

General Instructions

- (i) This booklet contains 26 questions, each provided with a complete, step-by-step solution.
- (ii) It comprises 6 single-correct multiple-choice questions.
- (iii) Attempt each question on your own before reviewing the given solution.

1. Which of the following solutions will have a maximum boiling point?

- (A) 1% glucose in water
- (B) 1% CaCl_2 in water
- (C) 1% sucrose in water
- (D) 1% NaCl in water

Correct Answer: (D) 1% NaCl in water

Solution:

Step 1: Concept. Elevation of boiling point is a colligative property:

$$\Delta T_b = i K_b m$$

where i is the van't Hoff factor (number of particles a solute gives on dissolving) and m is molality. So the solution that produces the largest number of dissolved particles boils highest.

Step 2: Same mass basis. All four are 1% by mass, so each has the same mass of solute in the same water. Moles = mass/ M , hence molality $\propto 1/M$. The effective particle count is therefore $\propto i/M$.

Step 3: Compare i/M .

Glucose: $i = 1$, $M = 180 \Rightarrow 0.0056$

CaCl_2 : $i = 3$, $M = 111 \Rightarrow 0.027$

Sucrose: $i = 1$, $M = 342 \Rightarrow 0.0029$

NaCl: $i = 2$, $M = 58.5 \Rightarrow 0.0342$

Step 4: Decide. NaCl gives the largest i/M , so the most particles and the highest ΔT_b .

Why others are wrong: Glucose and sucrose are non-electrolytes ($i = 1$), so few particles. CaCl_2 gives 3 ions but its high molar mass makes its particle count fall just below NaCl.

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Quick Tip: Boiling point rises with $i \times$ molality. For equal mass %, compare i/M ; the smallest-mass strong electrolyte wins.



2. The order of reaction for which the unit of the velocity (rate) constant is $\text{mol L}^{-1} \text{s}^{-1}$ is:

- (A) First order
- (B) Second order
- (C) Zero order
- (D) None of these

Correct Answer: (C) Zero order

Solution:

Step 1: General unit of rate constant. For a reaction of order n , rate = $k[A]^n$. Since rate always has units $\text{mol L}^{-1} \text{s}^{-1}$, the unit of k is

$$k = \text{mol}^{(1-n)} \text{L}^{(n-1)} \text{s}^{-1}.$$

Step 2: Put $n = 0$. $k = \text{mol}^{(1-0)} \text{L}^{(0-1)} \text{s}^{-1} = \text{mol L}^{-1} \text{s}^{-1}$. This matches the given unit.

Step 3: Check the others. First order ($n = 1$): $k = \text{s}^{-1}$. Second order ($n = 2$): $k = \text{mol}^{-1} \text{L s}^{-1}$. Neither equals $\text{mol L}^{-1} \text{s}^{-1}$.

Step 4: Only a zero-order rate constant carries the units of rate itself, because for zero order rate = k .

Zero order (option iii)

Quick Tip: Use k unit = $\text{mol}^{(1-n)} \text{L}^{(n-1)} \text{s}^{-1}$. When rate = k , the order is zero.

3. The most active metal among the following is:

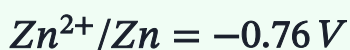
- (A) Fe
- (B) Zn
- (C) Ni
- (D) Cu

Correct Answer: (B) Zn

Solution:

Step 1: What 'most active' means. The most active (most reactive) metal is the strongest reducing agent, i.e. the one that loses electrons most easily. This is the metal with the most negative standard reduction potential and the highest position in the activity/electrochemical series.

Step 2: Compare standard reduction potentials.



$$Fe^{2+}/Fe = -0.44 V$$

$$Ni^{2+}/Ni = -0.25 V$$

$$Cu^{2+}/Cu = +0.34 V$$

Step 3: Rank. The most negative value belongs to zinc, so Zn is oxidised most readily and is the most active metal.

Step 4: Others. Cu is the least active (positive potential, a noble-ish metal); Fe and Ni lie in between.

Zn (option ii)

Quick Tip: Most active = most negative reduction potential = highest in the activity series. Compare Zn, Fe, Ni, Cu.



4. The velocity (rate) constant of a second order reaction is generally expressed as:

- (A) mole litre second
- (B) $\text{mole}^{-1} \text{litre}^{-1} \text{second}^{-1}$
- (C) $\text{mole litre}^{-1} \text{second}^{-1}$
- (D) $\text{mole}^{-1} \text{litre second}^{-1}$

Correct Answer: (D) $\text{mole}^{-1} \text{litre second}^{-1}$

Solution:

Step 1: Formula for the unit of k . For order n :

$$k = \text{mol}^{(1-n)} L^{(n-1)} s^{-1}.$$

Step 2: Substitute $n = 2$. $k = \text{mol}^{(1-2)} L^{(2-1)} s^{-1} = \text{mol}^{-1} L s^{-1}.$

Step 3: Read as words. $\text{mol}^{-1} \text{L s}^{-1} = \text{mole}^{-1} \text{litre second}^{-1}$.

Step 4: Match option. This is option (iv). Option (ii) $\text{mole}^{-1} \text{litre}^{-1} \text{second}^{-1}$ is wrong (extra litre^{-1}); option (iii) is the zero-order unit; option (i) has no reciprocal terms at all.

$\text{mole}^{-1} \text{litre second}^{-1}$ (option iv)

Quick Tip: Second order: $k = \text{mol}^{(1-n)} \text{L}^{(n-1)} \text{s}^{-1}$ with $n = 2$ gives $\text{mol}^{-1} \text{L s}^{-1}$.

5. The distinction between aldehydes and ketones can be made using:

- (A) Conc. H_2SO_4
- (B) Anhydrous ZnCl_2
- (C) Schiff reagent
- (D) Resorcinol

Correct Answer: (C) Schiff reagent

Solution:

Step 1: What is needed. We need a reagent that responds to aldehydes but not ketones.

Step 2: Schiff's reagent. Schiff's reagent is dilute rosaniline hydrochloride (magenta dye) decolourised by SO_2 . Aldehydes restore the pink/magenta colour, while ketones do not react.

Step 3: Apply. Add the unknown to Schiff's reagent: a pink colour appears with an aldehyde, no colour with a ketone. This cleanly distinguishes them.

Step 4: Why others fail. Conc. H_2SO_4 and anhydrous ZnCl_2 are

dehydrating/Lewis-acid catalysts, not a selective test. Resorcinol is a phenol, not a differentiating reagent for this pair.

Schiff reagent (option iii)

Quick Tip: Look for a reagent that only aldehydes turn pink. Think Schiff's (fuchsin) reagent.

6. In which cell does the following reaction take place?



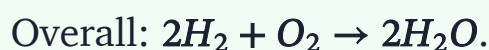
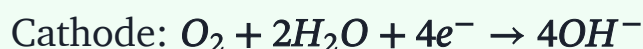
- (A) Lead accumulator battery
- (B) Fuel cell
- (C) Dry cell
- (D) None of these

Correct Answer: (B) Fuel cell

Solution:

Step 1: Identify the reaction. The overall change is hydrogen combining with oxygen to give water, releasing energy. A galvanic cell that runs on continuously supplied fuel gases is a fuel cell.

Step 2: The hydrogen-oxygen fuel cell. H_2 and O_2 are fed to porous electrodes in KOH.



Step 3: Rule out others. Lead accumulator uses Pb/PbO_2 in H_2SO_4 ;

the dry cell uses Zn/MnO_2 . Neither has this hydrogen-oxygen reaction.

Step 4: Hence the reaction occurs in a fuel cell.

Fuel cell (option ii)

Quick Tip: A cell fed continuously with H_2 and O_2 gases producing only water is a fuel cell.

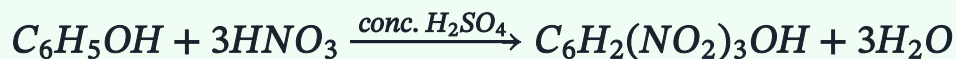
7. How will you obtain the following from phenol? (i) Picric acid (ii) Benzoquinone.

Correct Answer: —

Solution:

Step 1: (i) Picric acid from phenol. Picric acid is 2,4,6-trinitrophenol. The -OH group strongly activates the ring and directs incoming groups to the ortho and para positions, so nitration puts three nitro groups at positions 2, 4 and 6.

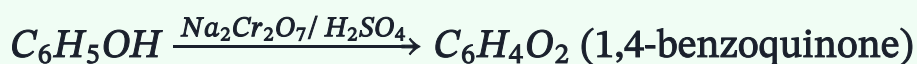
Reaction: Phenol is treated with concentrated HNO_3 in the presence of concentrated H_2SO_4 .



The product $C_6H_2(NO_2)_3OH$ is picric acid (2,4,6-trinitrophenol).

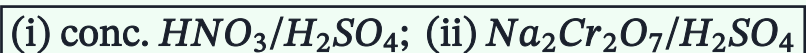
Step 2: (ii) Benzoquinone from phenol. Phenol is oxidised. On treatment with a strong oxidising agent such as sodium dichromate ($Na_2Cr_2O_7$) and sulphuric acid, phenol is converted into benzoquinone (1,4-benzoquinone / p-benzoquinone).

Reaction:



Here the -OH carbon and the para carbon are oxidised to two $C = O$ groups.

Step 3: Summary. Nitration gives picric acid; oxidation gives benzoquinone.



Quick Tip: Picric acid = trinitration of phenol with conc. HNO_3/H_2SO_4 ; benzoquinone = oxidation of phenol with acidified $Na_2Cr_2O_7$.

8. Write chemical equations of the Etard reaction and the Gattermann-Koch reaction.

Correct Answer: —

Solution:

Step 1: Etard reaction. Toluene is oxidised at its methyl group to benzaldehyde using chromyl chloride (CrO_2Cl_2) in carbon disulphide. A brown chromium complex forms first and is then hydrolysed to the aldehyde.



Controlled oxidation stops at the aldehyde stage (it does not go to the acid).

Step 2: Gattermann-Koch reaction. Benzene reacts with carbon

monoxide and hydrogen chloride in the presence of anhydrous $AlCl_3$ (with $CuCl$ as a helper) to give benzaldehyde. It behaves as a Friedel-Crafts type formylation.



Step 3: Summary. Both reactions are important routes to benzaldehyde: Etard from toluene, Gattermann-Koch from benzene.

Both give C_6H_5CHO

Quick Tip: Both make benzaldehyde: Etard oxidises toluene with CrO_2Cl_2 ; Gattermann-Koch formylates benzene with $CO + HCl/AlCl_3$.

9. Is the following reaction possible or not? Explain with reasons.



Correct Answer: —

Solution:

Step 1: What the reaction claims. It shows silver metal displacing zinc from zinc nitrate. For displacement, the free metal (Ag) must be more reactive than the metal in the salt (Zn).

Step 2: Compare reactivities. Zinc is far more reactive (more electropositive) than silver. Standard reduction potentials: $Zn^{2+}/Zn = -0.76 V$ and $Ag^+/Ag = +0.80 V$. Zinc sits above silver in the activity series.

Step 3: Test with cell potential. Here Ag would be oxidised (anode) and Zn^{2+} reduced (cathode):

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = (-0.76) - (+0.80) = -1.56 V$$

A negative E_{cell}° means $\Delta G = -nFE_{cell}^{\circ} > 0$, so the reaction is non-spontaneous.

Step 4: Conclusion. Silver cannot displace zinc; the reaction is NOT possible. In fact the reverse, $Zn + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2Ag$, is the feasible one.

Reaction not possible ($E_{cell}^{\circ} = -1.56 V$)

Quick Tip: Zn is above Ag in the activity series; Ag cannot displace Zn. Check E_{cell}° is negative.

◆

10. What is Lanthanide contraction? What are the consequences of Lanthanide contraction?

Correct Answer: —

Solution:

Step 1: Definition. Lanthanide contraction is the steady, small decrease in the atomic and ionic radii of the lanthanide elements (from La/Ce to Lu) as the atomic number increases across the series.

Step 2: Cause. As we move along the series, each added electron enters an inner $4f$ orbital. The $4f$ electrons shield the outer electrons from the nucleus very poorly (diffuse, poorly directed orbitals). So the effective nuclear charge felt by the outer electrons keeps rising,

pulling them inward and shrinking the size.

Step 3: Consequences.

(i) The atomic radii of the elements of the second (4d) and third (5d) transition series become almost the same (e.g. Zr and Hf, Nb and Ta), making these pairs very hard to separate.

(ii) The lanthanides themselves have closely similar sizes, so their chemical properties are very alike and separating them is difficult.

(iii) The basic strength of the hydroxides $M(OH)_3$ decreases from $La(OH)_3$ to $Lu(OH)_3$ as the ionic size falls.

(iv) There is a slight, regular variation in properties such as ionization enthalpy across the series.

Step 4: Summary. Poor 4f shielding causes a gradual size decrease, whose main results are the Zr/Hf-type resemblance, difficult separation and falling basicity.

Gradual $r \downarrow$ due to poor 4f shielding

Quick Tip: It is the gradual size decrease across 4f elements due to poor 4f shielding; recall Zr/Hf similarity and falling hydroxide basicity.

◆

11. The velocity constant K for a first order reaction was found to be $5.5 \times 10^{-14} \text{ s}^{-1}$. Calculate the half life of this reaction.

Correct Answer: —

Solution:

Step 1: Formula. For a first order reaction the half life is independent of initial concentration and is given by

$$t_{1/2} = \frac{0.693}{k}$$

Step 2: Substitute. $k = 5.5 \times 10^{-14} \text{ s}^{-1}$, so

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14}} \text{ s}$$

Step 3: Arithmetic. $\frac{0.693}{5.5} = 0.126$. Therefore

$$t_{1/2} = 0.126 \times 10^{14} = 1.26 \times 10^{13} \text{ s}$$

Step 4: State the result. The half life is about 1.26×10^{13} seconds (a very slow reaction, as expected from the tiny rate constant).

$$t_{1/2} \approx 1.26 \times 10^{13} \text{ s}$$

Quick Tip: First order half life $t_{1/2} = 0.693/k$; plug in $k = 5.5 \times 10^{-14} \text{ s}^{-1}$.

12. Draw a diagram to show the splitting of d-orbitals in an octahedral crystal field.

Correct Answer: —

Solution:

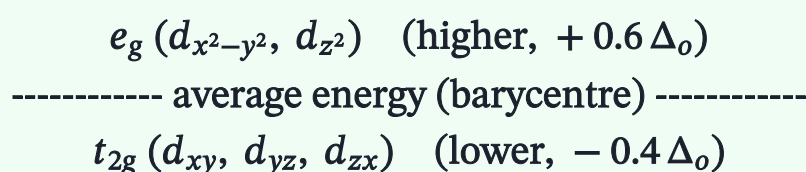
Step 1: Starting point. In a free (gaseous) metal ion the five d-orbitals (d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$, d_{z^2}) are degenerate, i.e. all have the same energy.

Step 2: Effect of six ligands. In an octahedral complex, six ligands approach the metal along the x , y and z axes. The two orbitals that

point directly along the axes, $d_{x^2-y^2}$ and d_{z^2} (the e_g set), face the ligands head-on and are repelled more, so their energy rises. The three orbitals lying between the axes, d_{xy} , d_{yz} , d_{zx} (the t_{2g} set), are repelled less, so their energy falls.

Step 3: The splitting. The degenerate level splits into a lower t_{2g} triplet and an upper e_g doublet, separated by the crystal field splitting energy Δ_o . Relative to the average (barycentre), t_{2g} is lowered by $0.4 \Delta_o$ each and e_g is raised by $0.6 \Delta_o$ each.

Step 4: Diagram (energy increases upward):



The gap between the two sets is Δ_o , the octahedral crystal field splitting energy.

$$t_{2g} (3 \text{ lower}) \text{ and } e_g (2 \text{ higher}), \text{ gap} = \Delta_o$$

Quick Tip: Five degenerate d-orbitals split into lower t_{2g} (3 orbitals) and higher e_g (2 orbitals), separated by Δ_o .

13. 0.32 g of a new compound was dissolved in 25 g of water. The freezing point of this solution was found to be -0.201°C . Determine the molecular weight of this new compound. For water $K_f = 1.86^\circ\text{C kg mol}^{-1}$.

Correct Answer: —

Solution:

Step 1: Concept. Depression in freezing point is a colligative property.

$$\Delta T_f = K_f \times m$$

where m is the molality of the solution.

Step 2: Find the depression in freezing point. Pure water freezes at 0°C , and the solution freezes at -0.201°C .

$$\Delta T_f = 0 - (-0.201) = 0.201^\circ\text{C}$$

Step 3: Write molality in terms of the unknown molar mass. With mass of solute $w_2 = 0.32\text{ g}$, mass of solvent $w_1 = 25\text{ g}$ and molar mass M_2 ,

$$m = \frac{w_2 \times 1000}{M_2 \times w_1}$$

so

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

Step 4: Rearrange for M_2 and substitute.

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1} = \frac{1.86 \times 0.32 \times 1000}{0.201 \times 25}$$

Step 5: Arithmetic. Numerator = $1.86 \times 0.32 \times 1000 = 595.2$.

Denominator = $0.201 \times 25 = 5.025$.

$$M_2 = \frac{595.2}{5.025} = 118.45\text{ g mol}^{-1}$$

$$M_2 \approx 118.4 \text{ g mol}^{-1}$$

Quick Tip: Use $\Delta T_f = K_f m$ with $\Delta T_f = 0.201 \text{ }^\circ\text{C}$, then write molality in terms of the unknown molar mass and solve.

14. Explain with reasons:

- (i) Transition metals show variable valency (variable oxidation states).
- (ii) Copper is considered a transition metal even though it has a completely filled d-orbital ($3d^{10}$) in its +1 state.

Correct Answer: —

Solution:

Part (i): Variable valency of transition metals.

Step 1: Transition metals have valence electrons in both the outer ns and the inner $(n - 1)d$ sub-shells. For example, for the first series the configuration is $3d^{1-10} 4s^{1-2}$.

Step 2: The energies of the $(n - 1)d$ and ns orbitals are very close, so the $4s$ and $3d$ electrons can both take part in bonding. Electrons are lost in steps, giving several stable oxidation states (for example Fe shows +2 and +3; Mn shows +2 up to +7).

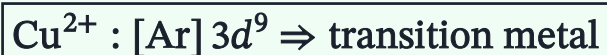
Step 3: Because successive oxidation states differ by removing one electron at a time and the energy required is small, the metals display variable valency.

Part (ii): Why copper is a transition metal.

Step 1: Definition. A transition element is one that has an incompletely (partially) filled d-orbital in its ground state or in at least one of its common oxidation states.

Step 2: The ground state configuration of copper is $[\text{Ar}] 3d^{10} 4s^1$. In its common and stable +2 oxidation state, Cu^{2+} has the configuration $[\text{Ar}] 3d^9$, which is a partially filled d-orbital.

Step 3: Since copper shows an incompletely filled d-orbital ($3d^9$) in its +2 state, it satisfies the definition and is classed as a transition metal, even though Cu^+ happens to be $3d^{10}$.



Quick Tip: Variable valency comes from the close energy of $(n - 1)d$ and ns electrons; copper qualifies because Cu^{2+} is $3d^9$, a partly filled d-orbital.

15. Explain electrode potential and standard electrode potential. The following reaction takes place in a cell:



Calculate the standard cell potential E_{cell}° of the cell. Given: $E_{(\text{Zn} \rightarrow \text{Zn}^{2+})}^{\circ} = 0.76 \text{ V}$ and $E_{(\text{Co} \rightarrow \text{Co}^{2+})}^{\circ} = 0.28 \text{ V}$ (oxidation potentials).

Correct Answer: —

Solution:

Definitions.

Electrode potential: When a metal electrode is dipped in a solution of its own ions, a potential difference is set up between the metal and the solution due to the tendency of the metal to lose electrons (oxidation) or to gain electrons (reduction). This potential difference is called the electrode potential.

Standard electrode potential (E°): It is the electrode potential

measured under standard conditions, that is, ion concentration **1 M**, temperature **298 K** and pressure **1 bar**, with respect to the standard hydrogen electrode (SHE) whose potential is taken as zero.

Numerical.

Step 1: Identify anode and cathode. In the cell reaction Zn is oxidised (loses electrons) so Zn is the anode; Co^{2+} is reduced so cobalt is the cathode.

Step 2: Formula. Using oxidation potentials,

$$E_{\text{cell}}^{\circ} = E_{\text{oxidation}(\text{anode})}^{\circ} + E_{\text{reduction}(\text{cathode})}^{\circ}$$

The reduction potential is the negative of the given oxidation potential: $E_{\text{reduction}(\text{Co}^{2+}/\text{Co})}^{\circ} = -0.28 \text{ V}$.

Step 3: Substitute.

$$E_{\text{cell}}^{\circ} = 0.76 + (-0.28)$$

Step 4: Arithmetic.

$$E_{\text{cell}}^{\circ} = 0.76 - 0.28 = 0.48 \text{ V}$$

$$\boxed{E_{\text{cell}}^{\circ} = 0.48 \text{ V}}$$

The positive value shows the reaction is spontaneous as written.

Quick Tip: Zn is the anode (oxidation), Co is the cathode. Convert the given oxidation potentials to reduction potentials and use $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$.

16. Discuss the factors that affect the velocity (rate) of a chemical reaction.

Correct Answer: —

Solution:

The rate (velocity) of a chemical reaction depends on the following main factors.

Step 1: Concentration of reactants. According to the law of mass action, the rate of a reaction is proportional to the concentration of the reactants. Increasing the concentration increases the number of reactant molecules per unit volume, so more effective collisions take place and the rate increases.

Step 2: Temperature. A rise in temperature increases the kinetic energy of the molecules, so a larger fraction of molecules have energy greater than the activation energy. As a rough rule the rate roughly doubles for every 10 °C rise (temperature coefficient).

Step 3: Nature of reactants. Ionic reactions are generally fast, while reactions involving breaking of strong covalent bonds are slower. The physical state (solid, liquid, gas) also matters.

Step 4: Surface area. For heterogeneous reactions, a greater surface area (for example a powdered solid) exposes more particles for collision and speeds up the reaction.

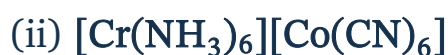
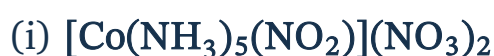
Step 5: Presence of a catalyst. A positive catalyst provides an alternative path with lower activation energy, greatly increasing the rate; a negative catalyst (inhibitor) decreases the rate.

Step 6: Effect of light (for photochemical reactions). Some reactions, such as the combination of H_2 and Cl_2 , are accelerated by light because light supplies the energy needed to start the reaction.

Rate depends on concentration, temperature, nature, surface area, catalyst and light.

Quick Tip: List and explain concentration, temperature, nature of reactants, surface area, catalyst and light as the main rate-controlling factors.

17. Explain the type of isomerism shown by the following complexes and give the structure of the isomers:



Correct Answer: —

Solution:

(i) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$ — **Linkage isomerism.**

Step 1: The NO_2 group is an ambidentate ligand: it can bind to the metal either through the nitrogen atom (nitro, $-\text{NO}_2$) or through an oxygen atom (nitrito, $-\text{ONO}$).

Step 2: Structures of the two isomers:

Nitro form: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ (Co–N bond), yellow.

Nitrito form: $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ (Co–O bond), red.

Both are octahedral with five NH_3 and one ambidentate ligand, and both have $(\text{NO}_3)_2$ as counter ions.

(ii) $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ — **Coordination isomerism.**

Step 1: Here both the cation and the anion are complex ions, so the ligands can be interchanged between the two metal centres.

Step 2: The isomer is $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which NH_3 ligands are now on cobalt and CN^- ligands on chromium. Both metals stay

octahedrally coordinated.

(iii) $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$ — Geometrical (cis–trans) isomerism.

Step 1: This is an octahedral complex of the MA_2B_4 type.

Step 2: The two isomers are:

cis isomer: the two NH_3 ligands occupy adjacent (90°) positions.

trans isomer: the two NH_3 ligands occupy opposite (180°) positions, with the four CN^- filling the remaining sites.

(i) Linkage, (ii) Coordination, (iii) Geometrical (cis/trans)

Quick Tip: NO_2 is ambidentate (linkage), two complex ions allow ligand swap (coordination), and an MA_2B_4 octahedral ion gives cis and trans (geometrical).

18. Explain the structure of Nucleic Acid.

Correct Answer: —

Solution:

Step 1: What nucleic acids are. Nucleic acids are long-chain biomolecules (biopolymers) that carry and transmit hereditary information. The two types are DNA (deoxyribonucleic acid) and RNA (ribonucleic acid). Their monomer unit is the nucleotide.

Step 2: Components of a nucleotide. Each nucleotide is made of three parts:

(a) A pentose sugar — β -D-2-deoxyribose in DNA and β -D-ribose in RNA.

(b) A nitrogen-containing base — purines (adenine A, guanine G) and pyrimidines (cytosine C, thymine T in DNA; uracil U replaces thymine in RNA).

(c) A phosphate group (H_3PO_4).

Step 3: Nucleoside and nucleotide. A base joined to the sugar (through an N-glycosidic bond) is a **nucleoside**. When a phosphate group is attached to the sugar of a nucleoside (through an ester bond), it becomes a **nucleotide**.

Step 4: Formation of the chain (primary structure). Nucleotides join together through phosphodiester linkages between the 3' carbon of one sugar and the 5' carbon of the next sugar, forming a long sugar-phosphate backbone with the bases projecting out.

Step 5: Secondary structure of DNA (Watson and Crick). DNA consists of two such polynucleotide strands coiled around each other in a right-handed **double helix**. The two strands run antiparallel and are held together by hydrogen bonds between complementary bases: adenine pairs with thymine ($\text{A} = \text{T}$, two H-bonds) and guanine pairs with cytosine ($\text{G} \equiv \text{C}$, three H-bonds).

Step 6: RNA structure. RNA is usually a single-stranded molecule containing ribose sugar and uracil in place of thymine.

Nucleic acid = repeating nucleotides (sugar + base + phosphate); DNA = double helix

Quick Tip: Describe the nucleotide (sugar + nitrogen base + phosphate), the phosphodiester backbone, and the antiparallel double helix of DNA with A-T and G-C base pairing.

19. Explain the ring structure of glucose. What happens when D-glucose reacts with the following reagents? (i) Bromine water (ii) Hydroxylamine.

Correct Answer: —

Solution:

Step 1: Why glucose needs a ring structure.

The open chain formula of glucose is an aldohexose, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO}$. A few facts are not explained by this open chain: glucose does not give the Schiff test, it does not form the hydrogensulphite addition product with NaHSO_3 , and it exists in two crystalline forms whose rotation slowly changes in water (mutarotation).

Step 2: Formation of the ring.

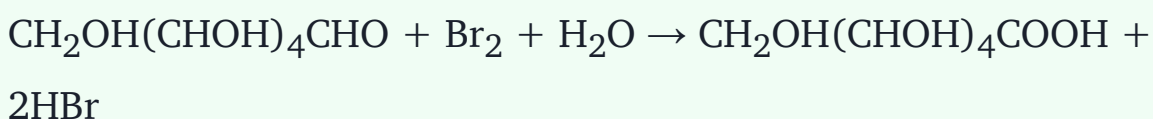
The oxygen of the C-5 hydroxyl group attacks the C-1 aldehyde carbon within the same molecule. This intramolecular addition forms a cyclic hemiacetal and a stable six-membered ring that contains one oxygen atom. This six-membered ring is called the pyranose form (glucopyranose).

Step 3: The anomeric carbon.

During ring closure C-1 becomes a new chiral centre called the anomeric carbon. The new -OH at C-1 can point below the ring (alpha form) or above it (beta form), giving alpha-D-glucose and beta-D-glucose, which are anomers. Their interconversion in solution explains mutarotation.

Step 4: (i) Reaction with bromine water.

Bromine water is a mild oxidising agent. It oxidises only the -CHO group to -COOH, giving gluconic acid, which confirms an aldehyde group.



Step 5: (ii) Reaction with hydroxylamine.

The -CHO group reacts with hydroxylamine (NH_2OH) to form glucose

oxime with loss of water, confirming a carbonyl (aldehyde) group.
 $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CHO} + \text{NH}_2\text{OH} \rightarrow \text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}=\text{NOH} + \text{H}_2\text{O}$

Quick Tip: Picture the C-5 -OH closing onto the C-1 -CHO to give a pyranose hemiacetal with alpha and beta anomers; bromine water gives gluconic acid and hydroxylamine gives the oxime.

20. (i) Write the IUPAC name of the following coordination compounds: (a) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ (b) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$. (ii) Write the electronic configuration of the following: (a) Cr^{3+} (b) Cu.

Correct Answer: —

Solution:

Step 1: Rules used.

The cation is named first, then the anion. Inside the complex, ligands are named in alphabetical order before the metal, negative ligands take an -o ending, and the metal oxidation state is shown by a Roman numeral. If the complex ion is an anion, the metal name ends in -ate.

Step 2: (a) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$.

Each oxalate ligand C_2O_4 carries a 2- charge and there are three, total 6-. Three K^+ give 3+, so chromium must be +3. The complex ion is an anion, so we use chromate. Name: potassium trioxalatochromate(III).

Step 3: (b) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$.

NH_3 is neutral (ammine) and carbonate CO_3 is 2-. The outer Cl is 1-, so the complex ion is 1+. Hence cobalt is +3. Ammine comes before

carbonato alphabetically. Name: pentaamminecarbonatocobalt(III) chloride.

Step 4: (a) Electronic configuration of Cr^{3+} .

Chromium ($Z = 24$) is $[\text{Ar}]3d^54s^1$. To make Cr^{3+} remove three electrons, first the 4s electron then two 3d electrons: $\text{Cr}^{3+} = [\text{Ar}]3d^3$.

Step 5: (b) Electronic configuration of Cu.

Copper ($Z = 29$). A fully filled 3d shell gives extra stability, so instead of $[\text{Ar}]3d^94s^2$ the actual configuration is $\text{Cu} = [\text{Ar}]3d^{10}4s^1$.

Quick Tip: Name cation before anion and use -ate for an anionic complex; recall the anomalous d-shell stabilities, so Cr^{3+} is $[\text{Ar}]3d^3$ and Cu is $[\text{Ar}]3d^{10}4s^1$.



21. Describe the method of identification of primary, secondary and tertiary amines. Classify the following compounds into primary, secondary and tertiary amines: (i) $\text{C}_6\text{H}_5\text{NHCH}_3$ (ii) $\text{CH}_3(\text{CH}_2)_2\text{NH}_2$ (iii) $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$.

Correct Answer: —

Solution:

Step 1: Basis of identification.

Amines are classed by how many carbon groups are joined to nitrogen: one in a primary amine, two in a secondary amine, three in a tertiary amine. The number of N-H bonds falls from two to one to zero, and the tests below use exactly this difference.

Step 2: Hinsberg test.

Each amine is shaken with benzenesulphonyl chloride (Hinsberg

reagent, $C_6H_5SO_2Cl$) and then treated with aqueous KOH.

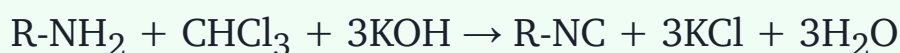
Primary amine: forms an N-substituted sulphonamide that still has one acidic N-H, so it dissolves in KOH to give a clear solution.

Secondary amine: forms a sulphonamide with no N-H, so it stays as an insoluble solid in KOH.

Tertiary amine: has no N-H and does not react.

Step 3: Carbylamine test.

On warming with chloroform and alcoholic KOH, only primary amines (aliphatic or aromatic) give an isocyanide (carbylamine) with a very unpleasant smell. Secondary and tertiary amines give no such smell, so the test is specific for primary amines.



Step 4: Classify the given compounds.

(i) $C_6H_5NHCH_3$ (N-methylaniline): nitrogen holds a phenyl group and a methyl group, that is two carbon groups, so it is a secondary amine.

(ii) $CH_3(CH_2)_2NH_2$ (propan-1-amine): nitrogen holds only one carbon chain, so it is a primary amine.

(iii) $(CH_3CH_2)_2NCH_3$ (N-ethyl-N-methylethanamine): nitrogen holds three carbon groups (two ethyl and one methyl), so it is a tertiary amine.

Quick Tip: Use the Hinsberg benzenesulphonyl chloride test (solubility in KOH) plus the carbylamine test for primary amines, then count the carbon groups on nitrogen to label each structure.

22. (i) Explain the nature of the C-X bond. Give an example of a compound having sp^3 C-X bonding. (ii) Write chemical equations of the following: (a) Carbylamine reaction (b) Hinsberg reaction.

Correct Answer: —

Solution:

Step 1: Nature of the C-X bond.

In a haloalkane the carbon-halogen (C-X) bond is a polar covalent bond. A halogen atom is more electronegative than carbon, so the shared electron pair is pulled towards the halogen. Carbon becomes slightly positive (delta plus) and the halogen slightly negative (delta minus). This polarity makes the carbon a target for nucleophiles.

Step 2: Trend in the bond.

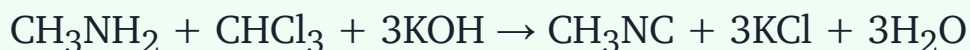
Electronegativity falls in the order $F > Cl > Br > I$, so C-F is the most polar. However the size of the halogen grows down the group, so C-X bond length increases and bond strength (bond enthalpy) decreases from C-F to C-I.

Step 3: Example with sp^3 C-X bonding.

In chloromethane, CH_3Cl , the carbon forms four sigma bonds and is sp^3 hybridised, so the C-Cl bond is an sp^3 C-X bond. Chloroethane, CH_3CH_2Cl , is another example.

Step 4: (a) Carbylamine reaction.

A primary amine heated with chloroform and alcoholic KOH gives a foul smelling isocyanide (carbylamine). Only primary amines respond.



Step 5: (b) Hinsberg reaction.

An amine reacts with benzenesulphonyl chloride (Hinsberg reagent). With a primary amine such as ethylamine it forms N-ethylbenzenesulphonamide and HCl.



The product still has an acidic N-H and dissolves in alkali, which is how a primary amine is recognised.

Quick Tip: The C-X bond is polar covalent (C is delta plus, X delta minus); use an sp^3 haloalkane such as CH_3Cl , and recall carbylamine uses $CHCl_3$ with alcoholic KOH while Hinsberg uses $C_6H_5SO_2Cl$.

23. Describe two methods of preparation of alkyl halides. Also give equations. Explain the following reactions of alkyl halides with examples: (i) Nucleophilic substitution reaction (ii) Elimination reaction.

OR

Write chemical equations of chlorination, nitration, sulphonation, Friedel-Crafts reaction and Wurtz (Fittig) reaction of chlorobenzene.

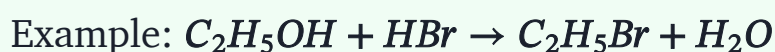
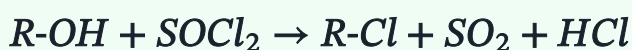
Correct Answer: —

Solution:

Option 1

Step 1: Two methods of preparation of alkyl halides.

(a) From alcohols: Alcohols react with halogen acids, phosphorus halides or thionyl chloride to replace the -OH group by -X.



(b) From alkenes (addition of hydrogen halide): Alkenes add HX following Markovnikov's rule (the halogen goes to the more substituted carbon).



Step 2: (i) Nucleophilic substitution reaction.

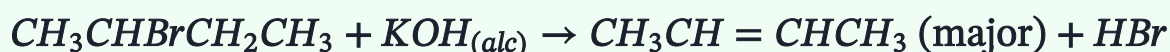
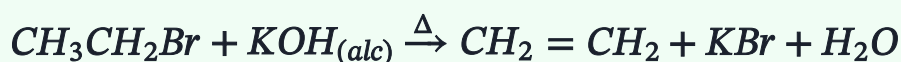
The carbon of the polar C-X bond bears a partial positive charge. A nucleophile (electron-rich species) attacks this carbon and replaces the halide, which departs as a good leaving group. It follows an SN1 route (two steps, through a carbocation) or an SN2 route (one concerted step, backside attack with inversion).

Example (hydrolysis): $CH_3CH_2Br + KOH_{(aq)} \rightarrow CH_3CH_2OH + KBr$

Example (cyanide): $CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$

Step 3: (ii) Elimination reaction.

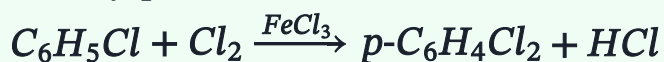
On heating with alcoholic KOH, an alkyl halide loses a hydrogen from the beta-carbon and the halogen from the alpha-carbon as HX, forming a carbon-carbon double bond (dehydrohalogenation, beta-elimination). When more than one alkene is possible, the more substituted alkene is the major product (Saytzeff rule).



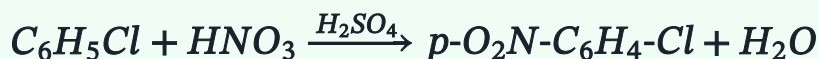
Option 2: Reactions of chlorobenzene.

Chlorine is an ortho/para director, so electrophilic substitutions give mainly the para isomer.

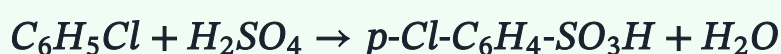
Step 1: Chlorination: With anhydrous $FeCl_3$, chlorobenzene gives mainly p-dichlorobenzene (with some ortho).



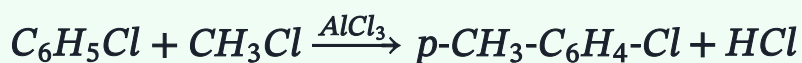
Step 2: Nitration: With concentrated HNO_3 and concentrated H_2SO_4 , it gives mainly p-nitrochlorobenzene.



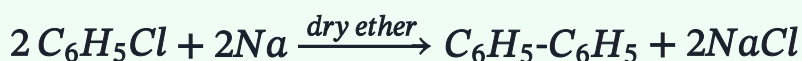
Step 3: Sulphonation: With concentrated (fuming) H_2SO_4 it gives mainly p-chlorobenzenesulphonic acid.



Step 4: Friedel-Crafts reaction: With CH_3Cl and anhydrous AlCl_3 (alkylation) it gives p-chlorotoluene (acylation with CH_3COCl gives p-chloroacetophenone).



Step 5: Wurtz (Fittig) reaction: Chlorobenzene with sodium metal in dry ether couples to give diphenyl (biphenyl).



Both alternatives complete

Quick Tip: For alkyl halides, recall preparation from alcohols or alkenes; a nucleophile swaps out the halide (SN_1/SN_2), while alcoholic KOH triggers beta-elimination to an alkene. For chlorobenzene, remember chlorine is an ortho/para director.

24. Write chemical equations of three methods of preparation and two chemical properties of benzaldehyde.

OR

Write short notes on the following: (i) Aldol condensation (ii) Cross aldol condensation (iii) Cannizzaro reaction (iv) Hell-Volhard-Zelinsky reaction (v) Kolbe electrolysis.

Correct Answer: —

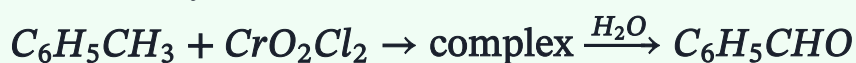
Solution:

Option 1: Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$)

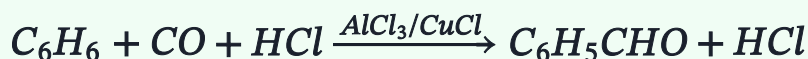
Step 1: Three methods of preparation.

(a) Etard reaction (from toluene): Toluene is oxidised with chromyl

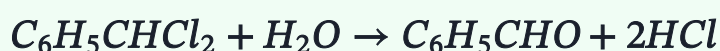
chloride in CS_2 ; the chromium complex on hydrolysis gives benzaldehyde.



(b) Gattermann-Koch reaction: Benzene reacts with carbon monoxide and HCl in presence of anhydrous $AlCl_3$ and $CuCl$.

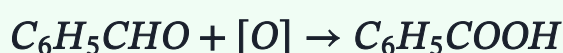


(c) Hydrolysis of benzal chloride: Benzal chloride on boiling with water (or aqueous alkali) gives benzaldehyde.

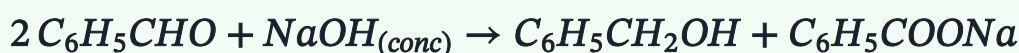


Step 2: Two chemical properties.

(a) Oxidation: Benzaldehyde is readily oxidised (even by air) to benzoic acid.

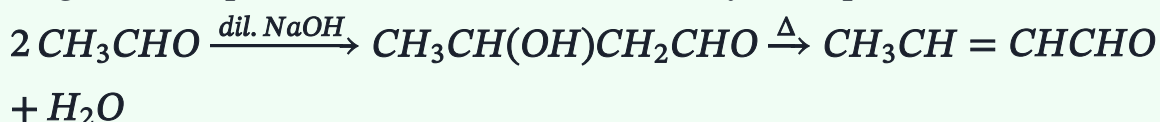


(b) Cannizzaro reaction: Benzaldehyde has no alpha-hydrogen, so with concentrated NaOH it undergoes disproportionation (self oxidation-reduction) giving benzyl alcohol and sodium benzoate.



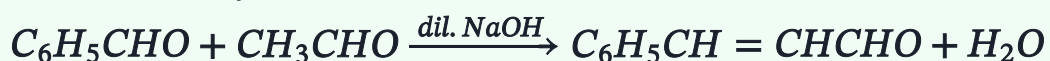
Option 2: Short notes.

(i) Aldol condensation: Aldehydes or ketones having an alpha-hydrogen, in the presence of dilute base, add to one another to give a beta-hydroxy aldehyde/ketone (an aldol); on heating this loses water to give an alpha,beta-unsaturated carbonyl compound.

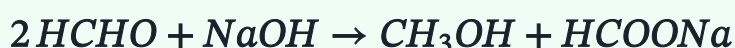


(ii) Cross aldol condensation: An aldol condensation between two different carbonyl compounds each carrying an alpha-hydrogen gives a mixture of four products. It is synthetically useful when one partner has no alpha-hydrogen (e.g. benzaldehyde with acetaldehyde gives

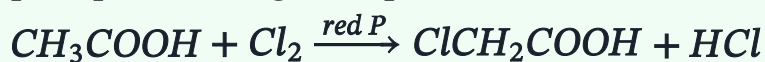
cinnamaldehyde).



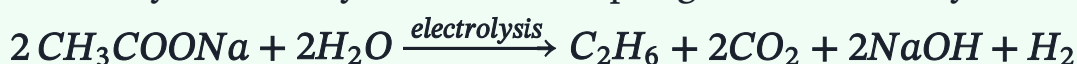
(iii) **Cannizzaro reaction:** Aldehydes with no alpha-hydrogen, on treatment with concentrated alkali, undergo disproportionation - one molecule is oxidised to the carboxylate salt and another is reduced to the alcohol.



(iv) **Hell-Volhard-Zelinsky (HVZ) reaction:** Carboxylic acids having an alpha-hydrogen react with Cl_2/Br_2 in presence of a little red phosphorus to give alpha-halo acids.



(v) **Kolbe electrolysis:** Electrolysis of an aqueous solution of the sodium or potassium salt of a carboxylic acid gives an alkane at the anode by decarboxylation and coupling of the two alkyl radicals.



Both alternatives complete

Quick Tip: Benzaldehyde has no alpha-hydrogen, so think Etard/Gattermann-Koch for preparation and oxidation/Cannizzaro for reactions. For the notes, sort the reactions by whether an alpha-hydrogen is present.

25. Explain by giving four examples that the alkoxy group (-OR) activates the aromatic ring towards electrophilic substitution.

OR

Describe two methods of preparation of phenol. Give two reactions that demonstrate the acidic nature of phenol. Compare the acidity of phenol with that of ethanol.

Correct Answer: —

Solution:

Option 1: Alkoxy (-OR) group activates the ring

Step 1: Nature of the group. An alkoxy group such as methoxy (-OCH₃) has an oxygen atom carrying lone pairs and joined directly to the benzene ring. Through its lone pair the oxygen pushes electron density into the ring by resonance (+R / +M effect), which easily outweighs its weak -I effect. So -OR is an **activating** group and an **ortho / para director**.

Step 2: Why it activates. The oxygen lone pair delocalises into the ring and builds up extra negative charge chiefly at the ortho and para carbons. This raises the ring's electron density, so the ring attracts an electrophile E^+ more strongly than plain benzene and reacts faster. The arenium-ion intermediate formed at o / p positions gets an extra resonance structure in which oxygen bears the positive charge (an oxonium form), lowering the activation energy.

Step 3: Four examples of electrophilic substitution on anisole

(C₆H₅OCH₃):

(i) **Halogenation:** $C_6H_5OCH_3 + Br_2 \xrightarrow{CH_3COOH}$ o- and p-bromoanisole (para major) + HBr. No catalyst is needed, unlike benzene.

(ii) **Nitration:** $C_6H_5OCH_3 + HNO_3 \xrightarrow{conc. H_2SO_4}$ o- and p-nitroanisole + H₂O.

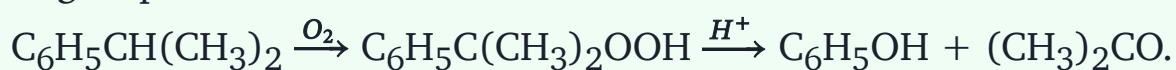
(iii) **Sulphonation:** $C_6H_5OCH_3 + conc. H_2SO_4 \rightarrow$ o- and p-methoxybenzenesulphonic acid + H₂O.

(iv) **Friedel-Crafts acylation:** $C_6H_5OCH_3 + CH_3COCl \xrightarrow{anhyd. AlCl_3}$ p-methoxyacetophenone + HCl.

Step 4: Conclusion. In each reaction substitution is faster than in benzene and occurs mainly at the ortho and para positions, which proves that the alkoxy group activates the aromatic ring and directs the electrophile to o / p.

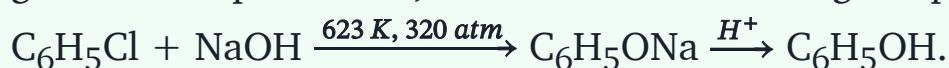
Option 2: Phenol preparation, acidity and comparison with ethanol

Step 1: Preparation (Method 1) - from cumene. Cumene (isopropylbenzene) is oxidised by air and then treated with dilute acid to give phenol and acetone:

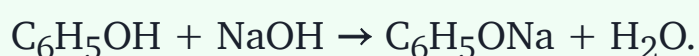


Step 2: Preparation (Method 2) - from chlorobenzene (Dow process).

Chlorobenzene is heated with aqueous NaOH at 623 K and 320 atm to give sodium phenoxide, which on acidification gives phenol:



Step 3: Acidic nature (Reaction 1) - with NaOH. Phenol dissolves in aqueous NaOH forming a salt, showing it is acidic:



Step 4: Acidic nature (Reaction 2) - with sodium metal. Phenol reacts with active metals liberating hydrogen gas, confirming the acidic O-H:
$$2\text{C}_6\text{H}_5\text{OH} + 2\text{Na} \rightarrow 2\text{C}_6\text{H}_5\text{ONa} + \text{H}_2\uparrow;$$

Step 5: Phenol vs ethanol. Phenol is much more acidic than ethanol. When phenol loses H^+ , the resulting phenoxide ion has its negative charge spread over the ring by resonance (onto the ortho and para

carbons), so it is well stabilised. When ethanol loses H^+ , ethoxide has no resonance and the electron-donating alkyl group (+I effect) pushes charge onto oxygen, intensifying it and destabilising the ion. A more stable conjugate base means a stronger acid, so

acidity: phenol ($pK_a \approx 10$) \gg ethanol ($pK_a \approx 16$)

Quick Tip: The oxygen of -OR donates its lone pair into the ring (+R effect), so it is an activating ortho/para director; for the OR-alternative, phenol's acidity comes from resonance stabilisation of the phenoxide ion, absent in ethoxide.

26. Define Molal depression constant. 48 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is dissolved in 600 g of water. Calculate (i) depression in freezing point and (ii) freezing point of the solution. [Given $K_f(\text{water}) = 1.86 \text{ }^\circ\text{C kg mol}^{-1}$]

OR

Define molality and explain mole fraction. Calculate the mole fraction of solute and solvent of a 20% aqueous $\text{C}_2\text{H}_6\text{O}_2$ solution.

Correct Answer: —

Solution:

Option 1: Molal depression constant and the freezing-point numerical

Step 1: Definition. The molal depression constant (cryoscopic constant, K_f) is the depression in freezing point produced when 1 mole of a non-volatile solute is dissolved in 1 kg (1000 g) of solvent. The working relation is $\Delta T_f = K_f \times m$, where m is the molality.

Step 2: Molar mass of the solute. For ethylene glycol $C_2H_6O_2$: $M = 2(12) + 6(1) + 2(16) = 24 + 6 + 32 = 62 \text{ g mol}^{-1}$.

Step 3: Moles of solute. $n = \frac{48}{62} = 0.774 \text{ mol}$.

Step 4: Molality. Mass of solvent = 600 g = 0.600 kg, so $m = \frac{0.774}{0.600} = 1.290 \text{ mol kg}^{-1}$.

Step 5: (i) Depression in freezing point. $\Delta T_f = K_f \times m = 1.86 \times 1.290 = 2.40$.

$$\Delta T_f = 2.4 \text{ }^\circ\text{C}$$

Step 6: (ii) Freezing point of the solution. Pure water freezes at $0 \text{ }^\circ\text{C}$, so the solution freezes $2.4 \text{ }^\circ\text{C}$ lower: $T_f = 0 - 2.4$.

$$T_f = -2.4 \text{ }^\circ\text{C}$$

Option 2: Molality, mole fraction, and the 20% solution

Step 1: Molality. Molality (m) is the number of moles of solute dissolved per kilogram of solvent: $m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$. It uses mass, so it does not change with temperature.

Step 2: Mole fraction. The mole fraction of a component is the ratio of its moles to the total moles of all components: $x_{\text{solute}} = \frac{n_2}{n_1 + n_2}$, $x_{\text{solvent}} = \frac{n_1}{n_1 + n_2}$, and the two add up to 1.

Step 3: Fix a basis. A 20% aqueous solution means 20 g of solute in

100 g of solution, so solute = 20 g and water = 100 - 20 = 80 g.

Step 4: Convert to moles. $n_{\text{solute}} = \frac{20}{62} = 0.3226 \text{ mol}$, $n_{\text{water}} = \frac{80}{18} = 4.444 \text{ mol}$.

Step 5: Total moles. $n_1 + n_2 = 0.3226 + 4.444 = 4.767 \text{ mol}$.

Step 6: Mole fractions. $x_{\text{solute}} = \frac{0.3226}{4.767} = 0.0677$, $x_{\text{solvent}} = \frac{4.444}{4.767} = 0.9323$ (sum = 1).

$$x_{\text{solute}} \approx 0.068, \quad x_{\text{solvent}} \approx 0.932$$

Quick Tip: Use $\Delta T_f = K_f \times m$ with $M(\text{C}_2\text{H}_6\text{O}_2) = 62$; for the OR-part take 100 g of solution (20 g solute + 80 g water) and apply $x = n/n_{\text{total}}$.