

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-5-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 2 hours

Maximum Marks: 35

General Instructions

- (i) This question paper contains **12** questions. **All** questions are compulsory.
- (ii) This question paper comprises of **three** sections- **Section A, B and C**.
- (iii) **Section A** – Q. No. 1 to 3 are very short-answer type questions carrying 2 marks each.
- (iv) **Section B** – Q. No. 4 to 11 are short-answer type questions carrying 3 marks each.
- (v) **Section C** – Q. No. 12 is case based question carrying 5 marks.
- (vi) Use of log tables and calculators is **not** allowed.

Section A (6 marks)

1. Answer the following questions (Do any two):

(a) Identify the order of reaction from the following unit for its rate constant: $\text{L mol}^{-1} \text{s}^{-1}$

(b) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

(c) Write the expression of integrated rate equation for zero order reaction.

[2 marks]

Solution:

Concept:

- For an order n reaction, $r = k[A]^n$. The units of k are $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$, since rate is concentration divided by time.
- A zero order reaction has a constant rate k , independent of reactant concentration; integration gives a linear decrease of concentration with time.

Step 1: (a) Identify the order from the units The given units are $\text{L mol}^{-1} \text{s}^{-1} = (\text{mol L}^{-1})^{-1} \text{s}^{-1}$. Comparing the concentration exponent with $1 - n$, we get $1 - n = -1$, so $n = 2$. Thus the reaction is second order.

Step 2: (b) Compare the two rates For the conversion $A \rightarrow B$, the rate of formation of B is $r = k[A]^2$. At unchanged temperature, k is unchanged. If $[A]$ becomes $3[A]$, then

$$\frac{r_{\text{new}}}{r_{\text{old}}} = \frac{k(3[A])^2}{k[A]^2} = 9.$$

The rate therefore becomes nine times its initial value.

Step 3: (c) State the integrated equation Integrating $-d[A]/dt = k$ between concentration $[A]_0$ at $t = 0$ and $[A]_t$ at time t gives

$$[A]_t = [A]_0 - kt, \quad k = \frac{[A]_0 - [A]_t}{t}.$$

Here k is the zero order rate constant. The equation applies while reactant remains and the reaction follows zero order kinetics.

Step 4: Conclusion (a) Second order; (b) the rate becomes nine times; (c) $[A]_t = [A]_0 - kt$. Any two of these parts may be attempted as directed.

Quick Tip to Solve: Compare the concentration power in the units of k with $1 - n$; for a concentration change, raise the multiplying factor to the reaction order.

2. Arrange the following in the increasing order of their property indicated:

(a) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)

(b) 4-Nitrobenzoic acid, benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (Acid strength)

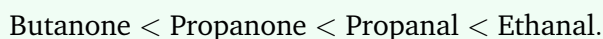
[2 marks]

Solution:

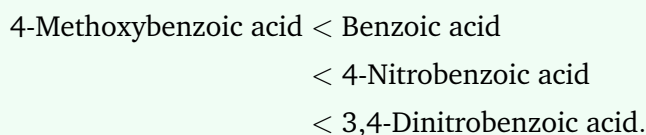
Concept:

- Nucleophilic addition is favoured by a more electrophilic carbonyl carbon and less steric hindrance. Alkyl groups donate electron density by the +I effect and hinder the approaching nucleophile.
- Acid strength increases when a substituent stabilises the carboxylate conjugate base by withdrawing electron density. Electron donation destabilises that anion and decreases acid strength.

Step 1: (a) Compare carbonyl compounds Aldehydes have only one alkyl group attached to the carbonyl carbon, whereas ketones have two. Hence aldehydes are more reactive towards nucleophilic addition than ketones. Within either pair, the larger ethyl group causes greater steric hindrance and electron donation than the methyl group: propanal is less reactive than ethanal, and butanone is less reactive than propanone. Combining these comparisons gives



Step 2: (b) Compare substituted benzoic acids The para methoxy group donates electron density through resonance; its net effect makes 4-methoxybenzoic acid weaker than benzoic acid. A nitro group strongly withdraws electron density through inductive and resonance effects, stabilising the carboxylate ion. Thus 4-nitrobenzoic acid is stronger than benzoic acid. A second nitro group gives additional electron withdrawal, making 3,4-dinitrobenzoic acid the strongest of the four. The increasing order is



Step 3: Conclusion (a) Butanone < propanone < propanal < ethanal. (b) 4-Methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3,4-dinitrobenzoic acid.

Quick Tip to Solve: For carbonyl addition compare aldehyde versus ketone first, then alkyl-group size. For acidity, count electron-withdrawing nitro groups and put the donating methoxy compound first.

3. Explain the following reactions:

(a) Wolff Kishner reduction

(b) Cannizzaro reaction

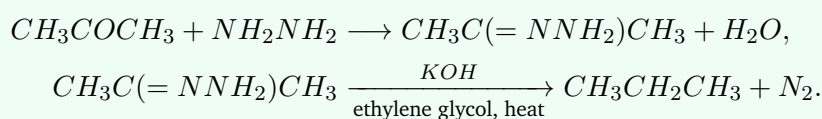
[2 marks]

Solution:

Concept:

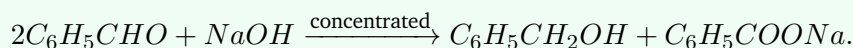
- Wolff-Kishner reduction replaces the carbonyl group $>C=O$ of an aldehyde or ketone by $>CH_2$, using hydrazine and strong base with heat.
- Cannizzaro reaction is the self oxidation-reduction of an aldehyde without an α -hydrogen in concentrated alkali: one molecule forms an alcohol and another forms a carboxylate salt.

Step 1: (a) Explain Wolff-Kishner reduction The aldehyde or ketone first reacts with hydrazine, NH_2NH_2 , to form its hydrazone. Heating the hydrazone with KOH in a high-boiling solvent such as ethylene glycol removes nitrogen and produces the corresponding hydrocarbon. For example, propanone gives propane:



The carbon skeleton is retained while oxygen is removed from the carbonyl group.

Step 2: (b) Explain Cannizzaro reaction Aldehydes lacking an α -hydrogen undergo disproportionation on treatment with concentrated aqueous $NaOH$ or KOH . Benzaldehyde is an example:



One benzaldehyde molecule is reduced to benzyl alcohol and the other is oxidised to sodium benzoate. In the alkaline reaction mixture the oxidation product is the carboxylate salt; acidification subsequently gives benzoic acid. The absence of an α -hydrogen distinguishes this reaction from aldol condensation.

Step 3: Conclusion Wolff-Kishner reduction converts aldehydes or ketones into hydrocarbons with hydrazine, KOH and heat. Cannizzaro reaction converts a non-enolisable aldehyde into an alcohol and a carboxylate salt in concentrated alkali.

Quick Tip to Solve: Remember the reagent contrast: hydrazine plus hot base removes carbonyl oxygen; concentrated alkali alone disproportionates an aldehyde that has no alpha hydrogen.

Section B (24 marks)

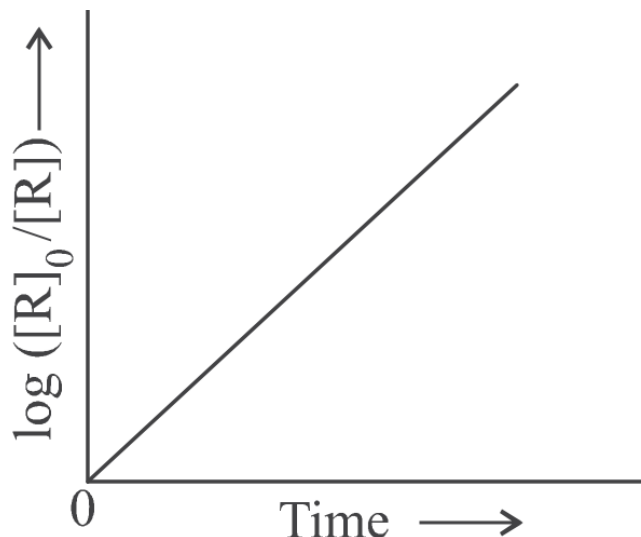
4. Observe the graph shown in figure and answer the following questions:

(a) What is the order of the reaction?

(b) What is the slope of the curve?

(c) Write the relationship between k and $t_{1/2}$ (half life period).

[3 marks]



Solution:

Concept:

- A first-order reaction obeys $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$, where $[R]_0$ and $[R]$ are the initial and time-dependent reactant concentrations.
- The slope of a straight-line plot is its change in ordinate divided by its change in abscissa; the half-life $t_{1/2}$ is the time for the reactant concentration to fall to half its initial value.

Step 1: (a) Identify the order from the plotted quantities The vertical axis is $\log([R]_0/[R])$, and the horizontal axis is time. Rearranging the integrated first-order rate equation gives

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

Thus this logarithmic quantity increases linearly from zero as time increases, exactly as in the given graph. A zero-order reaction instead gives a straight line for concentration against time, and a second-order reaction gives one for reciprocal concentration against time.

Step 2: (b) Read the coefficient of time as the slope Comparison with $y = mt + c$ gives $y = \log([R]_0/[R])$, $x = t$, and $c = 0$. Hence

$$m = \frac{\Delta \log([R]_0/[R])}{\Delta t} = \frac{k}{2.303}.$$

The slope is positive because the remaining reactant concentration decreases, making the ratio

Quick Tip to Solve: Check whether the axis says log or ln before writing the slope: common log introduces the factor 2.303.

$[R]_0/[R]$ increase. The factor 2.303 is essential because the ordinate uses the common logarithm.

Step 3: (c) Apply the half-life condition At $t = t_{1/2}$, put $[R] = [R]_0/2$ in the same equation:

$$k = \frac{2.303}{t_{1/2}} \log 2 = \frac{0.693}{t_{1/2}}.$$

This half-life is independent of the initial concentration for a first-order reaction.

Step 4: Conclusion (a) First order. (b) Slope = $k/2.303$. (c) $t_{1/2} = 0.693/k$, or $k = 0.693/t_{1/2}$.

Quick Tip to Solve: Check whether the axis says log or ln before writing the slope: common log introduces the factor 2.303.

5(a). (i) Write the IUPAC name of the following complex: $K_2[PdCl_4]$

(ii) Using crystal field theory, write the electronic configuration of d^5 ion, if $\Delta_o > P$.

(iii) What are Homoleptic complexes?

[3 marks]

Solution:

Concept:

- For an anionic complex, the metal name ends in “ate, and its oxidation state is written in Roman numerals.
- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. If $\Delta_o > P$, pairing in t_{2g} costs less energy than promotion to e_g .
- A homoleptic complex contains only one kind of ligand attached to the central metal atom or ion.

Step 1: (i) Determine oxidation state and name the complex The two potassium ions each have charge +1, so the complex ion is $[PdCl_4]^{2-}$. If the oxidation state of palladium is x , then

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

There are four chlorido ligands, giving tetrachlorido. Since the coordination entity is an anion, palladium becomes palladate. Name the potassium cation before the complex anion.

Step 2: (ii) Fill the orbitals for the given field strength The ion has five d electrons. Because $\Delta_o > P$, an electron pairs in a lower-energy t_{2g} orbital rather than occupying an upper e_g orbital. First place one electron in each of the three t_{2g} orbitals, then pair two of them. The resulting low-spin configuration is

$$t_{2g}^5 e_g^0.$$

It contains two electron pairs and one unpaired electron. The high-spin configuration $t_{2g}^3 e_g^2$ would correspond to the opposite inequality.

Step 3: (iii) Define a homoleptic complex Homoleptic complexes are coordination compounds in which the central metal is bonded to only one type of ligand. For example, $[Co(NH_3)_6]^{3+}$ has six ammine ligands and is homoleptic. The number of ligands may exceed one; the defining feature is that all are of the same kind.

Quick Tip to Solve: Use the complex charge to calculate the oxidation state first; compare splitting energy with pairing energy before filling the d orbitals.

Step 4: Conclusion (i) Potassium tetrachloridopalladate(II). (ii) $t_{2g}^5 e_g^0$, a low-spin configuration. (iii) Homoleptic complexes contain only one type of ligand bonded to the central metal.

Quick Tip to Solve: Use the complex charge to calculate the oxidation state first; compare splitting energy with pairing energy before filling the d orbitals.

OR

5(b)(i). Why chelate complexes are more stable than complexes with unidentate ligands? [1 mark]

Solution:

Concept:

- A chelating ligand binds to the same metal ion through two or more donor atoms and forms one or more rings.
- The chelate effect is the greater thermodynamic stability of such complexes compared with analogous complexes of unidentate ligands.

Step 1: Explain multiple attachment A chelating ligand remains attached through another donor atom even if one metal–donor bond temporarily breaks. Its detached donor group remains close to the metal and can bind again readily. Complete removal therefore requires loss of several attachments.

Step 2: Explain the stability advantage When multidentate ligands replace comparable unidentate ligands, several free ligand particles may be released into solution, producing a favourable increase in entropy. Together with ring formation and multiple attachment, this favours chelate formation and gives a larger formation constant under comparable conditions.

Step 3: Conclusion Chelate complexes are more stable because multidentate ligands form rings with multiple metal–ligand attachments, and their formation is generally favoured by the entropy increase associated with displacement of unidentate ligands.

Quick Tip to Solve: Mention ring formation and multiple donor attachments; the entropy advantage explains the thermodynamic chelate effect.

5(b)(ii). What is “spectrochemical series”? What is the difference between a weak field ligand and a strong field ligand? [2 marks]

Solution:

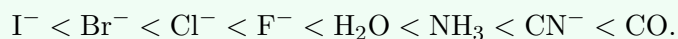
Concept:

- Crystal field splitting energy, Δ_o , is the energy gap between the lower t_{2g} and higher e_g orbital sets in an octahedral complex.
- Pairing energy, P , is the energy required to pair two electrons in the same orbital; comparing it with Δ_o determines electron occupation.

Step 1: Define the spectrochemical series The spectrochemical series is the experimentally determined

Quick Tip to Solve: Compare splitting with pairing energy: small splitting favours occupation before pairing; large splitting favours pairing first.

arrangement of ligands in increasing order of their crystal field splitting power. A representative order is



Ligands towards the left produce smaller splitting, whereas those towards the right produce larger splitting for comparable complexes.

Step 2: Compare weak and strong field ligands Weak field ligands such as Cl^- cause a small splitting. When $\Delta_o < P$, electrons occupy the higher orbitals before pairing in the lower ones, giving high spin complexes where a spin choice exists. Strong field ligands such as CN^- cause a large splitting. When $\Delta_o > P$, electrons pair in the lower orbitals before occupying the higher ones, giving low spin complexes where a spin choice exists.

Step 3: Conclusion The spectrochemical series ranks ligands by increasing splitting power. Weak field ligands produce smaller splitting and favour high spin configurations; strong field ligands produce larger splitting and favour low spin configurations.

Quick Tip to Solve: Compare splitting with pairing energy: small splitting favours occupation before pairing; large splitting favours pairing first.

6(a). (i) Define coagulation.

(ii) State Hardy-Schulze rule.

(iii) What is Electrophoresis?

[3 marks]

Solution:

Concept:

- Colloidal particles carry an electrical charge. Repulsion between particles of the same charge helps prevent their aggregation.
- An electrolyte can neutralise the charge of colloidal particles; an applied electric field can instead reveal their charge through directed movement.

Step 1: Define coagulation Coagulation is the process of precipitation of colloidal particles by aggregation. When their stabilising charge is removed or neutralised, the particles combine into larger aggregates which separate from the dispersion medium. Adding a suitable electrolyte is one way to bring about coagulation: its oppositely charged ions neutralise the charge on the colloidal particles.

Step 2: State the Hardy-Schulze rule The coagulating power of an electrolyte depends mainly on the valency of the ion carrying a charge opposite to that of the colloidal particles. The greater the valency of this ion, the greater is its coagulating power. For a negatively charged sol, cations are the effective coagulating ions; for example, the general order is $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^+$. For a positively charged sol, the effective ions are anions. The relevant valency is therefore that of the counter-ion, not the similarly charged ion.

Step 3: Define electrophoresis Electrophoresis is the movement of charged colloidal particles towards the oppositely charged electrode under an applied electric field. Positively charged particles move towards the cathode, whereas negatively charged particles move towards the anode. This directed

Quick Tip to Solve: Identify the sol's charge first: its counter-ions cause coagulation, and its particles move to the oppositely charged electrode.

motion provides evidence that the colloidal particles carry an electrical charge.

Step 4: Conclusion Coagulation is aggregation and precipitation of colloidal particles. The Hardy-Schulze rule states that higher counter-ion valency gives greater coagulating power. Electrophoresis is the movement of charged colloidal particles towards the electrode of opposite charge.

Quick Tip to Solve: Identify the sol's charge first: its counter-ions cause coagulation, and its particles move to the oppositely charged electrode.

OR

6(b). Write three differences between Physisorption and Chemisorption.

[3 marks]

Solution:

Concept:

- Adsorption is accumulation of an adsorbate at the surface of an adsorbent. Its type depends on the force holding the adsorbate at the surface.
- Physisorption involves weak van der Waals forces, while chemisorption involves chemical bonds between the adsorbate and the surface.

Step 1: Compare forces and heat of adsorption In physisorption, weak van der Waals forces hold the adsorbate. Its enthalpy of adsorption is relatively low, usually about $20\text{--}40\text{ kJ mol}^{-1}$. In chemisorption, chemical bonds hold the adsorbate, so the enthalpy of adsorption is much larger, usually about $80\text{--}240\text{ kJ mol}^{-1}$. The higher heat released in chemisorption reflects stronger bonding to the surface.

Step 2: Compare specificity Physisorption is not highly specific: a gas can be physically adsorbed on different surfaces because van der Waals attraction operates between many substances. Chemisorption is highly specific: it occurs only when the adsorbate can form a chemical bond with the particular surface. Thus, the chemical nature of both the adsorbate and the adsorbent determines whether chemisorption occurs.

Step 3: Compare the number of layers Physisorption can form several adsorbed layers, because molecules already adsorbed can attract further molecules by van der Waals forces. Chemisorption forms a monomolecular layer, because the adsorbate bonds directly to available surface sites. After these sites are occupied, another layer cannot form through the same chemical bonding to the adsorbent surface.

Step 4: Conclusion The three differences are weak forces and low heat of adsorption versus chemical bonds and high heat; low specificity versus high specificity; and multilayer versus monolayer adsorption, respectively, for physisorption and chemisorption.

Quick Tip to Solve: Recall the headings forces, specificity and layers; give a paired difference under each heading.

7. (a) Write any two consequences of Lanthanoid Contraction.

(b) Name the element of 3d series which exhibits the largest number of oxidation states. Give reason. [3 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series with increasing atomic number, caused by poor shielding by 4f electrons.
- Transition metals exhibit variable oxidation states because the $(n - 1)d$ and ns electrons have comparable energies and can participate in bonding.

Step 1: State two consequences of lanthanoid contraction First, corresponding elements of the second and third transition series have very similar radii. For example, zirconium and hafnium have almost identical sizes and consequently similar chemical properties. The expected size increase on adding an electron shell is largely offset by contraction across the intervening lanthanoids. Second, the basic strength of lanthanoid hydroxides decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. As the Ln^{3+} radius decreases, its polarising power increases and the hydroxide bond acquires greater covalent character, reducing basicity.

Step 2: Identify the element with the most oxidation states Manganese exhibits the largest number of oxidation states among the 3d elements, commonly ranging from +2 to +7. Its electronic configuration is $[\text{Ar}] 3d^5 4s^2$. It has five unpaired 3d electrons and two 4s electrons available for involvement in bonding. Since the energies of these orbitals are comparable, different numbers of these seven valence electrons can participate, allowing a wide range of oxidation states. The +7 state occurs, for example, in permanganate, MnO_4^- .

Step 3: Conclusion Two consequences are the close similarity in size and properties of Zr and Hf, and decreasing basicity of lanthanoid hydroxides from La to Lu. Manganese has the largest number of oxidation states in the 3d series because its $3d^5 4s^2$ configuration permits participation of different numbers of seven valence electrons.

Quick Tip to Solve: Connect contraction to increasing polarising power; for manganese, count five d and two s valence electrons.

8. Give reasons for the following statements:

(a) Copper does not displace hydrogen from acids.

(b) Transition metals and most of their compounds show paramagnetic behaviour.

(c) Zn, Cd and Hg are soft metals. [3 marks]

Solution:

Concept:

- Metal displacement of hydrogen from a non-oxidising acid depends on the electrode potential relative to the standard hydrogen electrode, whose standard reduction potential is zero.
- Unpaired electrons produce a magnetic moment and hence paramagnetism. Strong metallic

Quick Tip to Solve: For these three reasons, connect hydrogen displacement to electrode potential, magnetism to unpaired electrons, and softness to metallic-bond strength.

bonding requires effective participation of valence electrons in cohesion.

Step 1: (a) Compare copper with hydrogen The standard reduction potential of copper is positive: $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$. For the hypothetical displacement $\text{Cu} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2$, the standard cell potential is $0 - 0.34 = -0.34 \text{ V}$. The reaction is therefore not spontaneous under standard conditions. Copper lies below hydrogen in the activity series and cannot liberate hydrogen from ordinary non-oxidising acids. Oxidising acids can dissolve copper through reduction of the acid's oxidising species, rather than liberation of hydrogen.

Step 2: (b) Identify the origin of paramagnetism Transition metals and most of their ions possess partially filled d subshells containing unpaired electrons. The spin magnetic moments of these electrons are not completely cancelled, so the substances are attracted by an external magnetic field. In the spin-only approximation, $\mu = \sqrt{n(n+2)} \mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton. Species with all electrons paired are exceptions and are diamagnetic.

Step 3: (c) Relate softness to metallic bonding Zn, Cd and Hg have completely filled $(n-1)d^{10}$ subshells and ns^2 outer configurations. Their filled d subshells do not provide unpaired d electrons for the strong metallic bonding characteristic of many other d -block metals. Consequently their metallic bonding is relatively weak, accounting for their softness; mercury is liquid at ordinary room temperature.

Step 4: Conclusion Copper has a positive reduction potential and does not displace hydrogen from non-oxidising acids. Unpaired d electrons cause the usual paramagnetism of transition-metal species. Filled d^{10} subshells and relatively weak metallic bonding explain the softness of Zn, Cd and Hg.

Quick Tip to Solve: For these three reasons, connect hydrogen displacement to electrode potential, magnetism to unpaired electrons, and softness to metallic-bond strength.

9(a). Account for the following:

(i) pK_b of aniline is more than that of methylamine.

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

(iii) Primary amines have higher boiling points than tertiary amines.

[3 marks]

Solution:

Concept:

- A base accepts a proton through the nitrogen lone pair. Greater availability of that lone pair increases K_b and decreases $pK_b = -\log_{10} K_b$.
- Resonance, electron-releasing substituents, interaction with Lewis acids and intermolecular hydrogen bonding determine the relevant properties of amines.

Step 1: (i) Compare the basicity of aniline and methylamine In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less readily available to accept a proton. The phenyl group also exerts an electron-withdrawing inductive effect. In methylamine, the methyl group has a positive inductive effect and increases electron density at nitrogen; its lone pair is not delocalised into an aromatic ring. Methylamine is consequently the stronger base, with larger K_b .

Quick Tip to Solve: First ask whether the nitrogen lone pair is available; for boiling points, check for an N-H bond that can donate intermolecular hydrogen bonds.

Since $pK_b = -\log_{10} K_b$, aniline has the larger pK_b .

Step 2: (ii) Explain the failure of the Friedel–Crafts reaction The Lewis-acid catalyst, commonly anhydrous AlCl_3 , interacts strongly with the basic amino group of aniline. Nitrogen donates its lone pair to the Lewis acid, forming a salt-like coordination complex. This removes the lone pair from conjugation with the ring and makes the nitrogen-containing group strongly electron withdrawing. The aromatic ring is deactivated towards the electrophilic substitution needed for Friedel–Crafts alkylation or acylation. Thus aniline does not undergo the usual Friedel–Crafts reaction.

Step 3: (iii) Compare intermolecular attraction For comparable molecular masses, primary amines have higher boiling points than tertiary amines because primary amines contain $\text{N} - \text{H}$ bonds. A primary-amine molecule can donate a hydrogen bond to the nitrogen lone pair of another molecule, forming intermolecular $\text{N} - \text{H} \cdots \text{N}$ associations. Tertiary amines have no $\text{N} - \text{H}$ bond and cannot form such hydrogen bonds with one another in the pure liquid. More energy is needed to separate the hydrogen-bonded primary-amine molecules during boiling. Tertiary amines can nevertheless accept hydrogen bonds from water.

Step 4: Conclusion Aniline has higher pK_b because resonance reduces nitrogen-lone-pair availability. Its amino group binds the Friedel–Crafts Lewis-acid catalyst and deactivates the ring. Primary amines of comparable molecular mass boil higher because they form intermolecular hydrogen bonds, unlike pure tertiary amines.

Quick Tip to Solve: First ask whether the nitrogen lone pair is available; for boiling points, check for an $\text{N} - \text{H}$ bond that can donate intermolecular hydrogen bonds.

OR

9(b). (i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution: CH_3NH_2 , $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{NH}$

(ii) What is Hinsberg's reagent?

(iii) What is the role of pyridine in the acylation reaction of amines?

[3 marks]

Solution:

Concept:

- Basicity is the tendency of the nitrogen lone pair to accept a proton. In aqueous solution, electron donation by alkyl groups and hydration of the conjugate acid both affect basic strength.
- Hinsberg's reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, used to distinguish primary, secondary and tertiary amines.
- Acylation introduces an acyl group into an amine. Pyridine acts as a base to remove the hydrogen chloride formed when an acyl chloride is used.

Step 1: (i) Compare methylamines in water Methyl groups increase the availability of the nitrogen lone pair through their electron-releasing inductive effect. However, the protonated amine must also be stabilised by hydration. The bulky trimethylammonium ion is less effectively hydrated than the ions formed from primary and secondary methylamines. The secondary amine has a favourable

Quick Tip to Solve: For methylamines in water, remember the hydration-sensitive order tertiary < primary < secondary; name both the reagent and pyridine's acid-removing role explicitly.

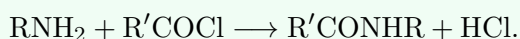
combination of electron donation and hydration. Thus, for these methylamines in aqueous solution, the increasing order is



Counting methyl groups alone would give the gas-phase tendency and would miss the solvent effect specified in the question.

Step 2: (ii) Name Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. It reacts with primary and secondary amines to form sulphonamide derivatives. Their different behaviour in alkali is useful in distinguishing amine classes; tertiary amines do not form these sulphonamides because they lack an N–H bond.

Step 3: (iii) Explain the role of pyridine Pyridine absorbs the HCl liberated during acylation, forming pyridinium chloride. For example,



If the acid accumulated, it would protonate the amine and decrease the availability of its lone pair for reaction. Pyridine therefore keeps the reaction medium basic and helps acylation proceed by removing the acid produced.

Step 4: Conclusion (i) $(\text{CH}_3)_3\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$; (ii) Hinsberg's reagent is $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$; (iii) pyridine removes the HCl formed during acylation as pyridinium chloride.

Quick Tip to Solve: For methylamines in water, remember the hydration-sensitive order tertiary < primary < secondary; name both the reagent and pyridine's acid-removing role explicitly.

10. A compound 'A' on reduction with iron scrap and hydrochloric acid gives compound 'B' with molecular formula $\text{C}_6\text{H}_7\text{N}$. Compound 'B' on reaction with CHCl_3 and alcoholic KOH produces an obnoxious smell of carbylamine due to the formation of 'C'. Identify 'A', 'B' and 'C' and write the chemical reactions involved. [3 marks]

Solution:

Concept:

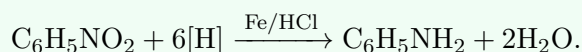
- Iron and hydrochloric acid reduce a nitro group, $-\text{NO}_2$, to a primary amino group, $-\text{NH}_2$, while retaining the carbon skeleton.
- The carbylamine test is given by primary amines. Heating a primary amine with chloroform and alcoholic potassium hydroxide forms a foul-smelling isocyanide, $\text{R}-\text{NC}$.

Step 1: Identify the amine B The molecular formula of B is $\text{C}_6\text{H}_7\text{N}$. Its positive carbylamine test establishes that it is a primary amine. Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, has exactly this molecular formula and contains a primary amino group attached to a benzene ring. Therefore B is aniline. A secondary or tertiary amine cannot explain the specified carbylamine reaction.

Step 2: Identify A and write the reduction The corresponding nitro compound is nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$. Reduction with iron scrap and hydrochloric acid converts its nitro group to the amino

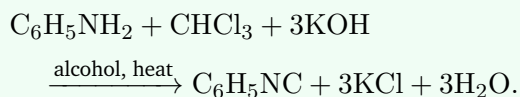
Quick Tip to Solve: A positive carbylamine test fixes the amine as primary; preserve its carbon skeleton when tracing back to the nitro compound and write the product as $\text{R}-\text{NC}$.

group of aniline:



Here $[\text{H}]$ denotes reducing hydrogen equivalents supplied by the reducing system. In the acidic reaction mixture the amine can occur as its anilinium salt; liberation of the free base gives aniline. The net reduction consumes six hydrogen equivalents and removes the two oxygen atoms as water.

Step 3: Identify C and write the carbylamine reaction Aniline reacts with chloroform and alcoholic potassium hydroxide on heating to form phenyl isocyanide, also called phenyl carbylamine:



The product has connectivity $\text{C}_6\text{H}_5 - \text{N} \equiv \text{C}$, so it is an isocyanide rather than benzonitrile, whose group is $-\text{C} \equiv \text{N}$. Formation of this isocyanide accounts for the obnoxious smell observed in the test.

Step 4: Conclusion A is nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$; B is aniline, $\text{C}_6\text{H}_5\text{NH}_2$; and C is phenyl isocyanide, $\text{C}_6\text{H}_5\text{NC}$.

Quick Tip to Solve: A positive carbylamine test fixes the amine as primary; preserve its carbon skeleton when tracing back to the nitro compound and write the product as $\text{R}-\text{NC}$.

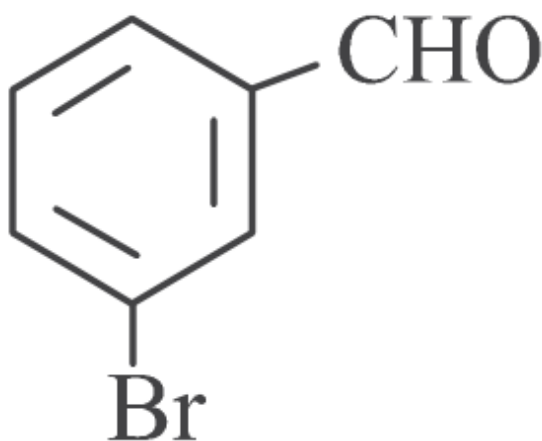
11(a). Complete the following:

(i) $\text{CH}_3\text{CN} \xrightarrow[2. \text{H}_2\text{O}]{1. \text{AlH}(\text{i-Bu})_2} \text{A} \xrightarrow[\text{H}^+]{\text{H}_2\text{N}-\text{OH}} \text{B}$. Identify A and B.

(ii) Write IUPAC name of the following compound:

(iii) Write chemical test to distinguish between the following compounds: Phenol and Benzoic acid.

[3 marks]



Solution:

Concept:

- DIBAL-H, $\text{AlH}(i\text{-Bu})_2$, partially reduces a nitrile; hydrolysis then gives the corresponding aldehyde with the same number of carbon atoms.
- Aldehydes condense with hydroxylamine, NH_2OH , to form oximes by elimination of water.
- Benzoic acid is sufficiently acidic to liberate carbon dioxide from aqueous sodium hydrogen carbonate, whereas phenol is not.

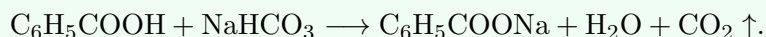
Step 1: (i) Identify the aldehyde and its oxime The nitrile carbon of CH_3CN becomes the aldehyde carbon after partial reduction and hydrolysis. Thus A is ethanal, CH_3CHO . Hydroxylamine reacts at the carbonyl group to produce B, ethanal oxime:



The oxime contains a carbon-nitrogen double bond; it is not an alcohol formed by further reduction.

Step 2: (ii) Name the substituted aromatic aldehyde The principal group is $-\text{CHO}$, so use benzaldehyde as the parent. Number the ring carbon attached to this group as 1 and choose the direction giving the bromine substituent the smaller locant. Bromine is on carbon 3, the meta position. The IUPAC name is 3-bromobenzaldehyde.

Step 3: (iii) Apply the sodium hydrogen carbonate test Add aqueous NaHCO_3 to separate samples. Benzoic acid gives brisk effervescence of CO_2 , whereas phenol gives no effervescence:



Benzoic acid is stronger than carbonic acid and displaces it from its salt. Phenol is weaker than carbonic acid, so it does not liberate this gas.

Step 4: Conclusion (i) A: ethanal, CH_3CHO ; B: ethanal oxime, $\text{CH}_3\text{CH}=\text{NOH}$. (ii) 3-bromobenzaldehyde. (iii) Aqueous NaHCO_3 gives CO_2 effervescence with benzoic acid and none with phenol.

Quick Tip to Solve: Preserve the nitrile carbon when finding A; for the ring name, start numbering at the carbon attached to CHO .

11(b). Convert the following:

(i) Benzoic acid to Benzaldehyde

(ii) Propan-1-ol to 2-Bromopropanoic acid

(iii) Acetaldehyde to But-2-enal

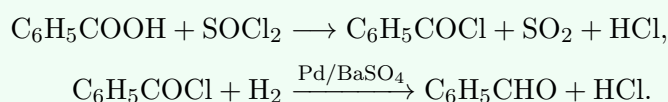
[3 marks]

Solution:

Concept:

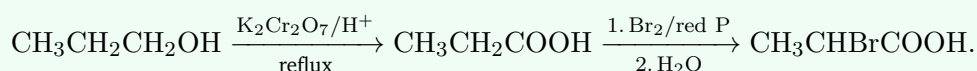
- Rosenmund reduction converts an acid chloride to an aldehyde using hydrogen and poisoned palladium on barium sulphate.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by bromine using Br_2 and red phosphorus, followed by hydrolysis.
- An aldehyde with alpha hydrogens undergoes aldol addition with dilute alkali; heating dehydrates the aldol to an alpha,beta-unsaturated aldehyde.

Step 1: (i) Benzoic acid to benzaldehyde First convert benzoic acid into benzoyl chloride using thionyl chloride. Then carry out Rosenmund reduction:



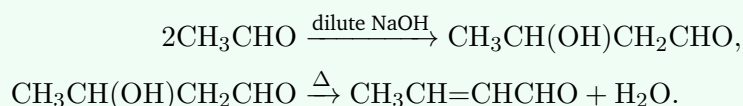
The poisoned catalyst limits reduction to the aldehyde. Direct strong reduction of the acid would instead give benzyl alcohol.

Step 2: (ii) Propan-1-ol to 2-bromopropanoic acid Oxidise the primary alcohol completely with acidified potassium dichromate under reflux. Brominate the resulting propanoic acid at its alpha carbon by the HVZ reaction:



The carbon next to $-\text{COOH}$ is carbon 2; hence alpha bromination gives the requested product without changing the three-carbon skeleton.

Step 3: (iii) Acetaldehyde to but-2-enal Treat ethanal with dilute sodium hydroxide to join two molecules by aldol addition. Heat the 3-hydroxybutanal obtained to remove water:



Numbering from the aldehyde carbon puts the double bond between carbons 2 and 3, so the dehydration product is but-2-enal.

Step 4: Conclusion (i) Benzoic acid $\rightarrow$ benzoyl chloride $\rightarrow$ benzaldehyde by Rosenmund reduction. (ii) Propan-1-ol $\rightarrow$ propanoic acid $\rightarrow$ 2-bromopropanoic acid by HVZ bromination. (iii) Acetaldehyde $\rightarrow$ 3-hydroxybutanal $\rightarrow$ but-2-enal by aldol condensation.

Quick Tip to Solve: Use selective reduction for the aldehyde, alpha bromination for the acid, and two ethanal molecules for the four-carbon enal.

Section C (5 marks)

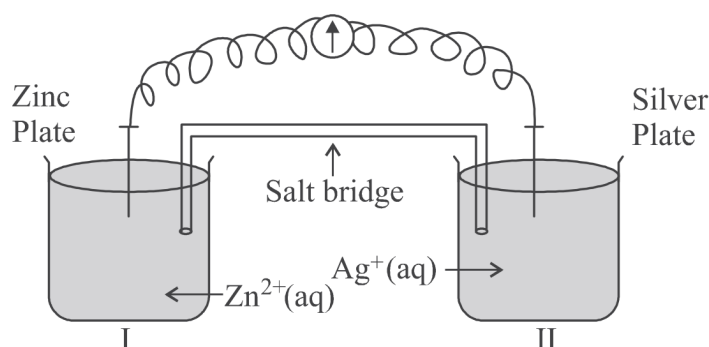
12(a). Read the passage given below and answer the questions that follow:

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E_{cell}° is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+} . This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by k and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.

Is silver plate the anode or cathode?

[1 mark]



Solution:

Concept:

- Oxidation occurs at the anode and reduction occurs at the cathode in every electrochemical cell.
- In the zinc-silver galvanic cell, zinc supplies electrons and silver ions accept them.

Step 1: Identify the source of electrons Zinc is oxidised in compartment I: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$. Electrons travel through the external wire from the zinc plate towards the silver plate.

Step 2: Identify the process at the silver plate Silver ions in compartment II gain these electrons and deposit as silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)}$. This is reduction, so the silver electrode is the cathode. It is the positive electrode of this spontaneously operating galvanic cell; it cannot be the anode because

Quick Tip to Solve: Follow electron gain at the silver plate: reduction always identifies the cathode, regardless of electrode sign.

silver ions are being reduced there.

Step 3: Conclusion The silver plate is the cathode; Ag^+ ions are reduced here.

Quick Tip to Solve: Follow electron gain at the silver plate: reduction always identifies the cathode, regardless of electrode sign.

12(b). What will happen if the salt bridge is removed?

[1 mark]

Solution:

Concept:

- The salt bridge completes the internal ionic circuit and maintains electrical neutrality in both half-cells.
- In this cell, zinc is oxidised to Zn^{2+} , while Ag^+ ions are reduced to silver.

Step 1: Examine the charge balance At the zinc electrode, oxidation produces positive ions in solution: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$. At the silver electrode, reduction removes positive ions: $\text{Ag}^+ + e^- \rightarrow \text{Ag}$. Ions from the salt bridge normally compensate these changes.

Step 2: Remove the ionic connection Without the salt bridge, positive charge accumulates in the zinc half-cell and excess negative charge develops in the silver half-cell. This charge separation opposes further electron transfer. The internal ionic circuit is interrupted, so sustained current cannot flow through the external wire.

Step 3: Conclusion The cell stops supplying sustained current when the salt bridge is removed, because electrical neutrality cannot be maintained in the half-cells.

Quick Tip to Solve: Remember that the wire carries electrons, while the salt bridge supplies the necessary ionic connection.

12(c). When does electrochemical cell behaves like an electrolytic cell?

[1 mark]

Solution:

Concept:

- A galvanic cell converts the energy of a spontaneous redox reaction into electrical energy.
- An electrolytic cell uses an external electrical source to drive a non-spontaneous reaction.

Step 1: Apply an opposing external voltage Connect an external source so that its potential opposes the natural cell potential E_{cell} . At an opposing potential equal to the cell emf, the net driving potential is zero and the cell current ceases.

Step 2: Increase the opposing voltage If the applied opposing potential becomes greater than the cell emf, current is forced in the reverse direction. The original galvanic reaction is reversed: electrical energy is consumed to drive a reaction that would not proceed spontaneously in that direction. The cell therefore operates as an electrolytic cell.

Step 3: Conclusion An electrochemical (galvanic) cell behaves as an electrolytic cell when an external

Quick Tip to Solve: Compare the opposing voltage with the cell emf: equality stops current; a larger voltage reverses it.

opposing potential greater than its cell emf is applied.

Quick Tip to Solve: Compare the opposing voltage with the cell emf: equality stops current; a larger voltage reverses it.

12(d). (i) What will happen to the concentration of Zn^{2+} and Ag^+ when $E_{\text{cell}} = 0$?

(ii) Why does conductivity of a solution decreases with dilution?

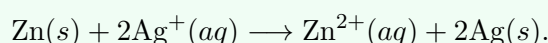
[2 marks]

Solution:

Concept:

- For a cell reaction, $\Delta G = -nFE_{\text{cell}}$; thus $E_{\text{cell}} = 0$ corresponds to equilibrium.
- Conductivity κ measures the ability of a unit volume of solution to conduct electricity and depends on the number of mobile ions per unit volume.

Step 1: Part (i): identify equilibrium The reaction of the zinc-silver cell is



During spontaneous operation, Zn^{2+} concentration increases and Ag^+ concentration decreases. When $E_{\text{cell}} = 0$, the reaction reaches equilibrium and there is no net progress of this reaction. Hence the concentrations of both ions remain constant at their equilibrium values; neither is required to become zero or equal to the other.

Step 2: Part (ii): consider dilution Adding solvent spreads the dissolved ions through a larger volume. The number of ions available to carry charge per unit volume decreases, so the conductivity of the solution decreases. This remains the relevant concentration effect even though dilution can increase ionic mobility or, for a weak electrolyte, the degree of ionisation. Conductivity must be distinguished from molar conductivity, which generally increases on dilution.

Step 3: Conclusion (i) The concentrations of Zn^{2+} and Ag^+ remain constant at equilibrium. (ii) Conductivity decreases on dilution because the number of conducting ions per unit volume decreases.

Quick Tip to Solve: At zero cell emf, think equilibrium; for conductivity, count ions per unit volume, not per mole.

OR

12(d). The molar conductivity of a 1.5 M solution of an electrolyte is found to be $138.9 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity of this solution.

[2 marks]

Solution:

Concept:

- Molar conductivity is related to conductivity by $\Lambda_m = 1000\kappa/C$, when C is in mol L^{-1} , κ in S cm^{-1} , and Λ_m in $\text{S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: With molarity in mol per litre and conductivity in S per centimetre, use $\kappa = \text{molar conductivity} \times C \text{ divided by } 1000$.

- The factor 1000 converts litres to cubic centimetres, since $1 \text{ L} = 1000 \text{ cm}^3$.

Step 1: Write the given data and rearrange The concentration is $C = 1.5 \text{ mol L}^{-1}$ and the molar conductivity is $\Lambda_m = 138.9 \text{ S cm}^2 \text{ mol}^{-1}$. Rearranging the relation gives

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

Equivalently, the concentration per cubic centimetre is $1.5/1000 \text{ mol cm}^{-3}$, which can be multiplied directly by the molar conductivity.

Step 2: Substitute and check the units

$$\begin{aligned}\kappa &= \frac{138.9 \times 1.5}{1000} \\ &= \frac{208.35}{1000} \\ &= 0.20835 \text{ S cm}^{-1}.\end{aligned}$$

The units also agree: $(\text{S cm}^2 \text{ mol}^{-1})(\text{mol cm}^{-3}) = \text{S cm}^{-1}$. The concentration is given in molarity, so omitting the conversion factor would make the conductivity a thousand times too large.

Step 3: Conclusion The conductivity of the solution is $\kappa = 0.20835 \text{ S cm}^{-1}$ (approximately 0.208 S cm^{-1}).

Quick Tip to Solve: With molarity in mol per litre and conductivity in S per centimetre, use $\kappa = \text{molar conductivity times } C \text{ divided by } 1000$.