UP Board Class 12 Chemistry 2026 Set 347 DZ Question Paper with Solutions

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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 formula is used to calculate osmotic pressure?

(A) $\pi = CRT$

(B) $\pi = VRT$

(C) $\pi = PVT$

(D) $\pi = nRT$

Correct Answer: (A) $\pi = CRT$

Solution:

Step 1: Osmotic pressure (π) is the colligative property equal to the extra pressure that must be applied to a solution to stop the inflow of solvent through a semipermeable membrane.

Step 2: The van't Hoff equation for a dilute solution is $\pi V = nRT$, where n is moles of solute, V the volume of solution, R the gas constant and T the temperature.

Step 3: Rearranging, $\pi = \frac{n}{V}RT$. Since molar concentration $C = \frac{n}{V}$, this becomes

$$\boxed{\pi = CRT}$$

Step 4: So option (i) is correct. Option (iv) $\pi = nRT$ is dimensionally wrong (it omits volume). Options (ii) and (iii) are meaningless combinations of symbols.

Quick Tip: Use the van't Hoff relation $\pi V = nRT$ and replace n/V by molar concentration C.

2. What is the coordination number of Co in the complex $K_3[Co(C_2O_4)_3]$?

(A) 3

(B) 4

(C) 5

(D) 6

Correct Answer: (D) 6

Solution:

Step 1: The coordination number is the number of ligand donor atoms directly bonded (coordinated) to the central metal ion.
Step 2: The ligand here is oxalate $(C_2O_4)^{2-}$, which is a bidentate ligand: each oxalate binds the metal through two oxygen donor atoms.
Step 3: There are three oxalate ligands. Donor atoms $= 3 \times 2 = 6$.
Step 4: Hence the coordination number of Co is 6, so option (iv) is correct. The number of ligand molecules (3) is not the coordination number, which is why option (i) is wrong.

Quick Tip: Oxalate is bidentate; three oxalate ligands each occupy two sites.

3. Which of the following is not a transition metal?

(A) Cu

(B) Cr

(C) Fe

(D) Na

Correct Answer: (D) Na

Solution:

Step 1: A transition metal is an element whose atom (or a stable ion) has a partially filled d-subshell.
Step 2: Check each element. Cr $(3d^5 4s^1)$, Fe $(3d^6 4s^2)$ and Cu $(3d^{10} 4s^1)$; Cu forms $Cu^{2+}(3d^9)$ with a partly filled d-orbital, so all three are transition (d-block) metals.
Step 3: Sodium (Na) has configuration $1s^2 2s^2 2p^6 3s^1$. It is an s-block alkali metal with no d-electrons and no partially filled d-orbital.
Step 4: Therefore Na is not a transition metal, so option (iv) is correct.

Quick Tip: Look for the element with no partially filled d-orbital; it is an s-block alkali metal.

4. Which of the following is an aldehyde?

(A) CH_3–CO–H (acetaldehyde)

(B) CH_3–CH_2–CO–CH_3 (butan-2-one)

(C) CH_3–CH_2–CO–CH_2–CH_3 (pentan-3-one)

(D) CH_3–CO–CH_3 (acetone)

Correct Answer: (A) CH_3–CO–H (acetaldehyde)

Solution:

Step 1: An aldehyde contains the carbonyl group with at least one hydrogen atom attached to the carbonyl carbon, i.e. the –CHO group. A ketone has the carbonyl carbon bonded to two carbon atoms (C–CO–C).

Step 2: Option (i) CH_3–CO–H is CH_3CHO (acetaldehyde). Its carbonyl carbon carries an H atom, so it is an aldehyde.

Step 3: Options (ii), (iii) and (iv) are butan-2-one, pentan-3-one and acetone respectively; in each the carbonyl carbon is flanked by two carbons, making them ketones, not aldehydes.

Step 4: Hence the aldehyde is option (i).

Quick Tip: An aldehyde has an H on the carbonyl carbon (–CHO); ketones have two carbons on it.

5. Which test is used to differentiate between primary, secondary and tertiary amines?

(A) Brady test

(B) Tollen's test

(C) Hinsberg test

(D) Lucas test

Correct Answer: (C) Hinsberg test

Solution:

Step 1: The Hinsberg test uses benzenesulphonyl chloride ($C_6H_5SO_2Cl$), the Hinsberg reagent, to distinguish the three classes of amine.

Step 2: A primary amine gives an N-substituted sulphonamide having an acidic N–H that dissolves in aqueous KOH (soluble). A secondary amine gives a sulphonamide with no N–H, so it stays insoluble in KOH. A tertiary amine has no N–H to react and normally does not react at all.

Step 3: These different outcomes (soluble product / insoluble product / no reaction) identify 1°, 2° and 3° amines, so option (iii) is correct.

Step 4: Brady's test (2,4-DNP) and Tollen's test are for carbonyl compounds; Lucas test differentiates alcohols. Hence they are wrong here.

Quick Tip: Think of the reagent benzenesulphonyl chloride, which reacts differently with 1°, 2° and 3° amines.

6. Match the vitamins given in Column (I) with the diseases caused by their deficiency in Column (II):
Column (I): A) Vitamin A, B) Vitamin B_1, C) Vitamin C, D) Vitamin K, E) Vitamin B_{12}.
Column (II): a) Increase in clotting time of blood, b) Night blindness, c) Beri-beri, d) Pernicious anaemia, e) Scurvy.

(A) A-(d), B-(c), C-(e), D-(a), E-(b)

(B) A-(b), B-(c), C-(e), D-(a), E-(d)

(C) A-(a), B-(b), C-(c), D-(d), E-(e)

(D) A-(b), B-(a), C-(e), D-(d), E-(c)

Correct Answer: (B) A-(b), B-(c), C-(e), D-(a), E-(d)

Solution:

Step 1: Recall each vitamin's deficiency disease.
Step 2: Vitamin A deficiency causes night blindness → A-(b). Vitamin B_1 (thiamine) deficiency causes beri-beri → B-(c). Vitamin C (ascorbic acid) deficiency causes scurvy → C-(e).
Step 3: Vitamin K is needed for blood clotting, so its deficiency increases the clotting time of blood → D-(a). Vitamin B_{12} deficiency causes pernicious anaemia → E-(d).
Step 4: The complete match A-(b), B-(c), C-(e), D-(a), E-(d) is option (ii), so option (ii) is correct.

Quick Tip: Vitamin A → night blindness, B_1 → beri-beri, C → scurvy, K → clotting, B_{12} → pernicious anaemia.

7. What is an ideal solution? Mention the characteristics of an ideal solution.

Correct Answer: —

Solution:

Step 1: Definition. An ideal solution is a solution that obeys Raoult's law over the entire range of concentration, at all temperatures. That is, the partial vapour pressure of each component equals its mole fraction times the vapour pressure of the pure component: $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$.

Step 2: Molecular reason. In an ideal solution the intermolecular forces between the two different molecules A–B are nearly the same as the forces A–A and B–B in the pure liquids. Example: benzene and toluene, or n-hexane and n-heptane.

Step 3: Characteristics.

(i) It obeys Raoult's law at every concentration.

(ii) Enthalpy of mixing is zero: $\Delta H_{mix} = 0$ (no heat absorbed or released on mixing).

(iii) Volume change on mixing is zero: $\Delta V_{mix} = 0$ (total volume equals the sum of the volumes of the components).

Step 4: Conclusion. Hence an ideal solution shows no deviation from Raoult's law, with $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$ because A–B interactions equal A–A and B–B interactions.

$$\boxed{\Delta H_{mix} = 0,\ \Delta V_{mix} = 0}$$

Quick Tip: An ideal solution obeys Raoult's law at all concentrations with zero enthalpy and zero volume change of mixing.

8. Transition metals, with a few exceptions, are extremely hard and less volatile. Explain.

Correct Answer: —

Solution:

Step 1: Key idea. Hardness and low volatility of a metal both depend on the strength of the metallic bonding that holds the atoms together in the solid.

Step 2: Why the bonding is strong. Transition metals have both (n-1)d and ns electrons available for bonding. Because the d-orbitals contribute many unpaired electrons to the metallic bond, a large number of electrons take part in delocalised bonding. This gives very strong interatomic (metallic) bonds.

Step 3: Consequences. Strong metallic bonds are hard to deform, so the metals are very hard. Breaking these strong bonds to form vapour needs a lot of energy, so the metals have high melting and boiling points and are therefore less volatile.

Step 4: The exceptions. Metals such as Zn, Cd and Hg have a completely filled d-subshell (d^{10}), so their d-electrons do not take part in metallic bonding. Their bonding is weak; hence they are soft and comparatively volatile (mercury is even a liquid at room temperature).

Strong metallic bonding from unpaired d-electrons → hard, less volatile

Quick Tip: Unpaired d-electrons give strong metallic bonding; the soft, volatile exceptions (Zn, Cd, Hg) have a filled d^{10} shell.

9. Write the IUPAC names of the following coordination compounds:

(i) $[Co(en)_2ClBr]NO_3$

(ii) $[Ni(NH_3)_4][Pt(CN)_4]$

Correct Answer: —

Solution:

Part (i): $[Co(en)_2ClBr]NO_3$

Step 1: Name the ligands in alphabetical order with anionic ligand suffixes '-o': bromido, chlorido, and ethane-1,2-diamine (en). 'en' appears twice, so use the multiplying prefix 'bis' (as 'en' already contains a numerical part) → bis(ethane-1,2-diamine).

Step 2: Find the oxidation state of Co. The nitrate counter ion is NO_3^-, so the complex ion is $[Co(en)_2ClBr]^+$. Let Co = x: $x + 2(0) + (-1)_{Cl} + (-1)_{Br} = +1 \Rightarrow x = +3$.

Step 3: Assemble: ligands alphabetically (bromido, chlorido, bis(ethane-1,2-diamine)) + metal(oxidation state) + counter ion.

Name: bromidochloridobis(ethane-1,2-diamine)cobalt(III) nitrate.

Part (ii): $[Ni(NH_3)_4][Pt(CN)_4]$

Step 1: Both ions are complex. Name the cation first, then the anion. Cation $[Ni(NH_3)_4]^{2+}$: ammine ligand × 4 = tetraammine. Ni oxidation state: $x + 4(0) = +2 \Rightarrow x = +2$ → nickel(II).

Step 2: Anion $[Pt(CN)_4]^{2-}$: cyanido ligand × 4 = tetracyanido; the anionic complex takes the '-ate' suffix on the metal (platinate). Pt oxidation state: $x + 4(-1) = -2 \Rightarrow x = +2$ → platinate(II).

Step 3: Combine cation then anion.

Name: tetraamminenickel(II) tetracyanidoplatinate(II).

Quick Tip: Name ligands alphabetically with 'bis' for en; work out the metal oxidation states from the counter-ion charges, and give the anionic complex

an '-ate' ending.

10. Write the reaction mechanism of the unimolecular nucleophilic substitution (S_N1) reaction of 2-bromo-2-methylpropane.

Correct Answer: —

Solution:

Step 1: The substrate. 2-bromo-2-methylpropane is tert-butyl bromide, $(CH_3)_3C\text{-}Br$. Take its reaction with aqueous alkali (OH^-) as the nucleophile. An S_N1 reaction goes in two steps through a carbocation.

Step 2: Step I – slow ionisation (rate-determining). The polar C–Br bond breaks heterolytically. Bromine leaves with the bonding electron pair as bromide ion, and a tertiary carbocation is formed:

$$(CH_3)_3C\text{-}Br \rightarrow (CH_3)_3C^+ + Br^-$$

This step is slow because breaking the bond needs energy; it decides the overall rate. The tertiary carbocation is stabilised by the +I (hyperconjugation and inductive) effect of the three methyl groups.

Step 3: Step II – fast attack of nucleophile. The hydroxide ion (or water) quickly attacks the planar carbocation from either face and forms the product:

$$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3C\text{-}OH$$

giving 2-methylpropan-2-ol (tert-butyl alcohol).

Step 4: Rate law and conclusion. Since only the substrate is involved in the slow step, the rate depends on its concentration alone:

$$\boxed{\text{Rate} = k[(CH_3)_3C\text{-}Br]}$$

The reaction is first order (unimolecular), hence S_N1.

Quick Tip: Two steps: slow heterolysis to a stabilised tertiary carbocation (rate-determining), then fast attack by OH^-; rate depends only on the halide.

11. 45 g ethylene glycol is mixed with 600 g H_2O. Calculate the depression of freezing point of this solution. ($K_f = 1.86\ \text{K kg mol}^{-1}$)

Correct Answer: —

Solution:

Step 1: Formula. The depression in freezing point is $\Delta T_f = K_f \times m$, where m is the molality of the solution and K_f is the cryoscopic (molal freezing point depression) constant.

Step 2: Moles of solute. Ethylene glycol is $C_2H_6O_2$, molar mass $= 2(12) + 6(1) + 2(16) = 62\ \text{g mol}^{-1}$.

$$n = \frac{45}{62} = 0.7258\ \text{mol}$$

Step 3: Molality. Mass of solvent (water) = 600 g = 0.600 kg.

$$m = \frac{0.7258}{0.600} = 1.2097\ \text{mol kg}^{-1}$$

Step 4: Substitute and compute.

$$\Delta T_f = 1.86 \times 1.2097 = 2.25 \text{ K}$$

$$\boxed{\Delta T_f \approx 2.25 \text{ K}}$$

So the freezing point of the solution is lowered by about 2.25 K (2.25 °C) below that of pure water.

Quick Tip: Use $\Delta T_f = K_f m$; molar mass of ethylene glycol is 62 g/mol and solvent mass is 0.6 kg.

12. Represent α-D-(+)-glucopyranose and β-D-(+)-glucopyranose by Haworth structure.

Correct Answer: —

Solution:

Step 1: The pyranose ring. Glucose exists as a six-membered ring (one ring oxygen + five carbons), called a pyranose. In the Haworth projection the ring is drawn as a flat hexagon lying almost perpendicular to the paper, with the ring oxygen at the upper right and C1 (the anomeric carbon) at the far right.

Step 2: Fixed groups (same in both forms). Number the ring carbons clockwise C1 to C5. For D-glucose:

- C2 –OH points down.
- C3 –OH points up.
- C4 –OH points down.
- C5 carries the –CH_2OH group pointing up (this defines the D-

configuration).

Step 3: Difference at C1 (the anomeric carbon). The two forms (anomers) differ only in the direction of the –OH on C1:

• In **α-D-(+)-glucopyranose**, the C1 –OH points **downwards** (trans to the CH_2OH, i.e. on the opposite side).

• In **β-D-(+)-glucopyranose**, the C1 –OH points **upwards** (cis to the CH_2OH, i.e. on the same side).

Step 4: Summary of the Haworth structures.

α-D-glucopyranose: ring with O at top-right; C1–OH down, C2–OH down, C3–OH up, C4–OH down, C5–CH_2OH up, H atoms on the opposite side of each OH.

$\boxed{\alpha\text{-form : C1--OH is down}}$

β-D-glucopyranose: identical to the above except the C1–OH is up.

$\boxed{\beta\text{-form : C1--OH is up}}$

Quick Tip: Draw the flat pyranose hexagon with ring O at top-right; the anomers differ only at C1 – OH down for α, OH up for β.

13. Complete the following chemical reaction:

$$CH_3CH_2CH_2OH \xrightarrow{PBr_3} [A] \xrightarrow[\Delta]{Alc.\ KOH} [B]$$

Correct Answer: —

Solution:

Step 1: Identify the starting material and first reagent.
The starting compound is propan-1-ol, $CH_3CH_2CH_2OH$, a primary alcohol. PBr_3 (phosphorus tribromide) converts alcohols into alkyl bromides by replacing the $-OH$ group with a $-Br$ group.

Step 2: Form product [A].
$3\,CH_3CH_2CH_2OH + PBr_3 \rightarrow 3\,CH_3CH_2CH_2Br + H_3PO_3$
So [A] is 1-bromopropane, $CH_3CH_2CH_2Br$.

Step 3: React [A] with alcoholic KOH and heat.
Alcoholic KOH is a strong base and promotes elimination (dehydrohalogenation). It removes one H from the carbon next to the $C-Br$ bond and the Br atom, forming a double bond (Saytzeff/beta elimination).

Step 4: Form product [B].
$CH_3CH_2CH_2Br \xrightarrow[\Delta]{Alc.\,KOH} CH_3CH=CH_2 + KBr + H_2O$
So [B] is propene, $CH_3CH=CH_2$.

Final answer:

$$\boxed{[A] = CH_3CH_2CH_2Br, \quad [B] = CH_3CH=CH_2}$$

Quick Tip: PBr_3 replaces $-OH$ with $-Br$; alcoholic KOH then eliminates HBr to give an alkene.

14. Write the effect of catalyst on the rate of reaction.

Correct Answer: —

Solution:

Step 1: What a catalyst is.

A catalyst is a substance that increases the rate of a chemical reaction but is itself chemically unchanged in mass and composition at the end of the reaction.

Step 2: How it increases the rate.

A catalyst provides an alternative reaction path (a new mechanism) that has a lower activation energy (E_a) than the uncatalysed path. Because more colliding molecules now have energy equal to or greater than this lowered E_a, the fraction of effective collisions rises and the rate increases.

Step 3: Effect on forward and backward reactions.

A catalyst lowers the activation energy of both the forward and the backward reaction by the same amount. Hence it speeds up both equally.

Step 4: Effect on equilibrium and thermodynamics.

Since it accelerates forward and backward reactions equally, a catalyst does not change the position of equilibrium or the value of the equilibrium constant. It only helps the equilibrium to be reached faster. It also does not change ΔH or ΔG of the reaction.

Final answer: A catalyst increases the rate of reaction by lowering the activation energy through an alternative path, without altering the enthalpy change or the equilibrium state.

Quick Tip: A catalyst offers an alternative path of lower activation energy; it

speeds the reaction but does not shift the equilibrium.

15. Write short notes on the following:

(i) Aldol condensation

(ii) Cannizzaro's reaction

Correct Answer: —

Solution:

(i) Aldol condensation

Step 1: Requirement. Aldehydes and ketones that contain at least one alpha-hydrogen (a hydrogen on the carbon next to the carbonyl group) undergo this reaction.

Step 2: Reagent and first product. In the presence of a dilute base (such as dilute NaOH or KOH), two such molecules combine. One acts as a carbanion (nucleophile) and adds to the carbonyl carbon of the other, giving a beta-hydroxy aldehyde or ketone called an aldol.

$2\,CH_3CHO \xrightarrow{dil.\ NaOH} CH_3CH(OH)CH_2CHO$ (3-hydroxybutanal)

Step 3: Condensation step. On warming, the aldol loses a water molecule to form an alpha,beta-unsaturated carbonyl compound.

$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH = CHCHO + H_2O$ (but-2-enal)

(ii) Cannizzaro's reaction

Step 1: Requirement. Aldehydes that do NOT have any alpha-hydrogen undergo this reaction.

Step 2: Reagent. On treatment with concentrated alkali, such aldehydes undergo self oxidation and reduction (disproportionation).

Step 3: Products. One molecule is oxidised to the carboxylic acid salt and the other is reduced to the alcohol.

$2\,HCHO + NaOH \rightarrow CH_3OH + HCOONa$

With benzaldehyde: $2\,C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$

Quick Tip: Aldol needs an alpha-hydrogen with dilute base; Cannizzaro is disproportionation of aldehydes without alpha-hydrogen using concentrated alkali.

16. What is the colligative property? Write an expression for the determination of molar mass of solute using relative lowering in vapour pressure.

Correct Answer: —

Solution:

Step 1: Definition of colligative property.
Colligative properties are those properties of a dilute solution which depend only on the number of solute particles present and not on the chemical nature of the solute. The four colligative properties are: relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, and osmotic pressure.

Step 2: Raoult's law for relative lowering of vapour pressure.
When a non-volatile solute is added to a solvent, the vapour pressure of the solvent falls. According to Raoult's law, the relative lowering of vapour pressure equals the mole fraction of the solute:

$$\frac{p^\circ - p}{p^\circ} = x_2 = \frac{n_2}{n_1 + n_2}$$

where p° is the vapour pressure of pure solvent, p is that of the

solution, and n_1, n_2 are the moles of solvent and solute.

Step 3: Dilute solution approximation.
For a dilute solution n_2 is very small compared with n_1, so $n_1 + n_2 \approx n_1$:

$$\frac{p^\circ - p}{p^\circ} = \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1}$$

where w_1, w_2 are masses and M_1, M_2 are molar masses of solvent and solute.

Step 4: Expression for molar mass of solute.
Rearranging for M_2:

$$\boxed{M_2 = \frac{w_2 \times M_1 \times p^\circ}{w_1 (p^\circ - p)}}$$

Quick Tip: Use Raoult's law: relative lowering of vapour pressure equals mole fraction of solute; rearrange to get M_2.

17. For the following cell reaction, write the half reactions occurring at the anode and cathode and determine the electromotive force (EMF) of the cell:
$2Ag^+ + Cd \rightarrow 2Ag + Cd^{2+}$
(Given, $E^\circ_{Ag^+/Ag} = +0.80\ V$ and $E^\circ_{Cd^{2+}/Cd} = -0.40\ V$)

Correct Answer: —

Solution:

Step 1: Decide which species is oxidised and which is reduced.
In the cell reaction $2Ag^{+} + Cd \rightarrow 2Ag + Cd^{2+}$, cadmium metal loses electrons (its oxidation state goes from 0 to +2), so it is oxidised. Silver ions gain electrons (from +1 to 0), so they are reduced.

Step 2: Write the half reactions.
Oxidation occurs at the anode:

$$Cd \rightarrow Cd^{2+} + 2e^{-} \quad (anode)$$

Reduction occurs at the cathode:

$$2Ag^{+} + 2e^{-} \rightarrow 2Ag \quad (cathode)$$

Step 3: Formula for cell EMF.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

Here the cathode is the silver electrode and the anode is the cadmium electrode.

Step 4: Substitute the given values.

$$E^{\circ}_{cell} = E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Cd^{2+}/Cd} = (+0.80) - (-0.40)$$

Step 5: Arithmetic.

$$E^{\circ}_{cell} = 0.80 + 0.40 = 1.20\ V$$

The positive value confirms the reaction is spontaneous.

$$\boxed{E^\circ_{cell} = +1.20\ V}$$

Quick Tip: Cd is oxidised (anode), Ag+ is reduced (cathode); $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$.

18. What is Lanthanoid contraction? Write in increasing order of basic nature of oxides (Ln_2O_3) and hydroxides $[Ln(OH)_3]$ of Lanthanoids.

Correct Answer: —

Solution:

Step 1: Definition of Lanthanoid contraction.
The steady and regular decrease in the atomic and ionic radii of the lanthanoid elements with increasing atomic number, as we move from lanthanum (La) to lutetium (Lu), is called lanthanoid contraction.

Step 2: Cause.
As the atomic number increases across the series, the added electrons enter the inner $4f$ subshell. The $4f$ electrons shield the outer electrons from the nucleus very poorly (imperfect shielding). Therefore the effective nuclear charge felt by the outer electrons increases steadily, pulling them closer and causing a gradual decrease in size.

Step 3: Link size to basic strength.
As the ionic size of Ln^{3+} decreases from La^{3+} to Lu^{3+}, the covalent character of the $Ln - OH$ bond increases and the basic strength of the

oxides and hydroxides decreases. Thus $La(OH)_3$ is the most basic and $Lu(OH)_3$ is the least basic.

Step 4: Increasing order of basic nature.
Hydroxides:

$$Lu(OH)_3 < Yb(OH)_3 < \ldots < Ce(OH)_3 < La(OH)_3$$

Oxides:

$$Lu_2O_3 < Yb_2O_3 < \ldots < Ce_2O_3 < La_2O_3$$

That is, basic character increases from Lu to La (with decreasing atomic number).

Quick Tip: Poor shielding by 4f electrons shrinks the ions from La to Lu; smaller ion means weaker base, so La(OH)3 is most basic.

19. Write short notes on Etard reaction and Gattermann-Koch reaction. (2 + 2)

Correct Answer: —

Solution:

Etard reaction

Step 1 (Concept): The Etard reaction is used to prepare benzaldehyde from toluene. Toluene is oxidised in a controlled way by chromyl chloride (CrO_2Cl_2) so that only the methyl group is converted to the aldehyde group, and over-oxidation to benzoic acid is prevented.

Step 2 (Reagent and conditions): Toluene is treated with chromyl chloride (CrO_2Cl_2) in a solvent such as CS_2 or CCl_4. A brown solid chromium complex separates out.

$$C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} \text{Chromium complex (brown solid)}$$

Step 3 (Hydrolysis): The chromium complex is then hydrolysed with water to give benzaldehyde.

$$\text{Chromium complex} \xrightarrow{H_3O^+} C_6H_5CHO$$

So the overall product is **benzaldehyde**.

Gattermann-Koch reaction

Step 4 (Concept): The Gattermann-Koch reaction introduces a –CHO group directly onto the benzene ring (formylation), giving benzaldehyde from benzene.

Step 5 (Reagent and conditions): Benzene is treated with carbon monoxide (CO) and hydrogen chloride (HCl) gas in the presence of anhydrous $AlCl_3$ and cuprous chloride (CuCl) as catalyst.

$$C_6H_6 + CO + HCl \xrightarrow{\text{anhyd. } AlCl_3/CuCl} C_6H_5CHO$$

Step 6 (Result): The product is **benzaldehyde**. Here $AlCl_3$ is a Lewis acid catalyst and CuCl helps absorb CO.

$$\boxed{\text{Both reactions give benzaldehyde } (C_6H_5CHO)}$$

Quick Tip: Etard: toluene + chromyl chloride (CrO_2Cl_2) then hydrolysis. Gattermann-Koch: benzene + CO + HCl with anhydrous $AlCl_3$/CuCl. Both give benzaldehyde.

20. Explain the crystal field splitting in octahedral complexes with the help of a diagram. (4)

Correct Answer: —

Solution:

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

Step 2 (Approach of ligands): In an octahedral complex six ligands approach the metal ion along the three axes (the +x, −x, +y, −y, +z and −z directions). The lone pairs of the ligands create a negative electric field around the metal.

Step 3 (Effect on the two sets of orbitals): The two e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) lie **along** the axes, so they point straight at the ligands and feel strong repulsion. Their energy is **raised**. The three t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) lie **between** the axes, so they feel less repulsion and their energy is **lowered**.

Step 4 (Splitting): Thus the five degenerate d orbitals split into two sets. The energy gap between them is called the crystal field splitting energy, Δ_o (o = octahedral).

Step 5 (Barycentre rule): The average energy stays constant (barycentre). The t_{2g} set is lowered by $0.4\,\Delta_o$ (i.e. $-0.4\Delta_o$ each) and the e_g set is raised by $0.6\,\Delta_o$ each, so the centre of gravity is

unchanged.

Step 6 (Diagram, described):

$$\underbrace{d_{x^2-y^2},\ d_{z^2}}_{e_g\ (\text{higher},\ +0.6\Delta_o)}$$

---- barycentre (average energy) ----

$$\underbrace{d_{xy},\ d_{yz},\ d_{zx}}_{t_{2g}\ (\text{lower},\ -0.4\Delta_o)}$$

Free ion (5 degenerate d orbitals) → spherical field (all raised equally) → octahedral field (split into lower t_{2g} and higher e_g).

Step 7 (Result): The magnitude of Δ_o decides whether the complex is high spin (weak field, small Δ_o) or low spin (strong field, large Δ_o), and it explains the colour and magnetic behaviour of the complex.

$$\boxed{e_g : +0.6\Delta_o, \quad t_{2g} : -0.4\Delta_o}$$

Quick Tip: Six ligands along the axes split the five d orbitals into lower t_{2g} (between axes) and higher e_g (along axes); the gap is Δ_o, with t_{2g} at $-0.4\Delta_o$ and e_g at $+0.6\Delta_o$.

21. Explain Kohlrausch's law. If Λ_m° for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2 mol$^{\−1}$, calculate Λ° for HAc. (4)

Correct Answer: —

Solution:

Step 1 (Statement of Kohlrausch's law): Kohlrausch's law of independent migration of ions states that at infinite dilution (when the electrolyte is completely dissociated), the limiting molar conductivity of an electrolyte is the sum of the individual limiting molar conductivities of its cation and anion.

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

where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion, and ν_+, ν_- are the number of cations and anions per formula unit.

Step 2 (Use): This law lets us calculate Λ_m° of a weak electrolyte (like acetic acid, HAc) which cannot be found by extrapolation, by combining the Λ_m° values of suitable strong electrolytes.

Step 3 (Set up the combination): Write HAc in terms of the given salts:

$$\Lambda^\circ(HAc) = \Lambda^\circ(HCl) + \Lambda^\circ(NaAc) - \Lambda^\circ(NaCl)$$

Check the ions: HCl gives $H^+ + Cl^-$; NaAc gives $Na^+ + Ac^-$; subtracting NaCl removes $Na^+ + Cl^-$, leaving $H^+ + Ac^-$ = HAc. Correct.

Step 4 (Substitute the values):

$$\Lambda^\circ(HAc) = 425.9 + 91.0 - 126.4$$

Step 5 (Arithmetic):

$$425.9 + 91.0 = 516.9$$

$$516.9 - 126.4 = 390.5$$

$$\boxed{\Lambda^\circ(HAc) = 390.5\ S\,cm^2\,mol^{-1}}$$

Quick Tip: By Kohlrausch's law of independent ion migration, $\Lambda^\circ(HAc) = \Lambda^\circ(HCl) + \Lambda^\circ(NaAc) - \Lambda^\circ(NaCl)$.

22. Write short notes on the following: (i) Denaturation of proteins (ii) Name and structural formula of bases present in the nucleic acid. (2 + 2)

Correct Answer: —

Solution:

(i) Denaturation of proteins

Step 1 (Meaning): A protein found in a living system with a unique three-dimensional shape and biological activity is called a native protein. When this native protein is subjected to a physical change (such as a rise in temperature) or a chemical change (such as a change in pH, or adding acid, alcohol or heavy-metal salts), it loses its natural shape and its biological activity. This process is called **denaturation**.

Step 2 (What happens at the molecular level): During denaturation the hydrogen bonds and other weak forces that hold the secondary and tertiary structure are broken. The coiled and folded chains (the helix uncoils and the globules unfold), so the secondary and tertiary structures are destroyed, but the **primary structure** (the sequence of amino acids joined by peptide bonds) remains intact.

Step 3 (Examples): Coagulation of egg white on boiling, and curdling of milk (due to the formation of lactic acid by bacteria) are common examples of denaturation.

(ii) Bases present in nucleic acids

Step 4 (Two families): The nitrogen-containing bases in nucleic acids are of two types:

• **Purines** (fused double-ring): **Adenine (A)** and **Guanine (G)**.

• **Pyrimidines** (single ring): **Cytosine (C)**, **Thymine (T)** and **Uracil (U)**.

Step 5 (Where they occur): DNA contains A, G, C and T. RNA contains A, G, C and U (thymine is replaced by uracil).

Step 6 (Names and structural description / formulae):

• **Adenine** (6-aminopurine), $C_5H_5N_5$: a purine ring bearing an –NH_2 group at position 6.

• **Guanine** (2-amino-6-oxopurine), $C_5H_5N_5O$: a purine ring with an –NH_2 group at position 2 and a keto (=O) group at position 6.

• **Cytosine** (4-amino-2-oxopyrimidine), $C_4H_5N_3O$: a pyrimidine ring with an –NH_2 group at position 4 and a keto group at position 2.

• **Thymine** (5-methyl-2,4-dioxopyrimidine), $C_5H_6N_2O_2$: a pyrimidine ring with keto groups at positions 2 and 4 and a –CH_3 group at position 5.

• **Uracil** (2,4-dioxopyrimidine), $C_4H_4N_2O_2$: a pyrimidine ring with keto groups at positions 2 and 4 (same as thymine but without the –CH_3).

Purines: A, G; Pyrimidines: C, T, U

Quick Tip: Denaturation breaks the hydrogen bonds of the secondary and tertiary structure (primary stays intact), e.g. boiling an egg. Bases: purines A and G; pyrimidines C, T (DNA) and U (RNA).

23. Write the products of the following reactions:

(i) Phenol (C_6H_5OH) + $CHCl_3$ + aq. NaOH $\rightarrow$?

(ii) Phenol (C_6H_5OH) + Zn / $\Delta \rightarrow$?

OR

(i) Explain hydrogen bonding in o-nitrophenol and p-nitrophenol.

(ii) What is formed in the nitration of phenol with concentrated HNO_3?

Correct Answer: —

Solution:

Option 1 (products of reactions)

Step 1: Reaction (i) is the Reimer-Tiemann reaction. When phenol is treated with chloroform ($CHCl_3$) in the presence of aqueous NaOH, an aldehyde group (–CHO) is introduced at the ortho position of the ring.

Step 2: How it works. Aqueous NaOH first reacts with $CHCl_3$ to generate the electrophile dichlorocarbene, $:CCl_2$. NaOH also converts phenol into the phenoxide ion, which is highly activated at the ortho and para positions. The electron-rich ortho carbon attacks the dichlorocarbene, and on subsequent hydrolysis the $-CHCl_2$ group is converted to $-CHO$.

Step 3: Product of (i). The main product is **salicylaldehyde (2-hydroxybenzaldehyde, ortho-hydroxybenzaldehyde)**.

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow{\Delta} o\text{-}HO\text{-}C_6H_4\text{-}CHO + 3NaCl + 2H_2O$$

Step 4: Reaction (ii) is zinc-dust distillation. When phenol vapour is passed over heated zinc dust, the $-OH$ group is removed (reduced) and replaced by $-H$; zinc takes up the oxygen as ZnO.
Step 5: Product of (ii). The product is **benzene**.

$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$$

Option 2 (hydrogen bonding and nitration)

Step 1: Nature of H-bonding in o-nitrophenol. In o-nitrophenol the $-OH$ group and the $-NO_2$ group are on adjacent (ortho) carbons and lie close in space. The $-OH$ hydrogen bonds to an oxygen of the neighbouring $-NO_2$ group within the same molecule, forming a stable six-membered chelate ring. This is **intramolecular hydrogen bonding**.
Step 2: Consequence for o-nitrophenol. Because the $-OH$ is locked in an internal H-bond, the molecules do not associate strongly with one another. Hence o-nitrophenol has a **lower boiling point, is steam-volatile, and is less soluble in water**.
Step 3: Nature of H-bonding in p-nitrophenol. In p-nitrophenol the $-OH$ and $-NO_2$ groups are far apart (para positions), so an intramolecular bond is not possible. Instead the $-OH$ of one molecule bonds to the $-NO_2/-OH$ of another molecule. This is **intermolecular hydrogen bonding**, which links many molecules together.
Step 4: Consequence for p-nitrophenol. The strong intermolecular association gives p-nitrophenol a **higher boiling point, makes it non-steam-volatile, and more soluble in water** than the ortho isomer.
Step 5: Nitration of phenol with concentrated HNO_3. Phenol is very

strongly activated by the $-OH$ group, so concentrated nitric acid nitrates it at all three activated positions (two ortho and one para). The product is **2,4,6-trinitrophenol, commonly called picric acid**.

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} 2,4,6\text{-}(NO_2)_3C_6H_2OH + 3H_2O$$

Products: salicylaldehyde; benzene; and picric acid (2,4,6-trinitrophenol)

Quick Tip: (i) is Reimer-Tiemann (dichlorocarbene) giving salicylaldehyde; Zn/Δ removes –OH to give benzene. For the alternative, compare intramolecular chelation in o-nitrophenol with intermolecular association in p-nitrophenol, and remember conc. HNO_3 gives picric acid.

24. Write short notes on the following:

(i) Gabriel phthalimide reaction

(ii) Hoffmann bromamide reaction

OR

Write the following chemical reactions:

(i) Reaction of ethanolic NH_3 with C_2H_5Cl.

(ii) Reaction of ammonia with benzyl chloride, followed by reaction with two moles of CH_3Cl.

Correct Answer: —

Solution:

Option 1 (short notes)

(i) Gabriel phthalimide reaction

Step 1: Purpose. It is a method to prepare **pure aliphatic primary amines** ($R\text{-}NH_2$) that are free from secondary and tertiary amines.
Step 2: Form the potassium salt. Phthalimide is treated with alcoholic KOH. The N–H (which is acidic because it is between two carbonyl groups) is removed to give potassium phthalimide.
Step 3: Alkylation. Potassium phthalimide is heated with an alkyl halide ($R\text{-}X$). The nitrogen displaces the halide to give N-alkylphthalimide.
Step 4: Release the amine. The N-alkylphthalimide is hydrolysed with aqueous acid or base (or treated with hydrazine, Ing-Manske method) to set free the primary amine along with phthalic acid.

$$\text{Phthalimide} \xrightarrow{KOH} \text{K-phthalimide} \xrightarrow{R\text{-}X} \text{N-alkylphthalimide} \xrightarrow{\text{hydrolysis}} R\text{-}NH_2$$

Step 5: Limitation. **Aromatic (aryl) primary amines cannot be made** this way because aryl halides do not undergo the required nucleophilic substitution with potassium phthalimide.

(ii) Hoffmann bromamide reaction (degradation)
Step 1: Purpose. An amide is converted into a primary amine that has **one carbon atom fewer** than the starting amide.
Step 2: Reagents. A primary amide ($R\text{-}CONH_2$) is treated with bromine (Br_2) and a strong base (NaOH or KOH).
Step 3: Overall reaction.

$$R\text{-}CONH_2 + Br_2 + 4NaOH \rightarrow R\text{-}NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Step 4: Key feature. The carbonyl carbon is lost (leaves as carbonate), so the amine $R\text{-}NH_2$ has one carbon less than the amide. For example, acetamide (CH_3CONH_2, 2 carbons) gives methylamine (CH_3NH_2, 1

carbon).

Option 2 (chemical reactions)

(i) Ethanolic NH_3 with C_2H_5Cl.

Step 1: Ethyl chloride undergoes nucleophilic substitution with ammonia (ammonolysis) to give ethylamine.

$$C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$$

Step 2: Ethylamine is itself a nucleophile, so with excess C_2H_5Cl it is further alkylated in steps to diethylamine, triethylamine, and finally the quaternary tetraethylammonium chloride.

$$C_2H_5NH_2 \xrightarrow{C_2H_5Cl} (C_2H_5)_2NH \xrightarrow{C_2H_5Cl} (C_2H_5)_3N \xrightarrow{C_2H_5Cl} (C_2H_5)_4N^+Cl^-$$

(ii) Ammonia with benzyl chloride, then two moles of CH_3Cl.

Step 1: Benzyl chloride reacts with ammonia to give benzylamine.

$$C_6H_5CH_2Cl + NH_3 \rightarrow C_6H_5CH_2NH_2 + HCl$$

Step 2: Benzylamine has two N–H bonds; reaction with two moles of methyl chloride methylates both, giving N,N-dimethylbenzylamine.

$$C_6H_5CH_2NH_2 + 2CH_3Cl \rightarrow C_6H_5CH_2N(CH_3)_2 + 2HCl$$

Final product: N,N-dimethylbenzylamine

Quick Tip: Gabriel synthesis makes pure aliphatic primary amines (not aromatic ones) via potassium phthalimide; Hoffmann bromamide degrades an amide with Br_2/NaOH to an amine with one carbon less. In the alternative, ammonolysis gives ethylamine, and benzyl chloride + NH_3 then 2 CH_3Cl gives N,N-dimethylbenzylamine.

25. Rate constant K for a first order reaction is found $5.5 \times 10^{-14}\ \text{s}^{-1}$. Calculate the half-life of this reaction.

OR

For the following first order reaction — $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ — the initial concentration of N_2O_5 at 318 K was $1.24 \times 10^{-2}\ \text{mol L}^{-1}$. After 60 min it became $0.20 \times 10^{-2}\ \text{mol L}^{-1}$. Calculate the rate constant at 318 K.

Correct Answer: —

Solution:

Option 1 (Half-life from rate constant)

Step 1: For a first order reaction the rate does not depend on the initial concentration, and the half-life $t_{1/2}$ is related to the rate constant k by the standard formula:

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

Here $0.693 = \ln 2$, the natural logarithm of 2.

Step 2: Substitute the given rate constant $k = 5.5 \times 10^{-14}\ \text{s}^{-1}$:

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

Step 3: Carry out the arithmetic. First $\frac{0.693}{5.5} = 0.126$. Then divide by 10^{-14}, which multiplies by 10^{14}:

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

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

Option 2 (Rate constant from concentration data)

Step 1: For a first order reaction the integrated rate law is:

$$k = \frac{2.303}{t}\ \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is the initial concentration and $[A]$ the concentration after time t.

Step 2: Insert the given data: $[A]_0 = 1.24 \times 10^{-2}$, $[A] = 0.20 \times 10^{-2}\ \text{mol L}^{-1}$, $t = 60\ \text{min}$.

$$\frac{[A]_0}{[A]} = \frac{1.24 \times 10^{-2}}{0.20 \times 10^{-2}} = 6.2$$

Step 3: Take the logarithm: $\log 6.2 = 0.7924$.

Step 4: Substitute and compute:

$$k = \frac{2.303}{60} \times 0.7924 = \frac{1.825}{60} = 0.0304\ \text{min}^{-1}$$

Step 5: Convert to s^{-1} by dividing by 60:

$$k = \frac{0.0304}{60} = 5.07 \times 10^{-4}\ \text{s}^{-1}$$

$$\boxed{k = 0.0304\ \text{min}^{-1} = 5.07 \times 10^{-4}\ \text{s}^{-1}}$$

Quick Tip: For any first order reaction $t_{1/2} = 0.693/k$; to get k from concentrations use $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$. Watch the time units (min vs s).

26. Reactivity of haloarene increases if an electron withdrawing group ($-NO_2$) is present at the ortho or para position. Explain it with an example and give the reaction mechanism.

OR

Write short notes on the applications of the following: (i) DDT (ii) Freon (iii) Carbon tetrachloride (iv) Chloroform (v) Dichloromethane.

Correct Answer: —

Solution:

Option 1 (Effect of -NO2 on haloarene reactivity)

Step 1 (Why haloarenes are normally unreactive): In a haloarene the halogen is joined to an sp^2 carbon of the benzene ring. The lone pair of the halogen overlaps with the ring, giving the C–X bond partial double-bond character. This makes the bond short and strong, and the ring carbon becomes electron rich, so ordinary nucleophiles cannot attack easily.

Step 2 (Role of -NO2 at ortho/para): A strong electron withdrawing group such as $-NO_2$ pulls electron density away from the ring. When it sits at the ortho or para position relative to the halogen, it can

directly stabilise the negative charge that develops on the carbon during attack. This makes nucleophilic aromatic substitution far easier.

Step 3 (Example): Chlorobenzene reacts with NaOH only under very harsh conditions (about 623 K and 300 atm). But p-nitrochlorobenzene reacts with dilute NaOH much more readily; 2,4-dinitrochlorobenzene reacts even more easily; and 2,4,6-trinitrochlorobenzene (picryl chloride) is hydrolysed just by warm water. Reactivity rises as more $-NO_2$ groups are added at ortho/para positions.

$$p\text{-}O_2N\text{-}C_6H_4\text{-}Cl + NaOH \rightarrow p\text{-}O_2N\text{-}C_6H_4\text{-}ONa + NaCl$$

which on acidification gives p-nitrophenol.

Step 4 (Mechanism – addition then elimination): (a) The nucleophile OH^- adds to the ring carbon carrying the chlorine, breaking one ring double bond and forming a resonance-stabilised carbanion (the Meisenheimer intermediate). (b) The negative charge is delocalised onto the oxygen atoms of the ortho/para $-NO_2$ groups, which greatly stabilises this intermediate. (c) Chloride ion Cl^- is then eliminated, the ring regains its aromatic sextet, and the phenoxide (then phenol) is formed.

Step 5 (Why ortho/para only): Only when $-NO_2$ is ortho or para to the halogen can its resonance structures place the negative charge onto the nitro oxygen. A meta $-NO_2$ cannot stabilise the carbanion by resonance, so it does not increase reactivity.

Option 2 (Applications of the given compounds)

(i) DDT (p,p'-dichlorodiphenyltrichloroethane): A powerful, cheap and long-lasting insecticide. It was widely used to control malaria and typhus by killing mosquitoes and lice. Because it is very stable, it

accumulates in the environment and in animal tissue (bioaccumulation) and is toxic to fish and birds, so its use is now banned or heavily restricted in many countries.

(ii) Freon (chlorofluorocarbons, e.g. CF_2Cl_2, Freon-12): Used as the refrigerant gas in refrigerators and air conditioners and as a propellant in aerosol sprays. They are chemically unreactive and non-toxic to handle, but they reach the stratosphere and destroy the ozone layer, so they are being phased out.

(iii) Carbon tetrachloride (CCl_4): Used as an industrial solvent for oils, fats and resins, in dry cleaning, and earlier as a fire extinguisher liquid (Pyrene). Its vapours are dense and smother flames. It is toxic to the liver and, on heating, can release poisonous gases, so its use is now limited.

(iv) Chloroform ($CHCl_3$): An important solvent for fats, waxes, alkaloids and iodine, and a starting material for making the refrigerant Freon (R-22). It was once used as an anaesthetic but this was stopped because it harms the liver and heart. It is stored in dark, filled bottles to stop it forming poisonous phosgene gas on exposure to light and air.

(v) Dichloromethane (CH_2Cl_2, methylene chloride): A common solvent used as a paint remover, a propellant in aerosols, a metal cleaning and degreasing agent, and in the process of decaffeinating coffee. It is harmful to the central nervous system, so it must be used with care.

Quick Tip: Ortho/para $-NO_2$ stabilises the carbanion (Meisenheimer) intermediate by resonance onto its oxygen, driving addition–elimination. For the uses part, link each haloalkane to its solvent/refrigerant/insecticide role and its hazard.