CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/3 (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 are the dispersed phase and dispersion medium in milk? [1 mark]

Solution:

Concept:

- Milk is an emulsion: a colloidal system in which one liquid is dispersed as small droplets in another liquid.
- The dispersed phase forms the droplets; the dispersion medium is the continuous liquid surrounding them.

Step 1: Identify the droplets In milk, tiny globules of liquid fat are distributed throughout the aqueous portion. The fat is therefore the dispersed phase. Its liquid state makes milk an emulsion rather than a sol, in which solid particles would be dispersed.

Step 2: Identify the continuous phase Water forms the continuous surrounding phase in which the fat globules remain dispersed. Hence water is the dispersion medium, and milk is classified as an oil-in-water emulsion.

Step 3: Conclusion Dispersed phase: liquid fat (oil). Dispersion medium: water.

Quick Tip to Solve: For an oil-in-water emulsion, name oil as the droplets and water as the continuous medium.

2. Name the method used for refining of copper metal. [1 mark]

Solution:

Concept:

- Electrolytic refining purifies an impure metal by dissolving it at the anode and depositing pure metal at the cathode.
- In copper refining, impure copper is the anode, pure copper is the cathode, and acidified copper(II) sulphate solution is the electrolyte.

Step 1: Identify the refining method Copper is purified industrially by electrolytic refining. On passing current, copper atoms from the impure anode enter the electrolyte as copper(II) ions: $\mathrm{Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-}$.

Step 2: Explain purification Copper(II) ions gain electrons at the cathode: $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$. Pure copper is deposited, while insoluble noble-metal impurities collect as anode mud; more reactive impurities generally remain in solution.

Step 3: Conclusion The method is electrolytic refining (electrorefining).

Quick Tip to Solve: Remember the impure copper anode and pure copper cathode to identify electrolytic refining.

3. Why does NH_3 act as a Lewis base? [1 mark]

Solution:

Concept:

- A Lewis base is an electron-pair donor; a Lewis acid accepts an electron pair to form a coordinate bond.
- Nitrogen in ammonia has five valence electrons: three participate in N–H bonds and the remaining two form a lone pair.

Step 1: Locate the available electron pair In NH_3, nitrogen forms three covalent bonds with hydrogen atoms. It still possesses one unshared pair of electrons. This lone pair is available for donation without breaking an N–H bond.

Step 2: Apply the Lewis definition Ammonia donates its nitrogen lone pair to an electron-deficient species. For example, in $NH_3 + H^+ \rightarrow NH_4^+$, nitrogen supplies both electrons for the new coordinate bond. Electron-pair donation is the defining behaviour of a Lewis base.

Step 3: Conclusion NH_3 acts as a Lewis base because nitrogen has a lone pair of electrons that it can donate.

Quick Tip to Solve: For Lewis basicity, locate an available lone pair and identify the atom that donates it.

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

Solution:

Concept:

- Diazotisation converts a primary aromatic amine into an aromatic diazonium salt using nitrous acid in an acidic medium.
- Nitrous acid is generated in situ from sodium nitrite and hydrochloric acid; the reaction is carried out at 273–278 K.

Step 1: Recognise the functional-group conversion The amino group $-NH_2$ attached to an aromatic ring is converted into a diazonium group $-N_2^+$. The aromatic ring is retained, and the product is obtained as a salt, commonly the chloride.

Step 2: Associate the reaction with its name For aniline, the conversion can be represented by

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

The low temperature helps preserve the diazonium salt. This characteristic transformation is called diazotisation.

Step 3: Conclusion The conversion is known as diazotisation.

Quick Tip to Solve: Associate the conversion of aromatic amino groups to diazonium salts with diazotisation.

5. Which of the following is a fibre?

Nylon, Neoprene, PVC [1 mark]

Solution:

Concept:

- Fibres are polymers with high tensile strength and strong intermolecular attractions, so they can be drawn into strong threads.
- Nylon is a polyamide: hydrogen bonding between its amide groups gives chains the strength and organisation required for fibres.

Step 1: Classify nylon Nylon contains recurring amide linkages, $-CO-NH-$. Strong hydrogen bonding between neighbouring chains gives it high tensile strength. It is therefore used as a synthetic fibre in textiles, ropes and similar materials.

Step 2: Check the other listed polymers Neoprene is a synthetic rubber and is classified as an elastomer. PVC, polyvinyl chloride, is classified as a thermoplastic in the standard classification of these polymers. Thus neither is the fibre intended among the three names listed.

Step 3: Conclusion Nylon is the fibre.

Quick Tip to Solve: Use the standard trio: nylon is a fibre, neoprene is an elastomer, and PVC is a thermoplastic.

6. Write the products of hydrolysis of lactose. [1 mark]

Solution:

Concept:

- Lactose is a reducing disaccharide made from one glucose unit and one galactose unit joined by a glycosidic bond.
- Hydrolysis adds water across the glycosidic bond and releases the constituent monosaccharides.

Step 1: Identify the constituent units Lactose contains a galactose residue linked through a $\beta(1 \to 4)$ glycosidic bond to a glucose residue. Hydrolysis cleaves this linkage; it does not change the carbon skeleton of either monosaccharide.

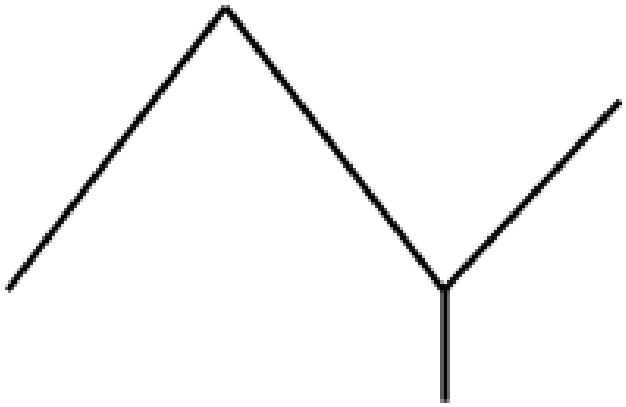
Step 2: Write the hydrolysis products On hydrolysis with dilute acid or the enzyme lactase, one mole of lactose yields one mole each of D-glucose and D-galactose:

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-galactose}}{C_6H_{12}O_6}.$$

Step 3: Conclusion The products are D-glucose and D-galactose, in equimolar amounts.

Quick Tip to Solve: Remember lactose as glucose plus galactose; sucrose instead gives glucose plus fructose.

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





Solution:

Concept:

- A tetrahedral carbon is a chiral centre when it is bonded to four different groups.
- A molecule containing one such asymmetric carbon has non-superimposable mirror images.

Step 1: Inspect the first molecule The first molecule is 2-chlorobutane, $CH_3CH(Cl)CH_2CH_3$. Its second carbon is attached to $-H$, $-Cl$, $-CH_3$ and $-CH_2CH_3$. All four groups are different, so this carbon is asymmetric.

Step 2: Check the other member of the pair The other is 1-chlorobutane, $ClCH_2CH_2CH_2CH_3$. Each carbon bears at least two identical hydrogen atoms, so it contains no asymmetric carbon and is achiral.

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

Quick Tip to Solve: At the chlorine-bearing carbon, compare methyl with ethyl: they are different groups.

8. Write the structure of 2-hydroxybenzoic acid. [1 mark]

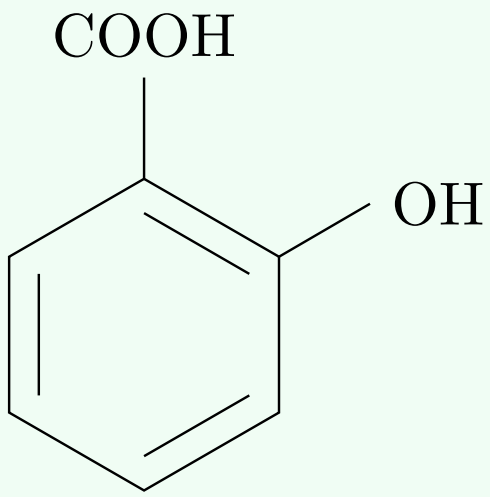
Solution:

Concept:

- In benzoic acid, the ring carbon attached to $-\mathrm{COOH}$ is numbered 1.
- The prefix 2-hydroxy places $-\mathrm{OH}$ on the adjacent ring carbon, giving the ortho isomer.

Step 1: Locate the carboxyl group Take a benzene ring bearing a $-\mathrm{COOH}$ group as the parent benzoic acid. The carboxyl group is attached through its carbon atom, so its connectivity is $\mathrm{C_6H_5-C(=O)-OH}$.

Step 2: Place the hydroxyl group Replace one hydrogen on the neighbouring ring carbon by $-\mathrm{OH}$. Thus the two substituents occupy positions 1 and 2; this compound is also called salicylic acid. Its condensed structural formula is $\mathrm{2-HO-C_6H_4-C(=O)-OH}$.



2-Hydroxybenzoic acid: adjacent hydroxyl and carboxyl groups

Step 3: Conclusion The structure is $\boxed{\mathrm{o-HO-C_6H_4-COOH}}$ (salicylic acid).

Quick Tip to Solve: Use COOH to fix carbon 1 first, then place OH directly next to it at carbon 2.

9. Complete the following equations:

(i) C + conc. H_2SO_4 $\rightarrow$

(ii) XeF_2 + H_2O $\rightarrow$ [2 marks]

Solution:

Concept:

- Hot concentrated sulphuric acid oxidises carbon to carbon dioxide and is itself reduced to sulphur dioxide.
- Xenon difluoride undergoes complete hydrolysis to xenon, hydrogen fluoride and oxygen; balance atoms in the final equation.

Quick Tip to Solve: For XeF2 hydrolysis, write Xe, HF and O2 first, then use two XeF2 to avoid a fractional oxygen coefficient.

Step 1: (i) Carbon with concentrated sulphuric acid Carbon changes from oxidation state 0 to +4 in CO_2, losing four electrons. Each sulphur atom changes from +6 to +4 in SO_2, gaining two electrons. Therefore two sulphuric acid molecules are required for each carbon atom. Balancing hydrogen and oxygen gives

$$C + 2H_2SO_4\,(\text{conc.}) \xrightarrow{\Delta} CO_2 + 2SO_2 + 2H_2O.$$

Step 2: (ii) Hydrolysis of xenon difluoride Water reacts with XeF_2 to liberate xenon and oxygen, while fluorine forms hydrogen fluoride. Using integer coefficients, the balanced reaction is

$$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2.$$

Both sides contain two xenon atoms, four fluorine atoms, four hydrogen atoms and two oxygen atoms.

Step 3: Conclusion The completed equations are $C + 2H_2SO_4\,(\text{conc.}) \rightarrow CO_2 + 2SO_2 + 2H_2O$ and $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$.

Quick Tip to Solve: For XeF2 hydrolysis, write Xe, HF and O2 first, then use two XeF2 to avoid a fractional oxygen coefficient.

10. Draw the structures of the following:

(i) XeO_3

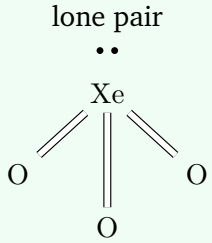
(ii) H_2SO_4 [2 marks]

Solution:

Concept:

- VSEPR theory predicts shape from the number of bonding domains and lone pairs around the central atom; a double bond counts as one domain.
- In XeO_3, xenon has three bonding domains and one lone pair; in H_2SO_4, sulphur has four bonding domains and no lone pair.

Step 1: (i) Structure of xenon trioxide Xenon is bonded to three oxygen atoms, conventionally represented by three $Xe = O$ bonds, and retains one lone pair. Thus there are four electron domains around xenon. Their arrangement is tetrahedral, but the molecular shape, described by the positions of the atoms alone, is trigonal pyramidal. The lone pair occupies the fourth direction above the three oxygen atoms.

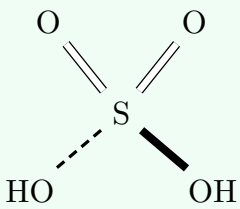


Trigonal pyramidal

Xenon trioxide: three Xe=O bonds and one lone pair

Quick Tip to Solve: For H2SO4, attach both hydrogens to oxygen; for XeO3, include the lone pair that makes the molecule pyramidal.

Step 2: (ii) Structure of sulphuric acid The central sulphur atom is bonded to two oxygen atoms by double bonds and to two hydroxyl oxygen atoms by single bonds. The hydrogen atoms are attached to oxygen, giving $HO-S(=O)_2-OH$. The four oxygen atoms have an approximately tetrahedral arrangement around sulphur; there is no lone pair on sulphur in this structure.



Tetrahedral

Sulphuric acid: tetrahedral arrangement about sulphur

Step 3: Conclusion XeO_3 is trigonal pyramidal with one lone pair on Xe; H_2SO_4 has tetrahedral oxygen coordination about S and connectivity $HO-S(=O)_2-OH$.

Quick Tip to Solve: For H2SO4, attach both hydrogens to oxygen; for XeO3, include the lone pair that makes the molecule pyramidal.

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

(i) Teflon

(ii) Buna-N [2 marks]

Solution:

Concept:

- A monomer is a small molecule that joins repeatedly to form a polymer. In addition polymerisation, a carbon-carbon double bond opens to form the polymer backbone.
- A homopolymer has one kind of monomer, whereas a copolymer is prepared using two or more different monomers.

Step 1: (i) Identify the monomer of Teflon Teflon is polytetrafluoroethene (PTFE). Its monomer is tetrafluoroethene, also called tetrafluoroethylene, $CF_2{=}CF_2$. Opening its double bond gives the repeating unit $-CF_2-CF_2-$; the fluorine atoms remain attached to the carbon chain.

Step 2: (ii) Identify both monomers of Buna-N Buna-N is a copolymer of buta-1,3-diene, $CH_2{=}CH-CH{=}CH_2$, and acrylonitrile (prop-2-enenitrile), $CH_2{=}CH-CN$. Thus two monomers must be named for Buna-N. The nitrile group distinguishes it from Buna-S, whose second monomer is styrene.

Step 3: Conclusion (i) Teflon: tetrafluoroethene. (ii) Buna-N: buta-1,3-diene and acrylonitrile.

Quick Tip to Solve: Remember that the N in Buna-N points to the nitrile-containing monomer acrylonitrile.

12. 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:

- The density of a cubic crystal is $\rho = \dfrac{ZM}{N_A a^3}$, where Z is the number of atoms per cell, M is the molar mass, N_A is Avogadro's constant and a is the cell edge.
- An f.c.c. cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms, counting the shared corner and face-centred atoms.

Step 1: Calculate the unit-cell volume Use centimetres for the edge because density is given in $\mathrm{g\,cm^{-3}}$. Hence

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

The mass of this cell is ρa^3, and it contains four atoms of mass M/N_A each.

Step 2: Substitute in the density relation Equating the two expressions for the cell mass gives

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

The factors 10^{-23} and 10^{23} cancel. Dividing by four accounts for the four atoms in each f.c.c. cell.

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

Quick Tip to Solve: For an f.c.c. lattice, insert Z = 4 and cube the entire edge length, including its power of ten.

13. (i) Write the type of magnetism observed when the magnetic moments are aligned in parallel and anti-parallel directions in unequal numbers.

(ii) Which stoichiometric defect decreases the density of the crystal? [2 marks]

Solution:

Concept:

- The net magnetisation of a solid depends on the vector sum of its constituent magnetic moments. Oppositely aligned moments can cancel completely or leave a resultant moment.
- Density is mass divided by volume. A vacancy defect lowers density when particles are removed from lattice sites without a comparable decrease in crystal volume.

Step 1: (i) Identify the magnetic ordering The moments point in parallel and antiparallel directions in unequal numbers. The two opposing contributions therefore do not cancel completely, so the crystal retains a resultant magnetic moment. This arrangement is ferrimagnetic. In antiferromagnetism the

Quick Tip to Solve: Unequal opposing moments indicate ferrimagnetism; missing ion pairs indicate a density-lowering Schottky defect.

opposing contributions cancel, whereas in ferromagnetism the moments align in the same direction.

Step 2: (ii) Identify the density-reducing defect The required stoichiometric defect is the Schottky defect. Equal numbers of cations and anions are missing from their normal lattice sites, preserving electrical neutrality and the ion ratio. The crystal loses mass while its volume remains practically unchanged, so its density decreases. In a Frenkel defect an ion moves to an interstitial site and the mass is retained.

Step 3: Conclusion (i) Ferrimagnetism. (ii) Schottky defect.

Quick Tip to Solve: Unequal opposing moments indicate ferrimagnetism; missing ion pairs indicate a density-lowering Schottky defect.

14. Define the following terms:

(i) Molar conductivity (Λ_m)

(ii) Secondary batteries [2 marks]

Solution:

Concept:

- Conductivity κ describes the conducting ability of an electrolyte solution. Molar conductivity relates this property to the amount of electrolyte present.
- A rechargeable electrochemical cell can operate as a galvanic cell during discharge and undergo the reverse chemical change when external electrical energy is supplied.

Step 1: (i) Define molar conductivity Molar conductivity, Λ_m, is the conductance of the volume of solution containing one mole of electrolyte when placed between electrodes one unit distance apart, with sufficient area to contain that volume. If c is the concentration in $\mathrm{mol\,cm^{-3}}$, then $\Lambda_m = \kappa/c$. For concentration C in $\mathrm{mol\,L^{-1}}$ and κ in $\mathrm{S\,cm^{-1}}$,

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

with unit $\mathrm{S\,cm^2\,mol^{-1}}$.

Step 2: (ii) Define secondary batteries Secondary batteries are batteries that can be recharged after discharge by passing an electric current through them in the opposite direction. Charging reverses the discharge reaction and regenerates the active materials, allowing repeated use. A lead storage battery is a familiar example.

Step 3: Conclusion Molar conductivity is the conductance associated with one mole of electrolyte in the specified electrode arrangement. Secondary batteries are rechargeable batteries with reversible cell reactions.

Quick Tip to Solve: State both the one-mole basis for molar conductivity and the reversal of the discharge reaction for a secondary battery.

15. Write the mechanism of the following reaction:

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

[2 marks]

Solution:

Concept:

- Ethanol is a primary alcohol. Its conversion to bromoethane with HBr is a nucleophilic substitution, proceeding by the S_N2 pathway after protonation of the hydroxyl group.
- The $-OH$ group is a poor leaving group, whereas protonated alcohol can lose a neutral water molecule. Bromide ion acts as the nucleophile.

Step 1: Protonate the alcohol The oxygen atom uses a lone pair to accept a proton from HBr. This produces an ethyloxonium ion and makes water the leaving group:

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

Protonation activates the carbon-oxygen bond for substitution; direct displacement of hydroxide from unprotonated ethanol is unfavourable.

Step 2: Displace water by bromide ion The bromide ion attacks the primary carbon bonded to oxygen from the side opposite the leaving group. Formation of the carbon-bromine bond and cleavage of the carbon-oxygen bond occur together:

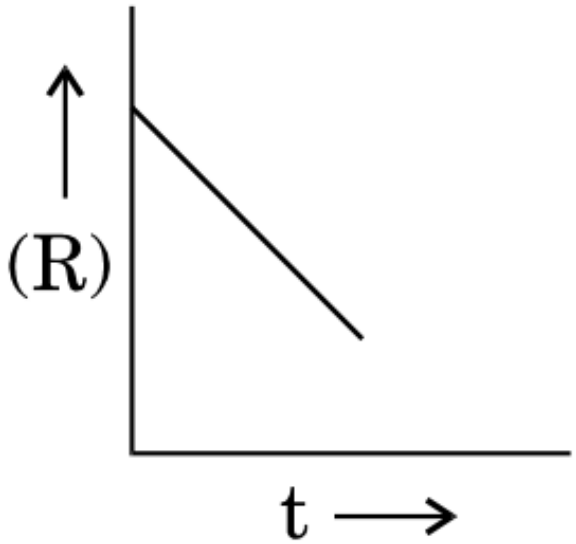
$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

The bonding electron pair of the carbon-oxygen bond goes to oxygen as water leaves. No free primary ethyl carbocation is formed, because that intermediate would be unstable.

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

Quick Tip to Solve: For a primary alcohol with HBr, protonate OH first, then show bromide displacing water in one step.

16. 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:

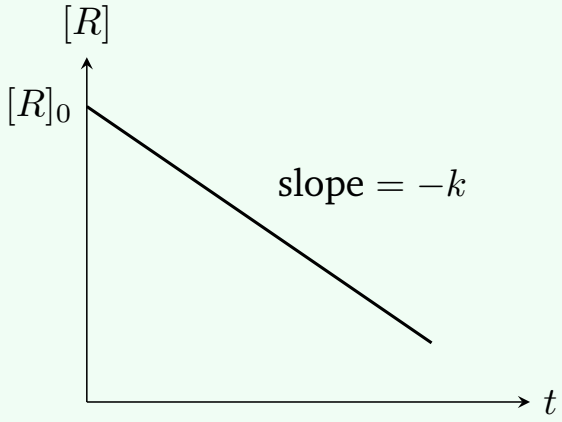
- For a zero-order reaction the rate is independent of reactant concentration: $-d[R]/dt = k$, where $[R]$ is the concentration of reactant R and k is the rate constant.
- Its integrated rate equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration. It has the straight-line form $y = c + mx$.

Step 1: Identify the order from the plotted variables The given graph plots reactant concentration itself against time and shows a straight line decreasing with time. Comparing this with

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

identifies a zero-order reaction. Equal intervals of time correspond to equal decreases in concentration, so the reaction rate is constant over the shown interval. A first-order reaction instead gives a straight line when $\ln[R]$, rather than $[R]$, is plotted against time.

Quick Tip to Solve: Check the vertical-axis quantity first: a straight decreasing concentration-time line identifies zero order.



Zero-order concentration-time plot with slope $-k$.

Step 2: Read the slope of the straight line With $[R]$ on the vertical axis and t on the horizontal axis, the coefficient of t in the integrated equation is the slope:

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

The negative sign shows consumption of R. The rate constant itself is positive and equals the magnitude of the slope. No numerical slope can be evaluated because the graph supplies no numerical coordinates.

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

Quick Tip to Solve: Check the vertical-axis quantity first: a straight decreasing concentration-time line identifies zero order.

17. Write the principle behind the froth floatation process. What is the role of collectors in this process? [2 marks]

Solution:

Concept:

- Froth floatation concentrates sulphide ores by exploiting the difference in wettability of ore particles and gangue particles by oil and water.
- Collectors, such as pine oil, fatty acids and xanthates, increase the non-wettability of sulphide mineral particles by water and favour their attachment to air bubbles.

Step 1: State the principle of separation Finely powdered sulphide ore is mixed with water and suitable reagents, and air is blown through the suspension. The sulphide ore particles are preferentially wetted by oil, whereas the earthy gangue is preferentially wetted by water. The ore particles attach to air bubbles and rise as froth, while the water-wetted gangue remains in the water or sinks. The mineral-rich froth is skimmed off and subsequently dried to recover the concentrated ore.

Step 2: Explain the action of collectors Collectors adsorb on the surfaces of sulphide mineral particles

Quick Tip to Solve: Link collectors to mineral surfaces and bubble attachment; the key principle is different wettability of ore and gangue.

and make them more hydrophobic, that is, less easily wetted by water. This promotes the adhesion of mineral particles to air bubbles, so that more ore is carried into the froth. For example, xanthates are used as collectors. Their role is to improve selective recovery of the ore; the essential separation still depends on the different wetting behaviour of ore and gangue.

Step 3: Conclusion Froth floatation uses preferential wetting: sulphide ore is wetted by oil and gangue by water. Collectors increase the water-repelling character of ore particles and help them attach to rising air bubbles.

Quick Tip to Solve: Link collectors to mineral surfaces and bubble attachment; the key principle is different wettability of ore and gangue.

18. Write the equations involved in the following reactions:

(i) Reimer - Tiemann reaction

(ii) Williamson synthesis [2 marks]

Solution:

Concept:

- Reimer–Tiemann reaction introduces a formyl group, $-\mathrm{CHO}$, mainly at the ortho position of phenol using chloroform and aqueous alkali, followed by acidification.
- Williamson synthesis forms an ether by nucleophilic substitution between a sodium alkoxide and a suitable alkyl halide.

Step 1: (i) Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The major organic product is salicylaldehyde (2-hydroxybenzaldehyde):

$$\mathrm{C_6H_5OH + CHCl_3 + 3NaOH} \xrightarrow[\text{then } H^+]{\text{heat}} \mathrm{o-HOC_6H_4CHO + 3NaCl + 2H_2O.}$$

The equation represents the overall reaction after work-up; the phenolic group is recovered on acidification.

Step 2: (ii) Williamson synthesis A sodium alkoxide attacks an alkyl halide and displaces halide ion:

$$\mathrm{RONa + R'X \longrightarrow ROR' + NaX.}$$

For example, sodium ethoxide reacts with bromoethane to form ethoxyethane:

$$\mathrm{C_2H_5ONa + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr.}$$

A primary alkyl halide is suitable because it permits easy substitution with little steric hindrance.

Step 3: Conclusion Reimer–Tiemann reaction gives mainly $\mathrm{o-HOC_6H_4CHO}$ from phenol; Williamson synthesis gives an ether, $\mathrm{ROR'}$, from an alkoxide and an alkyl halide.

Quick Tip to Solve: Associate Reimer–Tiemann with phenol plus chloroform, and Williamson with an alkoxide plus a primary alkyl halide.

19. (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:

- Complexes are named by listing ligands alphabetically, followed by the central metal and its oxidation state; the counter-ion is named separately.
- An octahedral complex with three bidentate ethane-1,2-diamine ligands can have non-superimposable mirror images and thus optical isomerism.
- Unpaired electrons produce paramagnetism; a complex with all electrons paired is diamagnetic. Oxidation state must be determined before assigning the metal's d-electron count.

Step 1: (i) Name the chromium complex The chloride outside the square brackets has charge -1, so the complex cation has charge $+1$. Ammonia is neutral and each coordinated chlorido ligand has charge -1. If chromium has oxidation state x,

$$x + 4(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

Place ammine before chlorido alphabetically, ignoring the multiplicative prefixes. The name is **tetraamminedichloridochromium(III) chloride**.

Step 2: (ii) Identify the isomerism The three bidentate en ligands occupy all six coordination sites around cobalt. Their two opposite spatial arrangements are mirror images that cannot be superimposed. Therefore $[\mathrm{Co(en)_3}]^{3+}$ exhibits **optical isomerism**, with Δ and Λ enantiomers.

Step 3: (iii) Compare the nickel complexes In $[\mathrm{NiCl_4}]^{2-}$, nickel is $+2$, giving $3d^8$. Chloride is a weak-field ligand, so the electrons are not forced to pair further. The tetrahedral sp^3 complex has **two unpaired electrons** and is paramagnetic. In $\mathrm{Ni(CO)_4}$, CO is neutral and nickel has oxidation state zero. In the complex, the strong-field CO ligands favour the paired $3d^{10}$ arrangement; four empty outer orbitals form sp^3 hybrids for bonding. This tetrahedral complex has **no unpaired electrons** and is diamagnetic. Thus identical tetrahedral geometry does not imply identical magnetic behaviour.

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

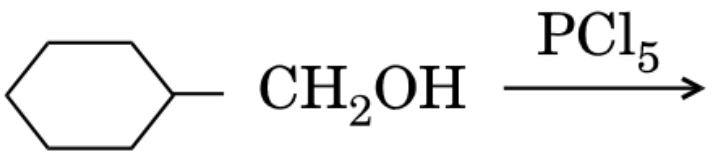
Quick Tip to Solve: Find nickel's oxidation state first: the chlorido complex contains Ni(II), while the neutral carbonyl contains Ni(0).

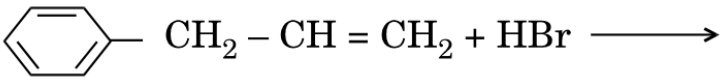
20. (a) Draw the structures of major monohalo products in each of the following reactions (i) and (ii), shown in order below.

(b) Which halogen compound in each of the following pairs will react faster in S_N2 reaction:

(i) CH_3Br **or** CH_3I

(ii) $(CH_3)_3C-Cl$ **or** CH_3-Cl [3 marks]





Solution:

Concept:

- Phosphorus pentachloride converts an alcohol into an alkyl chloride by replacing the $-OH$ group with chlorine.
- Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov's rule: hydrogen adds to the carbon already bearing more hydrogen atoms. Carbocation rearrangement can then give a more stable intermediate before bromide attacks.
- In an S_N2 reaction, a nucleophile attacks from the back of the carbon–halogen bond. Low steric hindrance and a better leaving group favour a faster reaction.

Step 1: (a)(i) Replace the alcoholic hydroxyl group The starting compound is cyclohexylmethanol: the CH_2OH group lies outside the saturated six-membered ring. Treatment with PCl_5 replaces only its hydroxyl group:

$$C_6H_{11}CH_2OH + PCl_5 \longrightarrow C_6H_{11}CH_2Cl + POCl_3 + HCl.$$

The product is (chloromethyl)cyclohexane; chlorine is attached to the side-chain carbon, not directly to the ring.

Step 2: (a)(ii) Add hydrogen bromide across the double bond No peroxide is specified. Protonation first gives the secondary carbocation at the middle carbon of the side chain:

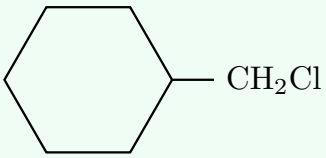
$$C_6H_5CH_2CH{=}CH_2 + H^+ \longrightarrow C_6H_5CH_2CH^+CH_3.$$

A 1,2-hydride shift from the adjacent benzylic carbon produces a resonance-stabilised benzylic carbocation. Bromide then attacks that carbon:

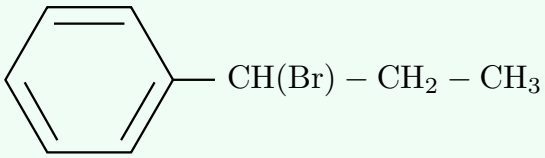
$$C_6H_5CH_2CH^+CH_3 \xrightarrow{\text{hydride shift}} C_6H_5CH^+CH_2CH_3 \xrightarrow{Br^-} C_6H_5CH(Br)CH_2CH_3.$$

The major product is therefore 1-bromo-1-phenylpropane. The rearrangement stabilises the positive charge by conjugation with the benzene ring. Both product structures are drawn below.

Quick Tip to Solve: For each SN2 pair, hold the common factor fixed: compare I versus Br for methyl halides, then methyl versus tertiary carbon for chlorides.



(i)



(ii)

Structures of the two monohalo products, in the order (i), (ii).

Step 3: (b)(i) Compare the leaving groups CH_3I reacts faster than CH_3Br. Both have the same unhindered methyl framework, so the leaving group decides the comparison. The C–I bond is weaker than C–Br and iodide is a better leaving group; displacement therefore occurs more readily in methyl iodide.

Step 4: (b)(ii) Compare steric hindrance CH_3Cl reacts faster than $(CH_3)_3CCl$. Both have chloride as the leaving group, but methyl chloride permits easy backside attack. Three methyl groups strongly shield the reacting carbon in tert-butyl chloride, suppressing the S_N2 pathway.

Step 5: Conclusion (a) The products are (i) $C_6H_{11}CH_2Cl$ and (ii) $C_6H_5CH(Br)CH_2CH_3$. (b) The faster compounds are (i) CH_3I and (ii) CH_3Cl.

Quick Tip to Solve: For each SN2 pair, hold the common factor fixed: compare I versus Br for methyl halides, then methyl versus tertiary carbon for chlorides.

21(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:

- Intermolecular hydrogen bonding requires a hydrogen attached directly to an electronegative atom such as nitrogen. Stronger intermolecular attraction raises the boiling point.
- Basicity in water depends on the electron density on nitrogen and the stability of the protonated amine through hydration; the inductive effect alone is insufficient.
- A Lewis acid accepts an electron pair. The nitrogen lone pair in aniline can therefore interact strongly with the Lewis acid catalyst $AlCl_3$.

Step 1: Explain the boiling-point difference For amines of comparable molecular mass, primary amines contain $N - H$ bonds and form intermolecular $N - H \cdots N$ hydrogen bonds. More energy is required to separate their molecules during boiling. Tertiary amines contain no $N - H$ bond and cannot hydrogen-bond with one another in the pure liquid, so their boiling points are lower.

Step 2: Explain why aniline fails in Friedel–Crafts reaction The lone pair of the nitrogen atom of aniline coordinates to the Lewis acid $AlCl_3$, the catalyst used for Friedel–Crafts reactions, to form a salt-like complex. The nitrogen in this complex has positive character and strongly withdraws electron

Quick Tip to Solve: For boiling points check for an N–H bond; for aqueous basicity compare hydration of the conjugate acids as well as the inductive effect.

density from the ring. The ring is consequently deactivated towards electrophilic substitution, so aniline does not undergo the usual Friedel–Crafts alkylation or acylation.

Step 3: Compare the two bases in aqueous solution Protonation gives $(CH_3)_2NH_2^+$ from dimethylamine and $(CH_3)_3NH^+$ from trimethylamine. Although three methyl groups exert a greater electron-releasing inductive effect, the bulky trimethylammonium ion is less effectively hydrated. The dimethylammonium ion has less steric shielding and is better stabilized by hydrogen bonding with water. This hydration advantage outweighs the additional inductive effect of the third methyl group.

Step 4: Conclusion (i) Primary amines have stronger intermolecular hydrogen bonding. (ii) Aniline forms a ring-deactivating complex with $AlCl_3$. (iii) Better hydration of $(CH_3)_2NH_2^+$ makes $(CH_3)_2NH$ more basic than $(CH_3)_3N$ in water.

Quick Tip to Solve: For boiling points check for an N–H bond; for aqueous basicity compare hydration of the conjugate acids as well as the inductive effect.

OR

21(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:

- Sn/HCl reduces an aromatic nitro group to an amino group. Nitrous acid, generated from $NaNO_2/HCl$, diazotises a primary aromatic amine at 273 K.
- Hydrolysis of a nitrile gives a carboxylic acid without changing the total number of carbon atoms; an acid heated with ammonia yields an amide.
- The Hofmann bromamide reaction converts $RCONH_2$ into RNH_2, with one fewer carbon atom in the organic product.

Step 1: Identify the aromatic sequence (i) Reduction of nitrobenzene gives aniline, so $A = C_6H_5NH_2$. Aniline is protonated in the acidic reaction medium; its amine structure is written for A in the sequence. Diazotisation then gives benzenediazonium chloride, and hydrolysis replaces the diazonium group by hydroxyl:

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

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

Thus $B = C_6H_5{-}N^+ \equiv N\,Cl^-$, benzenediazonium chloride, and $C = C_6H_5OH$, phenol. The nitrogen attached to the phenyl group carries the positive charge in the displayed diazonium representation; chloride is the counter-ion.

Step 2: Identify the aliphatic sequence (ii) Acidic hydrolysis of methyl cyanide gives ethanoic acid, so $A = CH_3C(=O)OH$. Ammonia first forms ammonium ethanoate, which loses water on heating to form ethanamide, $B = CH_3C(=O)NH_2$. Finally, bromine and potassium hydroxide cause Hofmann

Quick Tip to Solve: Follow the functional group at every arrow: nitro to amine to diazonium to phenol; nitrile to acid to amide to an amine with one fewer carbon.

degradation:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4,$$
$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O,$$
$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Hence $C = CH_3NH_2$, methylamine. The carbonyl carbon is removed in the final reaction, whereas the methyl group is retained.

Step 3: Conclusion (i) $A = C_6H_5NH_2$, $B = C_6H_5N_2^+Cl^-$, $C = C_6H_5OH$.
(ii) $A = CH_3COOH$, $B = CH_3CONH_2$, $C = CH_3NH_2$.

Quick Tip to Solve: Follow the functional group at every arrow: nitro to amine to diazonium to phenol; nitrile to acid to amide to an amine with one fewer carbon.

22. 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

(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:

- Values are identified by linking a person's or institution's actions to concern for others, responsibility and protection of human welfare.
- Analgesics relieve pain. Narcotic (opioid) analgesics are used to relieve severe pain, such as pain associated with terminal cancer.
- Artificial sweeteners provide sweetness in small quantities; saccharin is a standard example used as a sugar substitute for diabetic patients.

Step 1: Identify the values in part (i) (a) Dr. Satpal shows compassion, concern for the poor, social responsibility and a spirit of service. He organizes a health camp and helps provide medicines; reporting the widespread illness also shows alertness and a commitment to public welfare.

(b) NHRC shows sensitivity to suffering, protection of human rights and concern for the right to health and a dignified life. Its recommendations for medical care, financial assistance and specialized

Quick Tip to Solve: For the values part, cite an action from the passage; for severe terminal-cancer pain name narcotic analgesics, and give saccharin as the sweetener.

hospitals demonstrate responsibility towards vulnerable communities. These values are supported by the specific actions described in the passage.

Step 2: State the class of analgesics in part (ii) Narcotic analgesics, also called opioid analgesics, are chiefly used to relieve the severe pain of terminal cancer. Morphine is a standard example of this class. Their strong action on the central nervous system makes them suitable for severe pain; the question asks for the drug class, so the essential answer is narcotic analgesics.

Step 3: Give an artificial sweetener for part (iii) Saccharin is an appropriate example of an artificial sweetener that could be recommended as a sugar substitute to diabetic patients. It is much sweeter than sucrose, so only a small quantity is needed to provide sweetness. It supplies sweetness without requiring the corresponding quantity of ordinary sugar.

Step 4: Conclusion (i) Dr. Satpal: compassion, service and social responsibility; NHRC: protection of human rights, sensitivity and public welfare. (ii) Narcotic (opioid) analgesics, such as morphine. (iii) Saccharin.

Quick Tip to Solve: For the values part, cite an action from the passage; for severe terminal-cancer pain name narcotic analgesics, and give saccharin as the sweetener.

23. Define the following terms:

(i) Nucleotide

(ii) Anomers

(iii) Essential amino acids [3 marks]

Solution:

Concept:

- Nucleic acids are polymers of nucleotides; each nucleotide contains a base, a pentose sugar and a phosphate group.
- The anomeric carbon is the carbonyl carbon of an open-chain sugar that becomes a new stereocentre on ring formation.
- Amino acids are classified as essential or non-essential according to whether the human body can synthesise enough of them.

Step 1: (i) Nucleotide A nucleotide is the structural unit of a nucleic acid, consisting of a nitrogenous base linked to a pentose sugar, which is in turn esterified with phosphoric acid. The base may be a purine or a pyrimidine, and the sugar is ribose in RNA or 2-deoxyribose in DNA. Thus, a nucleotide is a nucleoside with a phosphate group, usually attached at the sugar's $5'$ position. For example, adenosine monophosphate is a nucleotide.

Step 2: (ii) Anomers Anomers are cyclic stereoisomers of a carbohydrate that differ in configuration only at the anomeric carbon. For an aldose this is carbon 1; for a ketose such as fructose it is carbon 2. For example, α-D-glucose and β-D-glucose differ only in the orientation of the hydroxyl group at carbon 1, while the configurations at the other stereocentres remain the same.

Step 3: (iii) Essential amino acids Essential amino acids are amino acids that the human body cannot

Quick Tip to Solve: Remember: nucleoside plus phosphate gives nucleotide; anomers differ at just the carbon created as a stereocentre during ring formation.

synthesise in adequate amounts and must therefore obtain through the diet. They are required for normal growth and protein synthesis. Valine, leucine and lysine are examples. The term essential refers to the need for a dietary supply; non-essential amino acids are also needed by the body but can be synthesised by it.

Step 4: Conclusion A nucleotide is a base-sugar-phosphate unit; anomers differ only at the anomeric carbon; essential amino acids must be supplied through food.

Quick Tip to Solve: Remember: nucleoside plus phosphate gives nucleotide; anomers differ at just the carbon created as a stereocentre during ring formation.

24. (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 reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per reaction as written and F is the Faraday constant.
- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.

Step 1: (a) Determine the electron transfer Magnesium is oxidised and copper(II) ions are reduced. The balanced half-reactions are

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

Adding these half-reactions gives the reaction in the question. Exactly two electrons are transferred per reaction as written, so $n = 2$. The electron count is taken from either half-reaction, rather than adding the electrons appearing in both.

Step 2: Calculate the standard Gibbs energy change Substitute the given positive cell potential into the thermodynamic relation:

$$\begin{aligned} \Delta_r G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -2 \times 96500 \times 2.71\,\text{J mol}^{-1} \\ &= -523030\,\text{J mol}^{-1} \\ &= -523.03\,\text{kJ mol}^{-1}. \end{aligned}$$

Here C $\times$ V = J. The negative sign agrees with the positive standard cell potential: the forward reaction is thermodynamically spontaneous under standard conditions.

Quick Tip to Solve: Find the electron count from one balanced half-reaction before using $-nFE^\circ$; a positive cell potential must give a negative Gibbs energy change.

Step 3: (b) Identify the Apollo power source The Apollo space programme used hydrogen-oxygen fuel cells to provide electrical power. Hydrogen acts as the fuel and oxygen as the oxidant. Their overall reaction is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

Besides supplying electrical energy, these cells produced water that could be used by the astronauts.

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

Quick Tip to Solve: Find the electron count from one balanced half-reaction before using $-nFE^\circ$; a positive cell potential must give a negative Gibbs energy change.

25. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	Time/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:

- At fixed volume and temperature, the partial pressure of a gas is proportional to its amount; the first-order law can therefore be written as $k = (2.303/t)\log(p_0/p_A)$.
- In $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$, one mole of reactant gives two moles of products. Total pressure rises, although reactant partial pressure falls.

Step 1: Express the partial pressures in terms of decomposition Let $p_0 = 0.4$ atm be the initial pressure of pure SO_2Cl_2. If the pressure corresponding to the amount decomposed at time t is x, stoichiometry gives

$$p_{SO_2Cl_2} = p_0 - x,$$
$$p_{SO_2} = x, \qquad p_{Cl_2} = x.$$

Hence the total pressure is $P_t = p_0 + x$. Thus $x = P_t - p_0$.

Step 2: Calculate the reactant pressure after the elapsed time For the second reading, $t = 100$ s and $P_t = 0.7$ atm. Thus

$$x = P_t - p_0 = 0.7 - 0.4 = 0.3\,\text{atm}.$$

The partial pressure of the remaining reactant is

$$p_A = p_0 - x = 2p_0 - P_t = 0.8 - 0.7 = 0.1\,\text{atm}.$$

Each product has pressure 0.3 atm, giving the correct total of 0.7 atm.

Quick Tip to Solve: For a gaseous decomposition $A \rightarrow B + C$ starting with pure A, use $p_A = 2p_0 - P_t$; total pressure itself is never the remaining reactant pressure.

Step 3: Apply the integrated first-order rate equation Use the initial and remaining reactant pressures in the logarithmic rate equation:

$$\begin{aligned} k &= \frac{2.303}{100} \log\left(\frac{0.4}{0.1}\right) \\ &= \frac{2.303}{100} \log 4 \\ &= \frac{2.303 \times 0.6021}{100} \\ &= 0.013866363\,\text{s}^{-1}. \end{aligned}$$

The pressure ratio is dimensionless; hence the unit of k is s^{-1}.

Step 4: Conclusion The rate constant is $\boxed{k \approx 1.39 \times 10^{-2}\,\text{s}^{-1}}$.

Quick Tip to Solve: For a gaseous decomposition $A \rightarrow B + C$ starting with pure A, use $p_A = 2p_0 - P_t$; total pressure itself is never the remaining reactant pressure.

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

Solution:

Concept:

- An emulsion is a colloidal dispersion of one liquid in another liquid with which it is immiscible. Both the dispersed phase and the dispersion medium are liquids.
- Emulsions are classified by the identity of the continuous liquid (dispersion medium): oil-in-water and water-in-oil. Here, oil denotes the water-immiscible liquid phase.

Step 1: Define an emulsion and identify its phases When very fine droplets of one immiscible liquid are distributed throughout another liquid, the resulting colloidal system is an emulsion. The droplets form the dispersed phase, while the liquid surrounding them is the continuous phase or dispersion medium. Thus, simply mixing two mutually soluble liquids does not produce an emulsion.

Step 2: Describe an oil-in-water emulsion In an oil-in-water emulsion, oil droplets are dispersed in a continuous aqueous medium. The dispersed phase is oil and the dispersion medium is water. Milk is an example: droplets of liquid fat are dispersed in an aqueous medium. It is therefore classified as an oil-in-water emulsion.

Step 3: Describe a water-in-oil emulsion In a water-in-oil emulsion, water droplets are dispersed in a continuous oily medium. The dispersed phase is water and the dispersion medium is oil or fat. Butter is the standard example: small water droplets are distributed throughout its continuous fat phase. Reversing the identities of the droplet and continuous phases changes the type of emulsion.

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

Quick Tip to Solve: In the name "oil-in-water", the liquid after "in" is the continuous medium; use the same rule for water-in-oil.

27. 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:

- Nitrogen is a second-period element and cannot expand its valence octet; phosphorus can form compounds with an expanded valence shell.
- Electron gain enthalpy depends on the attraction for the incoming electron and the repulsion it experiences in the occupied valence orbitals.
- The reducing action of phosphorus oxyacids is associated with their $\mathrm{P-H}$ bonds; these bonds are distinguished from their $\mathrm{O-H}$ bonds.

Step 1: Explain the difference between phosphorus and nitrogen (i) In the formal structure $(\mathrm{CH_3})_3\mathrm{P{=}O}$, phosphorus has three single bonds and one double bond, corresponding to ten electrons around it. Phosphorus can accommodate an expanded valence shell, so this compound exists. The analogous literal $(\mathrm{CH_3})_3\mathrm{N{=}O}$ structure would also place ten electrons around nitrogen. Nitrogen has only the second-shell valence orbitals and cannot exceed an octet, so this structure is not possible. Trimethylamine oxide can instead be represented with the charge-separated single-bond arrangement $(\mathrm{CH_3})_3\mathrm{N^+{-}O^-}$; this does not imply an allowed nitrogen-oxygen double bond in the printed formula.

Step 2: Compare electron addition to oxygen and sulphur (ii) Oxygen is smaller than sulphur. An incoming electron in oxygen must enter the compact, already occupied $2p$ subshell, where electron-electron repulsion is relatively high. In sulphur the added electron enters the larger, more diffuse $3p$ subshell and experiences less repulsion. Consequently electron addition releases less energy for oxygen: its electron gain enthalpy is less negative than that of sulphur.

Step 3: Count the phosphorus-hydrogen bonds (iii) Hypophosphorous acid, $\mathrm{H_3PO_2}$, has the connectivity $\mathrm{H_2P(=O)(OH)}$, with two $\mathrm{P-H}$ bonds. Phosphorous acid, $\mathrm{H_3PO_3}$, has the connectivity $\mathrm{HP(=O)(OH)_2}$, with only one $\mathrm{P-H}$ bond. The greater number of these reducing bonds makes $\mathrm{H_3PO_2}$ a stronger reducing agent. The total number of hydrogen atoms in the molecular formula alone does not give this comparison.

Step 4: Conclusion (i) Phosphorus permits the expanded-shell formal structure whereas nitrogen cannot expand its octet. (ii) Compact oxygen $2p$ orbitals cause greater repulsion for an added electron. (iii) $\mathrm{H_3PO_2}$ has two $\mathrm{P-H}$ bonds, compared with one in $\mathrm{H_3PO_3}$.

Quick Tip to Solve: For phosphorus oxyacids, write the connectivity and count $\mathrm{P-H}$ bonds before comparing reducing action; do not count all hydrogen atoms.

28(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 every element and the total electric charge. Dichromate changes to chromate in an alkaline medium without a change in chromium oxidation state.
- Permanganate accepts electrons during reduction. The specified number of electrons determines the oxidation state of the manganese product.

Step 1: Complete the dichromate-chromate conversion (i) Hydroxide ions convert the orange dichromate ion to yellow chromate ions. Two chromium atoms give two chromate ions, and water balances hydrogen and oxygen:

$$\mathrm{Cr_2O_7^{2-} + 2\,OH^- \longrightarrow 2\,CrO_4^{2-} + H_2O.}$$

There are two chromium, nine oxygen and two hydrogen atoms on each side. The total charge is -4 on each side. Chromium remains in oxidation state $+6$, so this is not a reduction.

Step 2: Complete the three-electron reduction of permanganate (ii) Manganese starts at $+7$ in $\mathrm{MnO_4^-}$. Acceptance of three electrons lowers its oxidation state to $+4$, giving $\mathrm{MnO_2}$. The four supplied hydrogen ions form two water molecules:

$$\mathrm{MnO_4^- + 4\,H^+ + 3\,e^- \longrightarrow MnO_2 + 2\,H_2O.}$$

Both sides contain one manganese, four oxygen and four hydrogen atoms. The charge on the left is $-1 + 4 - 3 = 0$, equal to the neutral products. Formation of $\mathrm{Mn^{2+}}$ would require five electrons, so it does not fit the printed equation.

Step 3: Conclusion The products are (i) $\mathrm{2\,CrO_4^{2-} + H_2O}$, and (ii) $\mathrm{MnO_2 + 2\,H_2O}$.

Quick Tip to Solve: Read the printed electron count first: three electrons change manganese from $+7$ to $+4$, whereas five would give $+2$.

28(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 commonly formed ions. A completely filled d^{10} subshell does not meet this criterion.

Quick Tip to Solve: For the potential comparison, write both reductions as d-electron changes: Mn goes from d4 to stable d5, while Cr goes from stable d3 to d4.

- Complex formation involves donation of lone pairs from ligands to a central metal ion. Small size, high charge density and available orbitals favour coordination.
- For a reduction couple M^{3+}/M^{2+}, a more positive standard reduction potential indicates a greater tendency for M^{3+} to accept an electron. Relative electronic stability contributes to this tendency.

Step 1: (i) Examine the d-electron configurations of zinc Zinc has the electronic configuration $[\mathrm{Ar}]3d^{10}4s^2$. Its common ion, Zn^{2+}, is formed by losing the two 4s electrons and has the configuration $[\mathrm{Ar}]3d^{10}$. Thus both the atom and its common ion have completely filled d subshells. Zinc is a d-block element, but it does not satisfy the electronic criterion for a transition element.

Step 2: (ii) Explain the formation of coordination complexes Transition-metal ions are relatively small and often carry high positive charges. Their high charge density attracts electron-rich ligands strongly. They also have suitable vacant orbitals that can accept the lone pairs donated by ligands to form coordinate bonds. Consequently, many ligands, such as water, ammonia and cyanide ions, can coordinate to transition-metal ions, producing a large number of complexes.

Step 3: (iii) Compare the stability changes during reduction For manganese, reduction converts Mn^{3+}, which is $3d^4$, into Mn^{2+}, which is $3d^5$. The product has the especially stable half-filled d subshell, so this reduction is strongly favoured. For chromium, reduction converts Cr^{3+}, which is $3d^3$, into Cr^{2+}, which is $3d^4$. In aqueous complexes, the d^3 configuration of Cr^{3+} has a stable t_{2g}^3 arrangement; reduction loses this stabilisation. Thus chromium(III) resists reduction relative to manganese(III), accounting for the much more positive E° of the $\mathrm{Mn}^{3+}/\mathrm{Mn}^{2+}$ couple.

Step 4: Conclusion (i) Zn and its common ion have filled $3d^{10}$ subshells. (ii) High charge density and suitable vacant orbitals favour coordination with ligands. (iii) Reduction of Mn^{3+} produces stable half-filled $3d^5$ Mn^{2+}, whereas reduction of stable $3d^3$ Cr^{3+} is less favourable.

Quick Tip to Solve: For the potential comparison, write both reductions as d-electron changes: Mn goes from d4 to stable d5, while Cr goes from stable d3 to d4.

OR

28(i). With reference to structural variability and chemical reactivity, write the differences between lanthanoids and actinoids. [5 marks total]

Solution:

Concept:

- Lanthanoids progressively fill the inner $4f$ subshell, whereas actinoids progressively fill the $5f$ subshell.
- Structural variability and chemical reactivity depend on the availability of valence electrons for bonding.

Step 1: Compare structural variability Lanthanoids show less structural variability because the deeply buried $4f$ electrons take little part in bonding and the $+3$ state predominates. Actinoids show greater structural variability: the $5f$, $6d$ and $7s$ levels are close in energy, allowing more electrons to participate in bonding and a wider range of oxidation states.

Quick Tip to Solve: Compare both requested properties explicitly: actinoids show more structural variability and are generally more reactive.

Step 2: Compare chemical reactivity Actinoids are generally more chemically reactive than lanthanoids. Their less effectively shielded, more accessible $5f$ electrons participate more readily in bonding; lanthanoids have more deeply buried $4f$ electrons.

Step 3: Conclusion Actinoids exhibit greater structural variability and generally greater chemical reactivity than lanthanoids.

Quick Tip to Solve: Compare both requested properties explicitly: actinoids show more structural variability and are generally more reactive.

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

Solution:

Concept:

- The usual oxidation state of lanthanoids is $+3$, but especially stable $4f$ configurations can also support other oxidation states.
- An empty $4f$ subshell, written $4f^0$, is one such stable configuration.

Step 1: Identify the lanthanoid Cerium, symbol Ce, is the lanthanoid well known to exhibit the $+4$ oxidation state, in addition to its common $+3$ state.

Step 2: Relate the state to electron configuration Cerium has the approximate ground-state configuration $[\mathrm{Xe}]\,4f^1 5d^1 6s^2$. Removal of four valence electrons gives Ce^{4+} with the xenon-core configuration $[\mathrm{Xe}]$, or $4f^0$. This stable empty $4f$ subshell accounts for its accessible $+4$ state.

Step 3: Conclusion The required member is $\boxed{\text{cerium (Ce)}}$.

Quick Tip to Solve: Remember cerium for the lanthanoid $+4$ state: Ce(IV) has the stable empty 4f subshell.

28(iii). Complete the following equation:

$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,\mathrm{e^-} \longrightarrow$$

Solution:

Concept:

- In acidic medium, permanganate is reduced from manganese in oxidation state $+7$ to $\mathrm{Mn^{2+}}$.
- A balanced redox half-reaction conserves both atoms and total electric charge; oxygen is balanced with water and hydrogen with $\mathrm{H^+}$.

Step 1: Determine the reduction product Manganese in $\mathrm{MnO_4^-}$ is in oxidation state $+7$. Acceptance of the five electrons shown reduces it to $+2$, so the manganese-containing product is $\mathrm{Mn^{2+}}$.

Step 2: Balance and check atoms and charge The four oxygen atoms form $4\mathrm{H_2O}$, using the eight hydrogen ions supplied. Both sides then contain one Mn atom, four O atoms and eight H atoms. The left-hand charge is $-1 + 8 - 5 = +2$, equal to the charge of $\mathrm{Mn^{2+}}$ on the right.

Quick Tip to Solve: The five electrons and eight hydrogen ions identify reduction of acidic permanganate to Mn(II).

Step 3: Conclusion

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

Quick Tip to Solve: The five electrons and eight hydrogen ions identify reduction of acidic permanganate to Mn(II).

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

Solution:

Concept:

- Paramagnetism arises from unpaired electrons; a greater number of unpaired electrons gives a larger spin-only magnetic moment.
- The spin-only moment is $\mu = \sqrt{n(n+2)}\,\mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton.

Step 1: Find the ionic configurations For Mn, $Z = 25$ and the neutral configuration is $[Ar]\,3d^5 4s^2$. Removing the two $4s$ electrons first and then one $3d$ electron gives Mn^{3+} : $[Ar]\,3d^4$. For Cr, $Z = 24$ and the neutral configuration is $[Ar]\,3d^5 4s^1$; removal of three electrons gives Cr^{3+} : $[Ar]\,3d^3$.

Step 2: Compare the unpaired electrons By Hund's rule, the $3d^4$ configuration has four unpaired electrons, whereas $3d^3$ has three. Their spin-only moments are therefore $\sqrt{24}\,\mu_B$ and $\sqrt{15}\,\mu_B$, respectively. The larger value belongs to Mn^{3+}.

Step 3: Conclusion $\boxed{Mn^{3+}}$ is more paramagnetic because it has four unpaired electrons, compared with three in Cr^{3+}.

Quick Tip to Solve: Remove 4s electrons before 3d electrons when forming transition-metal ions, then count unpaired d electrons.

29(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:

- The polar carbonyl group of ethanal, CH_3CHO, undergoes nucleophilic addition; the carbonyl carbon is attacked by an electron-rich reagent.
- Hydroxylamine forms an oxime by condensation with a carbonyl compound, eliminating water.
- Ethanal has alpha-hydrogen atoms and undergoes aldol addition with dilute alkali to give a beta-hydroxy aldehyde.

Quick Tip to Solve: With dilute alkali, join two ethanal molecules to form a four-carbon beta-hydroxy aldehyde; do not remove water unless heating is specified.

Step 1: Add hydrogen cyanide to ethanal Cyanide attacks the carbonyl carbon, followed by protonation of the oxygen. The carbonyl double bond becomes a single bond and the carbon gains both hydroxyl and cyano groups:

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

The product is ethanal cyanohydrin, also called 2-hydroxypropanenitrile. The original aldehyde hydrogen remains bonded to this carbon.

Step 2: Form the oxime with hydroxylamine The nitrogen of hydroxylamine reacts at the carbonyl carbon. Elimination of one water molecule replaces the carbonyl oxygen by $=N-OH$:

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

The product is ethanal oxime (acetaldoxime); the hydroxyl group remains attached to nitrogen.

Step 3: Carry out aldol addition with dilute alkali Dilute $NaOH$ removes an alpha-hydrogen from one ethanal molecule. The resulting enolate adds to a second ethanal molecule, and protonation gives the four-carbon beta-hydroxy aldehyde:

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

This product is 3-hydroxybutanal, commonly called aldol. Since heating is not specified, the required product is the addition product; dehydration to but-2-enal is not the reaction demanded here.

Step 4: Conclusion The products are (i) $CH_3CH(OH)CN$, ethanal cyanohydrin; (ii) $CH_3CH{=}NOH$, ethanal oxime; and (iii) $CH_3CH(OH)CH_2CHO$, 3-hydroxybutanal.

Quick Tip to Solve: With dilute alkali, join two ethanal molecules to form a four-carbon beta-hydroxy aldehyde; do not remove water unless heating is specified.

29(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 liberate carbon dioxide from sodium hydrogen carbonate; phenol is too weak an acid to do so.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver ions are reduced to metallic silver. A simple ketone does not give this test.

Step 1: Test benzoic acid and phenol with sodium hydrogen carbonate Add aqueous $NaHCO_3$ to separate samples. Benzoic acid gives brisk effervescence of CO_2, which turns limewater milky:

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

Quick Tip to Solve: Use bicarbonate to distinguish a carboxylic acid from phenol, and Tollens' reagent to distinguish a simple aldehyde from a ketone.

Phenol gives no effervescence under the same conditions, since it cannot displace carbonic acid from its salt. Thus gas evolution identifies benzoic acid.

Step 2: Test propanal and propanone with Tollens' reagent Warm separate samples gently with freshly prepared Tollens' reagent in a water bath. Propanal deposits a silver mirror on the inner surface of a clean test tube:

$$CH_3CH_2CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow$$

$$CH_3CH_2COO^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O.$$

Propanone gives no silver mirror because this simple ketone is not oxidised by Tollens' reagent. This difference distinguishes the aldehyde from the ketone.

Step 3: Conclusion Aqueous $NaHCO_3$ gives carbon dioxide with benzoic acid but not phenol. Tollens' reagent gives a silver mirror with propanal but not propanone.

Quick Tip to Solve: Use bicarbonate to distinguish a carboxylic acid from phenol, and Tollens' reagent to distinguish a simple aldehyde from a ketone.

OR

29(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. Electron-withdrawing groups stabilise a carboxylate ion by the negative inductive effect.
- Resonance between the two oxygen atoms of a carboxyl group changes its reactivity from that of an isolated aldehyde or ketone carbonyl group.

Step 1: Compare the stability of the conjugate bases Chloroacetic acid and acetic acid dissociate to form $ClCH_2COO^-$ and CH_3COO^-, respectively. The electronegative chlorine atom withdraws electron density through sigma bonds by its $-I$ effect. This disperses the negative charge on the chloroacetate ion and stabilises it, favouring acid dissociation. In acetic acid, the methyl group's $+I$ effect increases electron density and makes acetate relatively less stable. Hence chloroacetic acid releases a proton more readily.

Step 2: Explain the reduced carbonyl addition reactivity In RCOOH, a lone pair on the hydroxyl oxygen is conjugated with the carbonyl group. Resonance donation reduces the positive character of the carbonyl carbon, making it less susceptible to nucleophilic attack than the carbonyl carbon of an aldehyde or ketone. Thus carboxylic acids do not show the characteristic nucleophilic addition reactions of aldehydes and ketones, such as oxime formation. Their carboxyl group instead commonly undergoes reactions such as acid-base reactions and acyl substitution, for example esterification.

Step 3: Conclusion (i) The $-I$ effect of chlorine stabilises chloroacetate, so $ClCH_2COOH$ is stronger

Quick Tip to Solve: For acidity, compare conjugate-base stability; for carbonyl reactivity, check whether an adjacent oxygen donates a lone pair by resonance.

than CH_3COOH. (ii) Resonance donation by the hydroxyl oxygen reduces the electrophilicity of the carbonyl carbon in a carboxylic acid, suppressing the usual aldehyde/ketone addition reactions.

Quick Tip to Solve: For acidity, compare conjugate-base stability; for carbonyl reactivity, check whether an adjacent oxygen donates a lone pair by resonance.

29(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 into an aldehyde using hydrogen over poisoned palladium supported on barium sulphate.
- Cannizzaro's reaction is the disproportionation of an aldehyde without alpha-hydrogens in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Illustrate Rosenmund reduction Hydrogenate ethanoyl chloride using palladium on barium sulphate, with a poisoned catalyst to limit further reduction:

$$CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl.$$

Ethanoyl chloride is thereby reduced to ethanal. The reduced catalyst activity prevents the aldehyde from being readily reduced further to a primary alcohol. The general conversion is $RCOCl \longrightarrow RCHO$.

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

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

One benzaldehyde molecule is reduced to benzyl alcohol, while the other is oxidised to sodium benzoate. The two aldehyde molecules therefore furnish an alcohol and a carboxylate salt in equal molar amounts. Concentrated alkali and absence of alpha-hydrogen distinguish this reaction from aldol addition.

Step 3: Conclusion Rosenmund reduction gives ethanal from ethanoyl chloride using H_2 and poisoned $Pd/BaSO_4$. Cannizzaro's reaction of benzaldehyde with concentrated $NaOH$ gives benzyl alcohol and sodium benzoate, as shown in the balanced equations.

Quick Tip to Solve: Remember Rosenmund as acid chloride to aldehyde; for Cannizzaro choose an aldehyde with no alpha-hydrogen and write both alcohol and carboxylate products.

29(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:

- The iodoform test is given by methyl ketones containing the group $\mathrm{RCOCH_3}$. Iodine in aqueous alkali converts this group into yellow iodoform, $\mathrm{CHI_3}$.
- The carbonyl group alone is insufficient: a methyl group must be directly bonded to the carbonyl carbon.

Step 1: Examine the first ketone In $\mathrm{CH_3CH_2COCH_2CH_3}$, pentan-3-one, both groups attached to the carbonyl carbon are ethyl groups. It has no $-\mathrm{COCH_3}$ group and does not give the iodoform test.

Step 2: Examine the second ketone In $\mathrm{CH_3CH_2CH_2COCH_3}$, pentan-2-one, one group attached to the carbonyl carbon is methyl. Therefore it gives a yellow precipitate of $\mathrm{CHI_3}$ with iodine and aqueous alkali.

Step 3: Conclusion $\boxed{\mathrm{CH_3CH_2CH_2COCH_3}}$, pentan-2-one, gives the iodoform test.

Quick Tip to Solve: Locate the group $-\mathrm{COCH_3}$; a terminal methyl group elsewhere in the chain does not qualify.

30(a). Define the following terms:

(i) Molarity

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

Solution:

Concept:

- Molarity expresses concentration using the volume of the final solution, whereas molality uses the mass of solvent.
- For a dilute solution of a non-volatile non-electrolyte, boiling-point elevation obeys $\Delta T_b = K_b m$, where m is molality and K_b is a characteristic constant of the solvent.

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

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

Its unit is $\mathrm{mol\,L^{-1}}$. The denominator is the solution volume, including solute and solvent, and not the volume of solvent alone.

Step 2: (ii) Define molal elevation constant The molal elevation constant, or ebullioscopic constant, is the elevation in boiling point produced when one mole of a non-volatile non-electrolyte is dissolved in one kilogram of the solvent. Equivalently,

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

Its unit is $\mathrm{K\,kg\,mol^{-1}}$; it is numerically equal to the boiling-point elevation for a solution of unit

Quick Tip to Solve: Use litres of solution for molarity, but kilograms of solvent when defining the molality in $K_b = \Delta T_b/m$.

molality.

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

Quick Tip to Solve: Use litres of solution for molarity, but kilograms of solvent when defining the molality in $K_b = \Delta T_b/m$.

30(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:

- For a dilute solution, osmotic pressure is $\pi = iCRT = i(n/V)RT$, where C is molarity, R the gas constant and T the absolute temperature.
- Urea and glucose are non-electrolytes: neither dissociates into ions in water, so each has van't Hoff factor $i = 1$. Isotonic solutions at the same temperature have equal osmotic pressures and hence equal molarities.

Step 1: Calculate the molarity of urea The solution contains $15\,\text{g}$ of urea in $1\,\text{L}$ of solution. Using its molar mass,

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

The given volume is already the volume of solution, so no density conversion is required.

Step 2: Apply the isotonic condition Let w grams of glucose be present in one litre of its solution. Equal osmotic pressures at the same temperature give

$$C_uRT = C_gRT,$$
$$C_g = C_u = 0.25\,\text{mol L}^{-1}.$$

Thus the one-litre glucose solution also contains $0.25\,\text{mol}$. Equal molarities do not mean equal masses because the two molar masses differ.

Step 3: Convert glucose moles into mass Using the molar mass of glucose,

$$w = n_gM_g = (0.25\,\text{mol})(180\,\text{g mol}^{-1}) = 45\,\text{g}.$$

As a check, the glucose molar mass is three times the urea molar mass, so equal numbers of moles require three times the mass: $3 \times 15 = 45\,\text{g}$.

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

Quick Tip to Solve: For isotonic non-electrolytes at equal temperature and equal solution volumes, use the mass ratio equal to the molar-mass ratio.

OR

30(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 $p_A = x_A p_A^0$, $p_B = x_B p_B^0$, and $p = p_A + p_B$. Here x denotes mole fraction and p^0 the vapour pressure of the pure liquid.
- Positive deviation occurs when the escaping tendency of molecules is greater than in an ideal solution, giving vapour pressure above the Raoult-law prediction.

Step 1: Identify interactions in the pure liquids Ethanol molecules form intermolecular hydrogen bonds through their $-\mathrm{OH}$ groups. These attractions hold ethanol molecules together in the liquid. Acetone is a polar liquid, but it does not contain an $\mathrm{O-H}$ group and cannot form the same self-associated hydrogen-bond network.

Step 2: Explain the effect of mixing When acetone is added to ethanol, it disrupts some of the hydrogen bonds between ethanol molecules. Although ethanol and acetone can interact, the effective attraction in the mixture is weaker than the interactions holding the pure liquids together. Molecules therefore escape more readily into the vapour phase, and the observed vapour pressure is higher than the ideal value at the same composition and temperature.

Step 3: Conclusion The ethanol-acetone mixture shows $\boxed{\text{positive deviation}}$ from Raoult's law because mixing disrupts ethanol hydrogen bonding and increases the escaping tendency of molecules.

Quick Tip to Solve: For ethanol-acetone, connect disruption of ethanol hydrogen bonds to greater escaping tendency and hence higher vapour pressure.

30(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 the mass of solute in 100 g of solution. Thus a 10% (by mass) glucose solution contains 10 g of glucose and 90 g of water in every 100 g of solution.
- Molality is $m = n_{\text{solute}}/w_{\text{solvent}}$, where n is in moles and the solvent mass w is in kilograms. Molarity is $M = n_{\text{solute}}/V_{\text{solution}}$, where the solution volume V is in litres.

Step 1: Choose a 100 g sample and calculate glucose moles The mass-percentage statement gives the masses directly on a 100 g solution basis:

$$w_{\text{glucose}} = 10\,\text{g},$$
$$w_{\text{water}} = 100 - 10 = 90\,\text{g} = 0.090\,\text{kg},$$
$$n_{\text{glucose}} = \frac{10\,\text{g}}{180\,\text{g mol}^{-1}} = \frac{1}{18}\,\text{mol}.$$

Quick Tip to Solve: For a mass-percentage solution, choose 100 g: subtract the solute mass for molality, and divide the full 100 g by density for molarity.

The 100 g is the mass of the entire solution; it must not be used as the solvent mass.

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

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

Density is unnecessary here because molality depends on the mass of solvent, rather than the volume of solution.

Step 3: Convert solution mass to volume and calculate molarity Using the density of the solution, $\rho = 1.2\,\text{g mL}^{-1}$, the volume of our sample is

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

Hence the number of moles per litre of solution is

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

The density applies to the whole 100 g solution, so its volume is calculated from 100 g, not from the 90 g water mass.

Step 4: Conclusion The molality is $\boxed{0.617\,\text{mol kg}^{-1}}$, and the molarity is $\boxed{0.667\,\text{mol L}^{-1}}$.

Quick Tip to Solve: For a mass-percentage solution, choose 100 g: subtract the solute mass for molality, and divide the full 100 g by density for molarity.