert-butyl chloride and strongly obstruct the S_N2 pathway.

Step 4: Conclusion (a) $C_6H_{11}CH_2Cl$ and $C_6H_5CH_2CH(Br)CH_3$. (b) The faster compounds are (i) CH_3I, (ii) CH_3Cl.

Quick Tip to Solve: In each substitution pair, hold the common feature fixed: compare leaving groups for methyl halides and crowding for the two chlorides.

25(a). Account for the following:

(i) Primary amines (R-NH_2) have higher boiling point than tertiary amines (R_3N).

(ii) Aniline does not undergo Friedel-Crafts reaction.

(iii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. [3 marks]

Solution:

Concept:

- Boiling point reflects the strength of intermolecular forces. Primary amines contain N–H bonds and can form intermolecular hydrogen bonds.
- Aqueous basicity depends on both electron donation to nitrogen and stabilization of the protonated ion by hydration.

Step 1: Compare intermolecular association For primary and tertiary amines of comparable molar mass, a primary amine has N–H bonds and a nitrogen lone pair, so its molecules form intermolecular hydrogen bonds, $\mathrm{N-H\cdots N}$. A tertiary amine has no N–H bond and therefore cannot hydrogen-bond with other tertiary amine molecules. More energy is needed to separate the associated primary-amine molecules, so their boiling point is higher.

Step 2: Explain the failure of Friedel–Crafts reaction Aniline is a Lewis base because nitrogen has a lone pair. It reacts with the Lewis-acid catalyst $\mathrm{AlCl_3}$, forming an aniline–$\mathrm{AlCl_3}$ complex (often represented as a salt). Nitrogen consequently acquires positive character, and the ring becomes strongly deactivated towards electrophilic substitution. Thus the usual Friedel–Crafts alkylation or acylation does not occur.

Step 3: Compare basicity in water Protonation gives $(\mathrm{CH_3)_2NH_2^+}$ and $(\mathrm{CH_3)_3NH^+}$, respectively. Although three methyl groups exert a larger electron-releasing effect, the trimethylammonium ion is more sterically hindered and less effectively hydrated. The dimethylammonium ion has two N–H bonds and is better solvated. In water this stabilization outweighs the additional inductive effect, making dimethylamine the stronger base.

Step 4: Conclusion Primary amines have stronger self hydrogen bonding; aniline complexes with the Friedel–Crafts catalyst; and better hydration makes $(\mathrm{CH_3)_2NH}$ more basic than $(\mathrm{CH_3)_3N}$ in water.

Quick Tip to Solve: For aqueous amine basicity, compare hydration of the conjugate acids as well as the methyl-group inductive effect.

OR

25(b). Give the structures of A, B and C in the following reactions:

(i) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow{H_2O} C$

(ii) $CH_3CN \xrightarrow{H_2O/H^+} A \xrightarrow[\Delta]{NH_3} B \xrightarrow{Br_2+KOH} C$ [3 marks]

Solution:

Concept:

- Reduction of an aromatic nitro group gives an amino group; cold diazotisation produces an arenediazonium salt, which hydrolyses to a phenol.
- Acidic hydrolysis of a nitrile yields a carboxylic acid. Amide formation followed by Hofmann bromamide degradation gives an amine with one fewer carbon.

Step 1: Identify A, B and C in sequence (i) Tin and hydrochloric acid reduce the nitro group of nitrobenzene to an amino group; the organic product A is aniline, $C_6H_5 - NH_2$ (present as its salt in the acidic reaction mixture). Treatment with $NaNO_2/HCl$ at 273 K generates nitrous acid and diazotises aniline, giving B as benzenediazonium chloride, $C_6H_5 - N_2^+Cl^-$. Water hydrolyses the diazonium group with evolution of nitrogen, producing C as phenol, $C_6H_5 - OH$:

$$C_6H_5N_2^+Cl^- + H_2O \longrightarrow C_6H_5OH + N_2 + HCl.$$

Step 2: Identify A, B and C in sequence (ii) Acidic hydrolysis converts $-CN$ into $-COOH$, retaining the nitrile carbon. Hence A is ethanoic acid, $CH_3 - C(=O) - OH$. Ammonia first forms ammonium ethanoate, which loses water on heating to give B, ethanamide, $CH_3 - C(=O) - NH_2$. Bromine and potassium hydroxide cause Hofmann bromamide degradation. The carbonyl carbon is removed, so C is methylamine, $CH_3 - NH_2$:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Step 3: Conclusion (i) A: aniline, $C_6H_5NH_2$; B: benzenediazonium chloride, $C_6H_5N_2^+Cl^-$; C: phenol, C_6H_5OH.

(ii) A: ethanoic acid, CH_3COOH; B: ethanamide, CH_3CONH_2; C: methylamine, CH_3NH_2.

Quick Tip to Solve: Track the nitrile carbon: hydrolysis retains it, whereas the final Hofmann degradation removes the carbonyl carbon.

26. Define the following terms as related to proteins:

(i) Peptide linkage

(ii) Primary structure

(iii) Denaturation [3 marks]

Solution:

Concept:

- Proteins consist of amino acid residues joined by covalent peptide bonds in a definite sequence.
- Protein function depends on its spatial folding; disrupting that folding can destroy biological activity without breaking its peptide backbone.

Step 1: Define peptide linkage A peptide linkage is the amide bond $-\mathrm{C}(=\mathrm{O})-\mathrm{NH}-$ formed between the carboxyl group of one amino acid and the amino group of another, with elimination of one molecule of water. Thus two amino acids form a dipeptide:

$$\mathrm{H_2N-CH(R)-COOH + H_2N-CH(R')-COOH}$$

$$\longrightarrow \mathrm{H_2N-CH(R)-CO-NH-CH(R')-COOH + H_2O.}$$

The newly formed $-\mathrm{CO}-\mathrm{NH}-$ group joins the two amino acid residues.

Step 2: Define primary structure The primary structure of a protein is the specific sequence in which amino acid residues are joined by peptide linkages in its polypeptide chain. It specifies the order of residues from the amino-terminal end to the carboxyl-terminal end. Two chains having the same amino acids in different orders therefore have different primary structures.

Step 3: Define denaturation Denaturation is the loss of the native spatial structure and biological activity of a protein under the action of heat, a change in pH, or suitable chemicals. Interactions responsible for secondary and tertiary folding are disrupted and the chain unfolds; the peptide bonds and hence the primary structure remain intact. Coagulation of egg white on heating is a familiar example. Denaturation is therefore distinct from hydrolysis, which breaks peptide bonds.

Step 4: Conclusion Peptide linkage: $-\mathrm{CO}-\mathrm{NH}-$ between amino acid residues. Primary structure: their definite sequence. Denaturation: loss of native folding and activity while the primary structure is retained.

Quick Tip to Solve: Distinguish denaturation from hydrolysis: unfolding preserves the amino acid sequence, whereas hydrolysis breaks peptide bonds.

27. On the occasion of World Health Day, Dr. Satpal organized a 'health camp' for the poor farmers living in a nearby village. After check-up, he was shocked to see that most of the farmers suffered from cancer due to regular exposure to pesticides and many were diabetic. They distributed free medicines to them. Dr. Satpal immediately reported the matter to the National Human Rights Commission (NHRC). On the suggestions of NHRC, the government decided to provide medical care, financial assistance, setting up of super-speciality hospitals for treatment and prevention of the deadly disease in the affected villages all over India.

(i) Write the values shown by (a) Dr. Satpal and (b) NHRC.

(ii) What type of analgesics are chiefly used for the relief of pains of terminal cancer?

(iii) Give an example of artificial sweetener that could have been recommended to diabetic patients.

[3 marks]

Solution:

Concept:

- Social responsibility includes helping vulnerable people, providing care and reporting a public-health problem so that preventive action can follow.
- Narcotic analgesics relieve severe pain by acting on the central nervous system. Artificial sweeteners provide sweetness without using ordinary sugar.

Step 1: (i) Values shown by Dr. Satpal and NHRC (a) Dr. Satpal showed compassion, service to humanity and concern for the poor by organizing the camp and providing free medicines. Reporting the pesticide-related illness also shows professional responsibility and awareness of public health. (b) NHRC showed concern for human rights, social justice and the welfare of disadvantaged farmers. Its recommendations for treatment, financial assistance and hospitals show responsibility towards protecting life and health.

Step 2: (ii) Analgesics for terminal cancer pain Narcotic analgesics, also called opioid analgesics, are chiefly used to relieve the severe pain of terminal cancer. Morphine is a standard example. These drugs act on the central nervous system and are used under medical supervision for such intense pain.

Step 3: (iii) Sweetener for diabetic patients Saccharin is an example of an artificial sweetener suitable for this answer. It imparts sweetness and can substitute for ordinary sugar; unlike sucrose, it does not supply glucose through digestion in the same way.

Step 4: Conclusion Dr. Satpal showed compassion and social responsibility; NHRC showed concern for human rights and public welfare. Narcotic analgesics such as morphine relieve terminal cancer pain, and saccharin is an artificial sweetener.

Quick Tip to Solve: Link each value to a specific action in the passage, and name both the analgesic class and one example.

28(a). Define the following terms:

(i) Molarity

(ii) Molal elevation constant (K_b) [2 marks]

Solution:

Concept:

- Molarity expresses solute amount per unit volume of solution, whereas molality uses mass of solvent.
- For a dilute solution of a non-volatile non-electrolyte, elevation in boiling point is proportional to molality: $\Delta T_b = K_b m$.

Step 1: (i) Define molarity Molarity is the number of moles of solute dissolved per litre of solution. Thus,

$$M = \frac{n_{\text{solute}}}{V_{\text{solution}} \text{ in litres}}.$$

Its unit is mol L^{-1}. The denominator is the final volume of the solution, including both solute and solvent. Since this volume changes with temperature, molarity is temperature dependent.

Step 2: (ii) Define molal elevation constant The molal elevation constant, K_b, of a solvent is the elevation in its boiling point when one mole of a non-volatile non-electrolyte is dissolved in one kilogram of that solvent in the dilute-solution limit. Equivalently,

$$K_b = \frac{\Delta T_b}{m},$$

where $\Delta T_b = T_b(\text{solution}) - T_b(\text{pure solvent})$ and m is the molality. Its unit is K kg mol^{-1}, and it is a characteristic property of the solvent.

Step 3: Conclusion Molarity is moles of solute per litre of solution; K_b is the boiling-point elevation per unit molality of a dilute non-electrolyte solution.

Quick Tip to Solve: Use litres of solution for molarity, but kilograms of solvent when defining the molality in K_b.

28(b). A solution containing 15 g urea (molar mass = 60 g mol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. [3 marks]

Solution:

Concept:

- Osmotic pressure of a dilute solution is $\pi = CRT = nRT/V$, where C is molarity, R is the gas constant and T is absolute temperature.
- Isotonic solutions have equal osmotic pressures at the same temperature. Urea and glucose are non-electrolytes, so each has van't Hoff factor $i = 1$.

Step 1: Calculate the molarity of urea The mass of urea in one litre of solution is $15\,\text{g}$, and its molar

Quick Tip to Solve: For isotonic non-electrolyte solutions at the same temperature, equate moles per litre before converting to mass.

mass is $60\,\text{g mol}^{-1}$. Therefore,

$$n_u = \frac{15\,\text{g}}{60\,\text{g mol}^{-1}} = 0.25\,\text{mol}, \qquad C_u = \frac{0.25}{1} = 0.25\,\text{mol L}^{-1}.$$

The given litre refers to solution volume, so it can be used directly in the osmotic-pressure relation.

Step 2: Apply the isotonic condition Let C_g be the molarity of glucose. At the same temperature, equal osmotic pressures give

$$\pi_u = \pi_g \quad \Rightarrow \quad C_u RT = C_g RT \quad \Rightarrow \quad C_g = C_u = 0.25\,\text{mol L}^{-1}.$$

Both substances remain as molecules in solution, so there is no extra particle-number factor. Equal osmotic pressures imply equal molar concentrations, not equal masses per litre.

Step 3: Convert glucose amount into mass One litre of the glucose solution contains $n_g = C_g V = 0.25 \times 1 = 0.25\,\text{mol}$. Using the glucose molar mass,

$$w_g = n_g M_g = (0.25\,\text{mol})(180\,\text{g mol}^{-1}) = 45\,\text{g}.$$

This is three times the urea mass because glucose has three times the molar mass, while the two solutions contain equal numbers of solute molecules per litre.

Step 4: Conclusion The mass of glucose present in one litre of its solution is $\boxed{45\,\text{g}}$.

Quick Tip to Solve: For isotonic non-electrolyte solutions at the same temperature, equate moles per litre before converting to mass.

OR

28(a). What type of deviation is shown by a mixture of ethanol and acetone? Give reason. [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution is $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x_i is the liquid mole fraction and p_i^0 is the vapour pressure of pure component i.
- Positive deviation occurs when unlike intermolecular attractions are weaker than the attractions disrupted on mixing, so molecules escape more readily into the vapour.

Step 1: Compare the interactions before and after mixing Pure ethanol molecules are strongly associated through intermolecular hydrogen bonding between their hydroxyl groups. When acetone is added, acetone molecules come between ethanol molecules and disrupt part of this hydrogen-bonded association. Although ethanol can interact with the oxygen of acetone, the resulting interactions do not compensate fully for the strong ethanol–ethanol attractions broken during mixing.

Step 2: Relate the weaker attractions to vapour pressure The decreased effective attraction in the liquid makes escape of molecules into the vapour easier. Consequently the partial vapour pressures, and hence the total vapour pressure, exceed the values predicted for an ideal solution at the same

Quick Tip to Solve: First identify the strong bonding in pure ethanol; disruption of that association points to a higher vapour pressure.

composition and temperature:

$$p_{\text{total}} > x_{\text{ethanol}} p^0_{\text{ethanol}} + x_{\text{acetone}} p^0_{\text{acetone}}.$$

This is the characteristic pressure behaviour of positive deviation.

Step 3: Conclusion The ethanol–acetone mixture shows positive deviation from Raoult's law, because adding acetone disrupts hydrogen bonding between ethanol molecules and increases their escaping tendency.

Quick Tip to Solve: First identify the strong bonding in pure ethanol; disruption of that association points to a higher vapour pressure.

28(b). A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% (by mass). What would be the molality and molarity of the solution? (Density of solution = 1.2 g mL^{-1}) [3 marks]

Solution:

Concept:

- Mass percentage is $100 \times$ mass of solute/mass of solution. Thus a 10% by mass solution contains $10\,\text{g}$ glucose in $100\,\text{g}$ solution.
- Molality is $m = n_{\text{solute}}/w_{\text{solvent}}$, with solvent mass in kilograms. Molarity is $M = n_{\text{solute}}/V_{\text{solution}}$, with solution volume in litres.

Step 1: Choose a mass basis and find the moles of glucose Take $100\,\text{g}$ of the solution. The glucose mass is $10\,\text{g}$, while the mass of water is $100 - 10 = 90\,\text{g} = 0.090\,\text{kg}$. Using the given molar mass,

$$n_{\text{glucose}} = \frac{10\,\text{g}}{180\,\text{g mol}^{-1}} = \frac{1}{18}\,\text{mol} = 0.05556\,\text{mol}.$$

The solvent mass must exclude the dissolved glucose.

Step 2: Calculate molality using the mass of water Divide the number of moles of glucose by the mass of the solvent in kilograms:

$$m = \frac{1/18\,\text{mol}}{0.090\,\text{kg}} = 0.6173\,\text{mol kg}^{-1}.$$

No density is needed here because molality is based entirely on masses.

Step 3: Find solution volume and calculate molarity The density applies to the entire solution. Hence the volume of our $100\,\text{g}$ sample is

$$V = \frac{100\,\text{g}}{1.2\,\text{g mL}^{-1}} = 83.333\,\text{mL} = 0.083333\,\text{L}.$$

Therefore,

$$M = \frac{1/18\,\text{mol}}{0.083333\,\text{L}} = 0.6667\,\text{mol L}^{-1}.$$

Using the volume of water instead would be incorrect because molarity is defined per litre of solution.

Quick Tip to Solve: For mass percent, start with 100 g solution: subtract solute for molality, but use all 100 g with density for molarity.

Step 4: Conclusion $\boxed{m \approx 0.617\,\text{mol kg}^{-1}, \qquad M \approx 0.667\,\text{mol L}^{-1}}$.

Quick Tip to Solve: For mass percent, start with 100 g solution: subtract solute for molality, but use all 100 g with density for molarity.

29(a). Complete the following equations:

(i) $Cr_2O_7^{2-} + 2OH^- \rightarrow$

(ii) $MnO_4^- + 4H^+ + 3e^- \rightarrow$ [2 marks]

Solution:

Concept:

- A completed ionic equation must conserve both the number of atoms of each element and the total electric charge.
- In basic medium dichromate converts to chromate. In the given three-electron reduction, manganese changes from oxidation state $+7$ to $+4$, forming MnO_2.

Step 1: Complete the dichromate–hydroxide equation Two chromium atoms on the left require two chromate ions on the right. The two hydroxide ions supply the oxygen and hydrogen needed to form water. The balanced equation is

$$\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \longrightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}.$$

There are two Cr, nine O and two H atoms on each side. The charge is -4 on each side. Chromium remains in oxidation state $+6$; this conversion is not a redox change.

Step 2: Complete the permanganate reduction The three electrons reduce manganese from $+7$ to $+4$, so the manganese-containing product is manganese dioxide. Balance the remaining oxygen and hydrogen with water:

$$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \longrightarrow \text{MnO}_2 + 2\text{H}_2\text{O}.$$

Both sides contain one Mn, four O and four H atoms. The charge on the left is $-1 + 4 - 3 = 0$, matching the neutral products. The given three-electron count rules out Mn^{2+}, whose formation from permanganate requires five electrons.

Step 3: Conclusion (i) $\boxed{2\text{CrO}_4^{2-} + \text{H}_2\text{O}}$; (ii) $\boxed{\text{MnO}_2 + 2\text{H}_2\text{O}}$.

Quick Tip to Solve: Use the printed electron count first: three electrons give Mn(IV), whereas five electrons would give Mn(II).

29(b). Account for the following:

(i) Zn is not considered as a transition element.

(ii) Transition metals form a large number of complexes.

(iii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple.

[3 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.
- Complex formation is favoured by small metal-ion size, high charge density and available orbitals that can accept electron pairs from ligands.
- A more positive standard reduction potential means that reduction is more favourable. Half-filled d^5 and half-filled t_{2g}^3 arrangements provide additional stability in the relevant ions.

Step 1: (i) Examine the electronic configurations of zinc Zinc has the configuration $Zn : [Ar]3d^{10}4s^2$, while its usual ion has $Zn^{2+} : [Ar]3d^{10}$. Thus, neither the atom nor its common ion has an incompletely filled d subshell. Although zinc belongs to the d block, it does not satisfy the definition of a transition element.

Step 2: (ii) Explain the tendency to form complexes Transition-metal ions generally have relatively small sizes and appreciable positive charges, so they attract electron-pair donors strongly. They also possess suitable available orbitals to accept lone pairs from ligands and form coordinate bonds. Their different oxidation states and coordination numbers allow many combinations of metal ions and ligands, accounting for the large number of complexes.

Step 3: (iii) Compare the stability changes on reduction The relevant reductions are

$$Mn^{3+}(3d^4) + e^- \longrightarrow Mn^{2+}(3d^5),$$
$$Cr^{3+}(3d^3) + e^- \longrightarrow Cr^{2+}(3d^4).$$

Reduction of Mn^{3+} produces the especially stable half-filled $3d^5$ configuration, so it is strongly favoured. In contrast, Cr^{3+} has a stable $3d^3$ configuration (t_{2g}^3 in its octahedral aqua ion). Its reduction removes this favourable arrangement and gives $3d^4$. Consequently, reduction is much more favourable for the manganese couple, explaining its much more positive E°.

Step 4: Conclusion (i) Zn and its common ion have completely filled $3d^{10}$ subshells. (ii) Small size, high charge density and available acceptor orbitals favour complex formation by transition-metal ions. (iii) Reduction of Mn^{3+} gives stable $3d^5$, whereas reduction of stable $Cr^{3+}(3d^3)$ gives $3d^4$; hence $E^\circ_{Mn^{3+}/Mn^{2+}}$ is much more positive.

Quick Tip to Solve: For reduction potentials, write the d-electron counts on both sides first: formation of Mn(II), d5, favours reduction, while loss of Cr(III), d3, opposes it.

OR

29. (i) With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids.

(ii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(iii) Complete the following equation:

MnO_4^- + $8H^+$ + $5e^-$ $\rightarrow$

(iv) Out of Mn^{3+} and Cr^{3+}, which is more paramagnetic and why? (Atomic nos.: Mn = 25, Cr = 24) [5 marks]

Solution:

Concept:

- Lanthanoids fill the buried $4f$ orbitals, whereas actinoids fill $5f$ orbitals. The greater availability of $5f$, $6d$ and $7s$ electrons in actinoids produces a wider range of oxidation states and structures.
- A reduction half-equation conserves both atoms and charge. In acidic solution, oxygen is balanced using H_2O, hydrogen using H^+, and charge using electrons.
- Paramagnetism increases with the number n of unpaired electrons. The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\mu_B$, where μ_B is the Bohr magneton.

Step 1: (i) Compare structural variability and chemical reactivity Lanthanoids predominantly exhibit $+3$, with relatively similar structures throughout the series, because their buried $4f$ electrons contribute little to bonding. Actinoids show greater structural variability and more oxidation states: their $5f$, $6d$ and $7s$ orbitals have comparable energies and can participate in bonding. Actinoids are also generally more chemically reactive than lanthanoids, especially in the finely divided state.

Step 2: (ii) Identify the lanthanoid with a familiar +4 state Cerium, Ce, is well known to exhibit the $+4$ oxidation state, for example in CeO_2. Loss of four electrons from $[Xe]4f^15d^16s^2$ gives Ce^{4+} the stable noble-gas configuration $[Xe]$.

Step 3: (iii) Complete the acidic permanganate reduction Manganese changes from $+7$ in MnO_4^- to $+2$, accepting the five electrons specified. The balanced equation is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

Four water molecules balance oxygen and hydrogen. The charge on the left is $-1 + 8 - 5 = +2$, equal to the charge of Mn^{2+} on the right.

Step 4: (iv) Compare the unpaired electrons Remove $4s$ electrons before $3d$ electrons when forming these ions. Manganese has $[Ar]3d^54s^2$, so Mn^{3+} has $[Ar]3d^4$, with four unpaired electrons. Chromium has $[Ar]3d^54s^1$, so Cr^{3+} has $[Ar]3d^3$, with three unpaired electrons. Consequently,

$$\mu(Mn^{3+}) = \sqrt{24}\,\mu_B > \mu(Cr^{3+}) = \sqrt{15}\,\mu_B.$$

Step 5: Conclusion (i) Actinoids show greater structural variability and chemical reactivity than lanthanoids. (ii) Cerium exhibits $+4$. (iii) The products are $Mn^{2+} + 4H_2O$. (iv) Mn^{3+} is more paramagnetic: it has four unpaired electrons, compared with three in Cr^{3+}.

Quick Tip to Solve: For these ions remove 4s electrons first: Mn(III) is d4 and Cr(III) is d3. In the permanganate half-equation, check the total charge is +2 on both sides.

30(a). Write the products formed when CH_3CHO reacts with the following reagents:

(i) HCN

(ii) H_2N-OH

(iii) CH_3CHO in the presence of dilute NaOH [3 marks]

Solution:

Concept:

- An aldehyde has a polar carbonyl group: the carbonyl carbon is electrophilic and undergoes nucleophilic addition.
- Ethanal contains alpha-hydrogen atoms and therefore undergoes aldol addition with dilute alkali.

Step 1: Reaction with hydrogen cyanide Cyanide ion attacks the carbonyl carbon of ethanal; protonation of the oxygen then produces a cyanohydrin. The carbonyl double bond becomes a single bond, with hydroxyl and cyano groups attached to the same carbon.

$$CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$$

The product is ethanal cyanohydrin, also called 2-hydroxypropanenitrile.

Step 2: Reaction with hydroxylamine Hydroxylamine adds through its nitrogen atom to the carbonyl group. Subsequent elimination of water gives the carbon-nitrogen double bond of an oxime.

$$CH_3CHO + NH_2OH \longrightarrow CH_3CH{=}NOH + H_2O$$

The organic product is ethanal oxime (acetaldoxime). The aldehydic hydrogen remains attached to the carbon of the new double bond.

Step 3: Reaction with ethanal in dilute sodium hydroxide Dilute sodium hydroxide removes an alpha-hydrogen from one ethanal molecule. The resulting enolate attacks a second ethanal molecule, and protonation gives the beta-hydroxy aldehyde called an aldol.

$$2CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO$$

The product is 3-hydroxybutanal. Since heating is not specified, retain this aldol addition product; dehydration to but-2-enal is a subsequent reaction on heating.

Step 4: Conclusion The products are ethanal cyanohydrin, ethanal oxime and 3-hydroxybutanal, respectively.

Quick Tip to Solve: For dilute NaOH without heating, stop at the beta-hydroxy aldehyde; do not remove water.

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

(i) Benzoic acid and Phenol

(ii) Propanal and Propanone [2 marks]

Solution:

Concept:

- Carboxylic acids are sufficiently acidic to liberate carbon dioxide from sodium hydrogen carbonate; phenol is not.
- Tollens reagent oxidises an aliphatic aldehyde to carboxylate while silver ions are reduced to metallic silver; a simple ketone does not respond.

Step 1: Benzoic acid and phenol Add aqueous sodium hydrogen carbonate separately to the two samples. Benzoic acid gives brisk effervescence of carbon dioxide, whereas phenol gives no effervescence.

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 \uparrow + H_2O$$

The evolved gas turns limewater milky. This test distinguishes the carboxylic acid from the much weaker phenolic acid.

Step 2: Propanal and propanone Warm separate samples gently with freshly prepared Tollens reagent. Propanal forms a silver mirror (or a grey deposit of silver); propanone gives no silver mirror under these conditions.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$
$$\longrightarrow CH_3CH_2COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O$$

Propanal is oxidised to propanoate; the ketonic carbonyl group of propanone resists this mild oxidising reagent.

Step 3: Conclusion Use $NaHCO_3$: benzoic acid effervesces, phenol does not. Use Tollens reagent: propanal gives a silver mirror, propanone does not.

Quick Tip to Solve: Choose bicarbonate for the acid pair and Tollens reagent for the aldehyde-ketone pair.

OR

30(a). Account for the following:

(i) Cl-CH_2COOH is a stronger acid than CH_3COOH.

(ii) Carboxylic acids do not give reactions of carbonyl group. [2 marks]

Solution:

Concept:

- Acid strength increases when the conjugate base is stabilised: $RCOOH \rightleftharpoons RCOO^- + H^+$.
- Inductive withdrawal stabilises negative charge, while resonance donation into a carbonyl decreases its electrophilicity.

Step 1: Why chloroacetic acid is stronger Chlorine in $ClCH_2COOH$ is strongly electronegative and

Quick Tip to Solve: Compare conjugate-base stability for acidity, and carbonyl-carbon electrophilicity for addition reactions.

exerts a negative inductive ($-I$) effect through sigma bonds. It withdraws electron density and stabilises the negative charge of the chloroacetate ion, $ClCH_2COO^-$. In acetic acid, the methyl group instead has an electron-releasing $+I$ effect, which makes the acetate ion relatively less stable. The more stable conjugate base favours ionisation; hence chloroacetic acid is stronger than acetic acid.

Step 2: Why carboxylic acids do not show typical carbonyl addition The lone pair on the hydroxyl oxygen is delocalised into the carbonyl group of RCOOH. This resonance donation reduces the positive character of the carbonyl carbon, so it is less susceptible to nucleophilic attack than the carbonyl carbon of an aldehyde or ketone. Thus carboxylic acids do not give the characteristic nucleophilic addition reactions of aldehydes and ketones, such as cyanohydrin or oxime formation. Their reactions with nucleophiles generally involve substitution of the hydroxyl group, rather than simple addition across the carbonyl bond.

Step 3: Conclusion Chloroacetic acid is stronger because chlorine stabilises its conjugate base by the $-I$ effect. Resonance donation by $-OH$ reduces the electrophilicity of the carboxyl carbon.

Quick Tip to Solve: Compare conjugate-base stability for acidity, and carbonyl-carbon electrophilicity for addition reactions.

30(b). Write the chemical equations to illustrate the following name reactions:

(i) Rosenmund reduction

(ii) Cannizzaro's reaction [2 marks]

Solution:

Concept:

- Rosenmund reduction converts an acid chloride to an aldehyde using hydrogen over poisoned palladium on barium sulphate.
- An aldehyde without alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Rosenmund reduction For example, benzoyl chloride is hydrogenated over palladium supported on barium sulphate, with the catalyst poisoned to prevent further reduction of the aldehyde to an alcohol:

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

The organic product is benzaldehyde. The essential substrate is an acid chloride, and the controlled catalyst stops the reaction at the aldehyde stage.

Step 2: Cannizzaro reaction Benzaldehyde has no alpha-hydrogen and undergoes disproportionation with concentrated sodium hydroxide:

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

One molecule is oxidised to sodium benzoate and the other is reduced to benzyl alcohol. The coefficient two for the aldehyde is necessary because the oxidation and reduction occur together; the acidic product remains a carboxylate salt in the alkaline reaction mixture.

Quick Tip to Solve: For Cannizzaro, choose an aldehyde without alpha-hydrogen and balance two aldehyde molecules.

Step 3: Conclusion Rosenmund reduction gives benzaldehyde from benzoyl chloride; Cannizzaro reaction gives sodium benzoate and benzyl alcohol from benzaldehyde.

Quick Tip to Solve: For Cannizzaro, choose an aldehyde without alpha-hydrogen and balance two aldehyde molecules.

30(c). Out of CH_3CH_2-CO-CH_2-CH_3 and CH_3CH_2-CH_2-CO-CH_3, which gives iodoform test? [1 mark]

Solution:

Concept:

- Methyl ketones contain the group CH_3CO- and give a yellow precipitate of iodoform, CHI_3, with iodine and aqueous sodium hydroxide.
- The carbonyl carbon must be directly bonded to a methyl group; a terminal methyl group elsewhere in the molecule does not meet this condition.

Step 1: Examine the first ketone In $CH_3CH_2COCH_2CH_3$ (pentan-3-one), the carbonyl group is bonded to an ethyl group on each side. It has no CH_3CO- group and therefore does not give the iodoform test.

Step 2: Examine the second ketone In $CH_3CH_2CH_2COCH_3$ (pentan-2-one), the carbonyl group is directly bonded to CH_3. On warming with iodine and aqueous sodium hydroxide, this methyl ketone gives the characteristic yellow precipitate of CHI_3.

Step 3: Conclusion $\boxed{CH_3CH_2CH_2COCH_3}$ gives the iodoform test.

Quick Tip to Solve: Locate the carbonyl carbon first and check whether either directly attached group is methyl.