

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-3-2

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 is divided into **three** Sections – Section **A**, **B** and **C**.
- (iii) **Section - A** Q. Nos. **1** to **3** are very short answer type questions carrying **2** marks each.
- (iv) **Section - B** Q. Nos. **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)

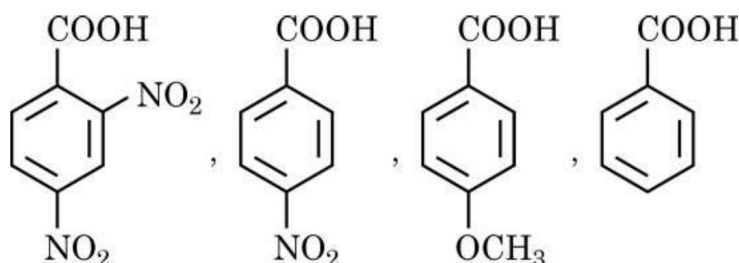
1. Arrange the following compounds in increasing order of their property as indicated in bracket: (Any two)

(i) $\text{CH}_3\text{-CHO}$, $\text{CH}_3\text{-CO-CH}_3$, $\text{CH}_3\text{-CO-C(CH}_3)_3$ (reactivity towards HCN)

(ii) $\text{CCl}_3\text{-COOH}$, $\text{CF}_3\text{-COOH}$, $(\text{CH}_3)_3\text{C-COOH}$ (acid strength)

(iii) (acid strength)

[2 marks]

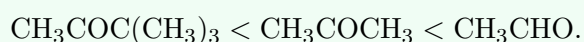


Solution:

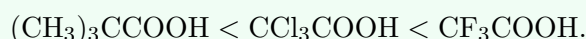
Concept:

- HCN adds through nucleophilic attack of CN^- on the carbonyl carbon. Greater electrophilicity and less steric hindrance favour attack.
- Electron-withdrawing groups stabilise a carboxylate ion and increase acid strength; electron-donating groups generally decrease it.

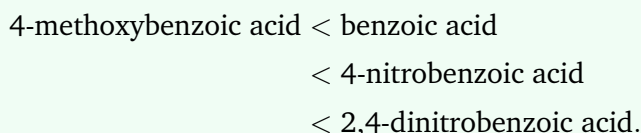
Step 1: (i) Carbonyl reactivity towards HCN The tert-butyl group hinders cyanide attack more than methyl. Alkyl electron donation also reduces carbonyl electrophilicity. Ethanal, with only one alkyl group and a small hydrogen atom, is least hindered and most electrophilic. The increasing order is



Step 2: (ii) Aliphatic acid strength The tert-butyl +I effect destabilises carboxylate. Trihalomethyl groups stabilise it by electron withdrawal (-I); more electronegative fluorine makes this effect stronger for CF_3 . Thus



Step 3: (iii) Aromatic acid strength Para methoxy resonance donation outweighs inductive withdrawal, making its acid weaker than benzoic acid. Nitro groups withdraw electrons through both inductive and resonance effects and stabilise benzoate. Two nitro groups increase acidity more than one, with the ortho substituent providing an additional ortho effect. Hence



Step 4: Conclusion (i) Bulky ketone < acetone < ethanal; (ii) tert-butyl acid < trichloroacetic

Quick Tip to Solve: For HCN addition compare crowding first; for acid strength compare how the substituent stabilises the conjugate base.

acid < trifluoroacetic acid; (iii) p-methoxybenzoic acid < benzoic acid < p-nitrobenzoic acid < 2,4-dinitrobenzoic acid. Any two orders suffice.

Quick Tip to Solve: For HCN addition compare crowding first; for acid strength compare how the substituent stabilises the conjugate base.

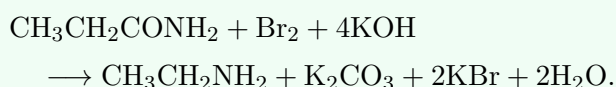
2. An Organic compound (A) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (B). Compound (B) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (C) and on reacting with $C_6H_5SO_2Cl$ forms a compound (D) which is soluble in alkali. Write the structures of (A), (B), (C) and (D). [2 marks]

Solution:

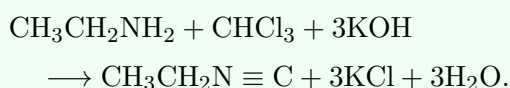
Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ to RNH_2 , removing the carbonyl carbon.
- A primary amine gives an offensive-smelling isocyanide in the carbylamine test and an alkali-soluble sulphonamide in the Hinsberg test.

Step 1: Identify A and B from bromamide degradation Since A reacts with bromine and KOH to form an amine, A is a primary amide. Its molecular formula C_3H_7NO identifies it as propanamide, $CH_3CH_2C(=O)NH_2$. Removal of its carbonyl carbon gives ethanamine, B, $CH_3CH_2NH_2$:

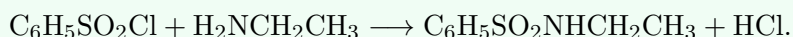


Step 2: Identify the carbylamine product C Ethanamine is a primary amine and gives ethyl isocyanide on heating with chloroform and alcoholic KOH :



Thus C is $CH_3CH_2N \equiv C$. The ethyl group is bonded to nitrogen; the product is an isocyanide, not the nitrile with an ethyl-carbon bond.

Step 3: Identify the Hinsberg product D Ethanamine reacts with benzenesulphonyl chloride to give N-ethylbenzenesulphonamide:



Therefore D has structure $C_6H_5S(=O)_2NHCH_2CH_3$. It retains an N-H bond, whose hydrogen is acidic because the sulphonyl group withdraws electrons. Alkali removes this proton, producing an ionic, soluble salt and explaining the stated solubility.

Step 4: Conclusion A is propanamide, $CH_3CH_2CONH_2$; B is ethanamine, $CH_3CH_2NH_2$.

C is ethyl isocyanide, $CH_3CH_2N \equiv C$; D is N-ethylbenzenesulphonamide, $C_6H_5SO_2NHCH_2CH_3$.

Quick Tip to Solve: Count one fewer carbon after Hofmann degradation, and write the isocyanide as R-N-C rather than R-C-N.

3. Define conductivity for the solution of an electrolyte. Why does the conductivity of a solution decrease with dilution? [2 marks]

Solution:

Concept:

- Conductivity κ is the reciprocal of resistivity: $\kappa = 1/\rho$. It measures the ability of a solution to conduct current per unit geometry.
- Current in an electrolyte is carried by ions; conductivity depends on the number of ions per unit volume as well as their charge and mobility.

Step 1: Define the conductivity of an electrolyte solution Conductivity is the conductance of a solution column of unit length and unit cross-sectional area. If the electrode separation is l , the area is A , and resistance is R , then

$$R = \rho \frac{l}{A}, \quad \kappa = \frac{1}{\rho} = \frac{l}{RA} = G \frac{l}{A},$$

where $G = 1/R$ is conductance. Equivalently, using centimetre units it is the conductance of the solution between electrodes one centimetre apart and of area one square centimetre. Its SI unit is S m^{-1} ; S cm^{-1} is also commonly used.

Step 2: Explain why dilution lowers conductivity Adding solvent increases the solution volume and lowers the concentration of ions, so fewer charge carriers occupy each unit volume. This lowers the current transported under the same applied electric field and hence lowers κ . For a weak electrolyte, dilution also increases its degree of ionisation; nevertheless, the number of ions per unit volume decreases overall. The distinction is between conductivity and molar conductivity: dilution can increase the conducting ability per mole while reducing the conducting ability per unit volume. Thus the observed decrease refers to conductivity, not molar conductivity.

Step 3: Conclusion Conductivity is the conductance of a unit-length, unit-area solution column, or the reciprocal of resistivity. It decreases on dilution because the number of ions carrying charge per unit volume decreases.

Quick Tip to Solve: Associate conductivity with ions per unit volume; associate molar conductivity with the conducting ability per mole.

Section B (24 marks)

4. Account for the following:

- Cr^{2+} is a strong reducing agent.
- Ti^{3+} is coloured whereas Sc^{3+} is colourless in aqueous solution.
- Zn , Cd and Hg are not called transition elements.

[3 marks]

Solution:

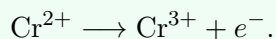
Concept:

- A reducing agent loses electrons and is itself oxidised. A stable resulting oxidation state favours this electron loss.

Quick Tip to Solve: Remove outer s electrons before d electrons when writing metal-ion configurations, then check the d-electron count.

- Ligands split d orbitals into different energy levels; absorption of visible light for a d–d transition produces colour in an ion with suitable d electrons.
- A transition element has an incompletely filled d subshell in its atom or in a commonly formed ion.

Step 1: (i) Explain the reducing nature of chromium(II) Chromium has $[\text{Ar}] 3d^5 4s^1$, so Cr^{2+} is $[\text{Ar}] 3d^4$. It readily loses an electron:



The product Cr^{3+} has the stable $3d^3$ configuration. In its octahedral aqueous complex, the three electrons singly occupy the lower-energy t_{2g} orbitals, giving t_{2g}^3 . The tendency to attain this stable state makes Cr^{2+} a strong reducing agent.

Step 2: (ii) Compare titanium(III) and scandium(III) Titanium is $[\text{Ar}] 3d^2 4s^2$, hence Ti^{3+} is $[\text{Ar}] 3d^1$. Its single d electron can absorb visible light and move between ligand-split d levels, so its aqueous ion is coloured. Scandium is $[\text{Ar}] 3d^1 4s^2$, hence Sc^{3+} is $[\text{Ar}] 3d^0$. With no d electron available for a d–d transition, its aqueous ion is colourless.

Step 3: (iii) Apply the definition of a transition element Zn, Cd and Hg atoms have configurations ending in $3d^{10} 4s^2$, $4d^{10} 5s^2$ and $5d^{10} 6s^2$, respectively. Their usual divalent ions lose the two outer s electrons and retain $3d^{10}$, $4d^{10}$ and $5d^{10}$. Thus their atoms and commonly formed ions have completely filled d subshells. Being in the d block alone does not satisfy the definition of a transition element.

Step 4: Conclusion Cr^{2+} readily forms stable Cr^{3+} ; Ti^{3+} is coloured because it is d^1 , whereas Sc^{3+} is colourless because it is d^0 . Zn, Cd and Hg are excluded from transition elements because their d subshells remain completely filled.

Quick Tip to Solve: Remove outer s electrons before d electrons when writing metal-ion configurations, then check the d-electron count.

5(a). Differentiate between the following:

(i) Adsorption and Absorption

(ii) Lyophobic Sol and Lyophilic Sol

(iii) Multimolecular Colloid and Macromolecular colloid.

[3 marks]

Solution:

Concept:

- Adsorption is accumulation at a surface, whereas absorption involves entry into the bulk of a substance.
- Colloids can be classified by affinity between dispersed phase and dispersion medium, and by the nature of their dispersed particles.

Step 1: (i) Adsorption and absorption In adsorption, molecules accumulate only on the surface of an adsorbent; it is a surface phenomenon. The concentration of the adsorbed substance is consequently greater at the surface than in the interior. For example, activated charcoal adsorbs gases on its surface. In absorption, a substance enters and is distributed throughout the bulk of another substance; it is a

Quick Tip to Solve: For each comparison, state the defining difference first and attach one example to each side.

bulk phenomenon. For example, anhydrous calcium chloride absorbs water. Thus the distinguishing feature is the location of the substance: surface accumulation versus penetration into the whole material.

Step 2: (ii) Lyophobic and lyophilic sols A lyophobic sol has little affinity between its dispersed phase and dispersion medium. It generally needs special preparation, is relatively unstable, and is readily coagulated by small quantities of electrolytes. Once precipitated, it does not readily reform simply by mixing with the medium; examples include gold and arsenic sulphide sols in water. A lyophilic sol has appreciable affinity between the dispersed phase and medium. It forms readily by mixing, is more stable, and is reversible: after separating the dispersed material, the sol can be formed again by adding the medium. Starch and gum sols in water are examples.

Step 3: (iii) Multimolecular and macromolecular colloids A multimolecular colloidal particle is an aggregate of many atoms or small molecules held together, commonly by van der Waals forces. The individual atoms or molecules are smaller than colloidal dimensions, but their aggregate lies in the colloidal size range; gold sol and sulphur sol are examples. In a macromolecular colloid, each dispersed particle is itself one large molecule whose dimensions fall within the colloidal range. Such molecules form colloidal solutions in suitable media; starch, proteins and cellulose are examples. Aggregation of many small units distinguishes the first type from a single large molecule in the second.

Step 4: Conclusion Adsorption occurs at a surface and absorption throughout the bulk. Lyophobic sols have little affinity for the medium and lower stability, while lyophilic sols have strong affinity and greater stability. Multimolecular particles are aggregates of small species, whereas macromolecular particles are individual giant molecules.

Quick Tip to Solve: For each comparison, state the defining difference first and attach one example to each side.

OR

5(b). (I) Define the following terms:

(i) Zeta Potential

(ii) Coagulation

(II) Why a negatively charged sol is obtained when AgNO_3 solution is added to KI solution? [3 marks]

Solution:

Concept:

- Colloidal particles acquire charge by preferential adsorption of ions; counterions form an electrical double layer around them.
- Zeta potential is associated with the fixed and diffused parts of the electrical double layer. Like charges help keep sol particles dispersed.
- Coagulation occurs when particles aggregate and separate from the dispersion medium after their stabilising charge is neutralised.

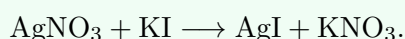
Step 1: (I)(i) Define zeta potential Zeta potential, or electrokinetic potential, is the potential difference

Quick Tip to Solve: Identify the reagent in excess: KI supplies adsorbed iodide and gives a negative AgI sol, whereas excess silver nitrate gives a positive sol.

between the fixed layer and the diffused layer of opposite charges surrounding a colloidal particle. The fixed layer accompanies the particle, whereas the diffused layer contains more mobile counterions. This electrical double layer explains why equally charged particles repel one another and why a charged sol remains dispersed.

Step 2: (I)(ii) Define coagulation Coagulation is the process of precipitation of colloidal particles by their aggregation into larger particles. When the stabilising charge is neutralised, repulsion between particles decreases; the particles come together and separate out as a precipitate. A suitable electrolyte can cause coagulation because its oppositely charged ions neutralise the charge on the sol particles.

Step 3: (II) Explain the negative silver iodide sol Adding silver nitrate solution to potassium iodide solution produces silver iodide:



Since silver nitrate is added to potassium iodide, iodide ions are present in excess in the dispersion medium. The freshly formed AgI particles preferentially adsorb I^- , an ion common to silver iodide. This adsorption gives the particles a negative charge. Potassium ions form the counterion layer around these negatively charged particles. Thus, adsorption of iodide explains the charge; the neutral chemical formula of AgI alone does not.

Step 4: Conclusion Zeta potential is the potential difference between the fixed and diffused layers; coagulation is aggregation and precipitation of colloidal particles. The AgI sol is negatively charged because its particles preferentially adsorb excess I^- from KI solution.

Quick Tip to Solve: Identify the reagent in excess: KI supplies adsorbed iodide and gives a negative AgI sol, whereas excess silver nitrate gives a positive sol.

6(a). What happens when

(i) Propanone is treated with CH_3MgBr and then hydrolysed?

(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction?

[3 marks]

Solution:

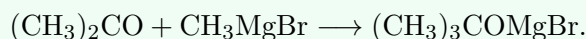
Concept:

- A Grignard reagent adds its alkyl group to the carbonyl carbon; hydrolysis of the resulting magnesium alkoxide gives an alcohol.
- An aldehyde reacts with excess alcohol in the presence of an acid catalyst to form an acetal and water.
- Aldehydes without an α hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is reduced and another is oxidised.

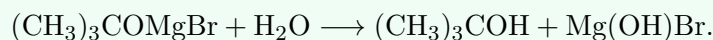
Step 1: (i) React propanone with methylmagnesium bromide In dry ether, the methyl group of CH_3MgBr adds to the electrophilic carbonyl carbon of propanone. The two methyl groups already

Quick Tip to Solve: Track the carbonyl carbon: Grignard adds a methyl group, excess ethanol replaces oxygen by two ethoxy groups, and Cannizzaro gives one alcohol and one carboxylate.

attached to this carbon remain intact, so the intermediate is a tertiary magnesium alkoxide:

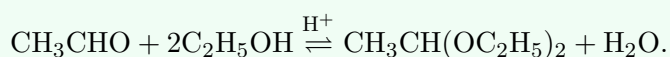


Hydrolysis protonates the oxygen and forms 2-methylpropan-2-ol (tert-butyl alcohol):



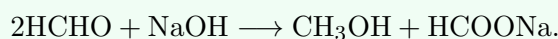
Water is added only after the Grignard addition, since it would otherwise destroy the reagent.

Step 2: (ii) React ethanal with excess ethanol and acid Ethanal first forms a hemiacetal with ethanol. In excess ethanol and with an acid catalyst, the hemiacetal reacts further, replacing its hydroxyl group by a second ethoxy group. The acetal product is 1,1-diethoxyethane:



Excess ethanol favours acetal formation in this reversible reaction. Both ethoxy groups attach to the carbon that originally carried the aldehyde oxygen.

Step 3: (iii) Carry out the Cannizzaro reaction of methanal Methanal has no alpha carbon and therefore no alpha hydrogen. With concentrated sodium hydroxide, it undergoes self-oxidation and reduction. One methanal molecule is reduced to methanol while another is oxidised to sodium methanoate:

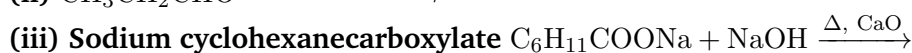
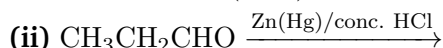
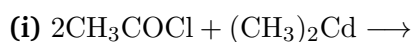


The alkaline reaction mixture contains the carboxylate salt, not free methanoic acid. The two carbon-containing products occur in equal molar amounts.

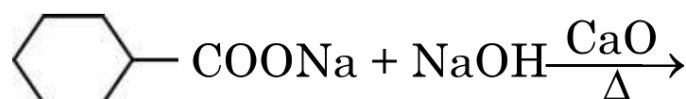
Step 4: Conclusion The products are (i) 2-methylpropan-2-ol, $(\text{CH}_3)_3\text{COH}$; (ii) the acetal 1,1-diethoxyethane, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$; and (iii) methanol and sodium methanoate, CH_3OH and HCOONa .

Quick Tip to Solve: Track the carbonyl carbon: Grignard adds a methyl group, excess ethanol replaces oxygen by two ethoxy groups, and Cannizzaro gives one alcohol and one carboxylate.

6(b). Write the main product in the following reactions:



[3 marks]



Solution:

Concept:

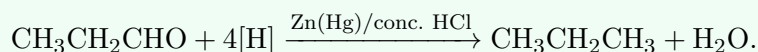
- Dialkylcadmium reacts with acyl chlorides to give ketones: each alkyl group replaces chlorine in an acyl chloride.
- Clemmensen reduction with zinc amalgam and concentrated hydrochloric acid converts $-\text{CHO}$ into $-\text{CH}_3$.
- Soda lime decarboxylates sodium carboxylates on heating: $\text{RCOONa} + \text{NaOH} \longrightarrow \text{RH} + \text{Na}_2\text{CO}_3$.

Step 1: (i) Reaction with dimethylcadmium The acyl chloride is ethanoyl chloride and the transferred alkyl group is methyl. Combining $\text{CH}_3\text{CO}-$ with $-\text{CH}_3$ forms propanone. Both methyl groups of one dimethylcadmium molecule are used:



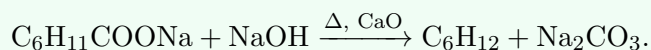
The reagent gives a ketone without further addition to the carbonyl group.

Step 2: (ii) Clemmensen reduction of propanal Reduction removes the aldehyde oxygen while retaining the three-carbon skeleton. The terminal aldehyde carbon becomes a methyl carbon:



Here $[\text{H}]$ denotes reducing hydrogen equivalents. The organic product is an alkane; these reagents do not stop at the alcohol stage.

Step 3: (iii) Soda-lime decarboxylation The printed ring is saturated, so the salt is sodium cyclohexanecarboxylate, $\text{C}_6\text{H}_{11}\text{COONa}$. Heating with soda lime removes the carboxyl carbon as carbonate and replaces the carboxylate substituent with hydrogen:



All six ring carbons remain. No double bond is introduced, so the product is cyclohexane.

Step 4: Conclusion The main products are (i) propanone, CH_3COCH_3 ; (ii) propane, $\text{CH}_3\text{CH}_2\text{CH}_3$; and (iii) cyclohexane, C_6H_{12} .

Quick Tip to Solve: Cadmium adds methyl, Clemmensen preserves the carbon skeleton, and soda lime removes only the carboxyl carbon.

7. What is Lanthanoid contraction? What is the cause of Lanthanoid contraction? Write two consequences of Lanthanoid contraction. [3 marks]

Solution:

Concept:

- Lanthanoids involve progressive filling of the $4f$ subshell, whose electrons shield the nuclear charge poorly.
- Greater effective nuclear charge draws the electron cloud closer to the nucleus; the comparable ionic radii are those of Ln^{3+} ions.

Step 1: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic radii and, especially, the radii of trivalent lanthanoid ions Ln^{3+} , with increasing atomic number from lanthanum to lutetium. Thus successive members have slightly smaller sizes rather than the increase one might expect merely from adding electrons.

Step 2: Explain its cause As atomic number increases, an additional proton increases the nuclear charge, while the differentiating electron enters the inner $4f$ subshell. The $4f$ electrons shield one another poorly from the nucleus. Their added shielding cannot fully compensate for the increase in nuclear charge. Consequently, the effective nuclear attraction felt by the electrons rises across the series, drawing the electron cloud inward and decreasing the radius.

Step 3: State two consequences (1) The elements of the second and third transition series have very similar radii. For example, zirconium and hafnium have nearly equal sizes because the intervening lanthanoid contraction offsets the size increase expected on entering the next period. As a result, Zr and Hf have closely similar chemical properties and are difficult to separate.

(2) The basic character of lanthanoid hydroxides decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. As the Ln^{3+} ion becomes smaller, its charge density and polarising power increase. The metal–oxygen bond acquires greater covalent character, and the hydroxide becomes less basic.

Step 4: Conclusion Lanthanoid contraction is the gradual size decrease caused by poor shielding by $4f$ electrons. Two consequences are the similarity of Zr and Hf and the decreasing basicity of lanthanoid hydroxides across the series.

Quick Tip to Solve: Link the chain explicitly: poor $4f$ shielding increases effective nuclear attraction, reducing size and increasing polarising power.

8(a). (i) Which acid of the following pair would you expect to be stronger?

F-CH₂-COOH or CH₃-COOH

(ii) Arrange the following compounds in increasing order of their boiling points:

CH₃CH₂OH, CH₃-CHO, CH₃-COOH

(iii) Give simple chemical test to distinguish between Benzaldehyde and Acetophenone.

[3 marks]

Solution:

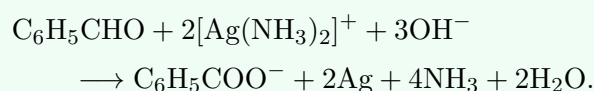
Concept:

- Electron-withdrawing groups increase carboxylic acid strength by stabilising the conjugate carboxylate ion through the negative inductive effect.
- Boiling point increases with intermolecular attraction. Alcohols form hydrogen bonds; carboxylic acids form strongly hydrogen-bonded dimers.
- Tollens' reagent is ammoniacal silver nitrate. Aldehydes reduce it to metallic silver while being oxidised to carboxylate ions; ordinary ketones do not.

Step 1: (i) Compare the acid strengths Fluorine in FCH₂COOH withdraws electron density through sigma bonds. Its $-I$ effect stabilises the negative charge of FCH₂COO⁻, favouring loss of H⁺. The methyl group in ethanoic acid has a $+I$ effect and does not provide this stabilisation. Thus fluoroethanoic acid dissociates more readily and is stronger.

Step 2: (ii) Compare intermolecular attractions Ethanal has dipole-dipole attractions but lacks an O – H bond, so its molecules cannot hydrogen-bond with one another. Ethanol forms intermolecular hydrogen bonds. Ethanoic acid forms dimers held by two hydrogen bonds, giving stronger association and requiring more energy to separate molecules into vapour. Hence boiling points increase from ethanal to ethanol to ethanoic acid.

Step 3: (iii) Perform Tollens' test Warm separate samples with freshly prepared Tollens' reagent in clean test tubes. Benzaldehyde gives a silver mirror on the inner wall; acetophenone gives no silver mirror. Benzaldehyde is oxidised to benzoate in this alkaline medium:



Acetophenone is a ketone and does not reduce this reagent. Fehling's test is unsuitable here because benzaldehyde, an aromatic aldehyde, does not give the usual positive Fehling's test.

Step 4: Conclusion (i) FCH₂COOH is stronger. (ii) CH₃CHO < CH₃CH₂OH < CH₃COOH is the increasing boiling point order. (iii) Benzaldehyde gives a silver mirror with Tollens' reagent; acetophenone does not.

Quick Tip to Solve: Choose Tollens' test for this pair: aromatic benzaldehyde gives a silver mirror even though its Fehling's test is negative.

8(b). (i) Which will undergo faster nucleophilic addition reaction? Acetaldehyde or Propanone

(ii) What is the composition of Fehling's reagent?

(iii) Draw structure of the semicarbazone of Ethanal.

[3 marks]

Solution:

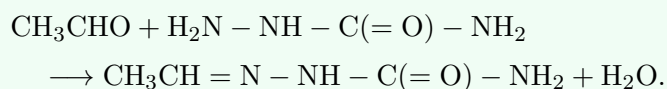
Concept:

- Nucleophiles attack the electrophilic carbonyl carbon. Electron-releasing alkyl groups and steric crowding both reduce the rate of nucleophilic addition.
- Fehling's reagent is freshly made by mixing aqueous copper(II) sulphate with an alkaline solution of sodium potassium tartrate.
- Semicarbazide, $\text{H}_2\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, condenses with a carbonyl compound through its terminal hydrazino $-\text{NH}_2$ group, eliminating water to form a semicarbazone.

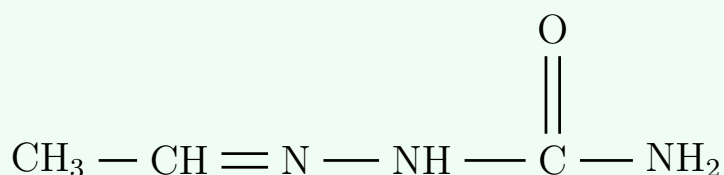
Step 1: (i) Compare acetaldehyde and propanone Acetaldehyde has one methyl group and one hydrogen attached to its carbonyl carbon; propanone has two methyl groups. The two methyl groups of propanone donate electron density by their $+I$ effect, decreasing the positive character of the carbonyl carbon. They also hinder nucleophilic approach more than the smaller hydrogen atom. Both the electronic and steric factors favour faster nucleophilic addition to acetaldehyde.

Step 2: (ii) State the reagent composition Fehling's solution A is an aqueous solution of copper(II) sulphate, CuSO_4 . Fehling's solution B is an alkaline solution of sodium potassium tartrate (Rochelle salt), containing sodium hydroxide. Equal volumes of A and B are mixed freshly before use. Tartrate complexes copper(II), preventing copper(II) hydroxide precipitation.

Step 3: (iii) Form the semicarbazone of ethanal The terminal $-\text{NH}_2$ group of semicarbazide reacts with the carbonyl group of ethanal. Loss of water replaces $\text{C} = \text{O}$ by $\text{C} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$:



The hydrogen originally attached to the aldehydic carbon remains attached in the product. The amide carbonyl remains intact.



Structure of ethanal semicarbazone

Step 4: Conclusion (i) Acetaldehyde reacts faster. (ii) Fehling's reagent contains aqueous copper(II) sulphate and alkaline sodium potassium tartrate solution. (iii) Ethanal semicarbazone is $\text{CH}_3\text{CH} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, as drawn above.

Quick Tip to Solve: Keep the ethanal carbon's hydrogen and semicarbazide's amide carbonyl: replace only ethanal's oxygen by the semicarbazide nitrogen chain.

9. Give reasons:

- (i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.
(ii) Aniline does not give Friedel-Crafts reaction.
(iii) Although $-\text{NH}_2$ group is o/p directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of *m*-nitroaniline.

[3 marks]

Solution:

Concept:

- Alkyl halides undergo nucleophilic substitution with ammonia and amines. An amine product still has a nitrogen lone pair and can react further.
- Free $-\text{NH}_2$ donates its lone pair and directs electrophiles to ortho and para positions; protonated $-\text{NH}_3^+$ is electron withdrawing and meta directing.

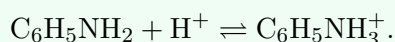
Step 1: (i) Successive alkylation forms a mixture Ammonolysis initially produces a primary amine, RNH_2 . This product is itself a nucleophile and reacts with further alkyl halide. Successive alkylation forms secondary and tertiary amines and finally a quaternary ammonium salt:



Consequently, ammonolysis gives a mixture whose separation is difficult, rather than a pure primary amine. Using excess ammonia favours the primary product but does not remove this general limitation.

Step 2: (ii) Aniline combines with the Lewis acid catalyst Nitrogen in aniline has a lone pair and acts as a Lewis base. It coordinates strongly with the Friedel-Crafts catalyst AlCl_3 , forming a salt-like Lewis acid-base complex. The nitrogen lone pair becomes unavailable for donation to the ring, which is strongly deactivated towards electrophilic substitution. Thus, aniline does not undergo ordinary Friedel-Crafts alkylation or acylation.

Step 3: (iii) Protonation changes the directing group In the strongly acidic nitrating mixture, aniline is protonated to anilinium ion:



The $-\text{NH}_3^+$ group has no lone pair available for resonance donation to the ring. It is electron withdrawing, deactivating and meta directing. Therefore, nitration of the protonated species gives a substantial amount of *m*-nitroaniline after work-up. The ortho/para directing rule applies to free aniline, not to its protonated form in this medium.

Step 4: Conclusion (i) Further alkylation gives a mixture of products. (ii) Complex formation with AlCl_3 deactivates aniline. (iii) The meta-directing anilinium ion formed in the acidic medium accounts for the good yield of *m*-nitroaniline.

Quick Tip to Solve: Check whether the nitrogen lone pair remains free in the reaction medium before applying the amino group's ortho/para directing effect.

10. (a) Using valence bond theory, predict the hybridization and magnetic character of the following: $[\text{CoF}_6]^{3-}$ [Atomic number of Co = 27]
- (b) Write IUPAC name of the following complex: $[\text{CoBr}_2(\text{en})_2]^+$
- (c) How many ions are produced from the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ in solution? [3 marks]

Solution:

Concept:

- In valence bond theory, a six-coordinate complex uses six hybrid orbitals. Weak-field ligands do not force pairing of the metal's d electrons; unpaired electrons cause paramagnetism.
- In complex nomenclature, neutral ethane-1,2-diamine (en) has zero charge and each bromido ligand has charge -1 . Counterions outside square brackets dissociate while ligands within the coordination sphere remain bound.

Step 1: (a) Determine the metal configuration and hybridization Let the cobalt oxidation state in $[\text{CoF}_6]^{3-}$ be x . Then $x + 6(-1) = -3$, so cobalt is Co^{3+} . For atomic number 27, neutral cobalt is $[\text{Ar}]3d^74s^2$; removal of two $4s$ electrons and one $3d$ electron gives $[\text{Ar}]3d^6$. Fluorido is a weak-field ligand and does not cause pairing of the $3d$ electrons. The high-spin d^6 configuration has four unpaired electrons. Two vacant inner $3d$ orbitals are therefore unavailable, and the complex uses one $4s$, three $4p$ and two $4d$ orbitals to give sp^3d^2 hybridization. It is an outer-orbital octahedral complex and is paramagnetic because of these four unpaired electrons.

Step 2: (b) Name the complex cation For $[\text{CoBr}_2(\text{en})_2]^+$, the charge balance is $x - 2 = +1$, giving cobalt oxidation state $+3$. Name ligands alphabetically, ignoring numerical prefixes: bromido precedes ethane-1,2-diamine. There are two bromido ligands and two bidentate ethane-1,2-diamine ligands; the latter uses the prefix bis. Since the complex is cationic, the metal name remains cobalt. Its name is dibromidobis(ethane-1,2-diamine)cobalt(III) ion.

Step 3: (c) Count particles formed by dissociation The printed formula has two chloride counterions outside the coordination sphere. In solution it dissociates as

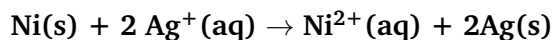


One formula unit thus produces one complex cation and two chloride anions, a total of three ions. The six ammonia molecules are coordinated ligands and are not counted as separate ions.

Step 4: Conclusion (a) sp^3d^2 hybridization; paramagnetic with four unpaired electrons. (b) Dibromidobis(ethane-1,2-diamine)cobalt(III) ion. (c) Three ions per formula unit.

Quick Tip to Solve: Find the oxidation state before assigning the d -electron count, and count only the entire complex ion plus counterions when calculating ions in solution.

11(a). Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following cell:



Given that $E^\circ_{\text{cell}} = 1.05 \text{ V}$, $1F = 96,500 \text{ C mol}^{-1}$.

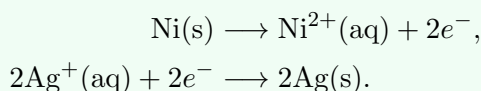
[3 marks]

Solution:

Concept:

- Standard reaction Gibbs energy satisfies $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- Since $\Delta_r G^\circ = -RT \ln K_c$, at the usual textbook temperature of 298 K, $E^\circ_{\text{cell}} = (0.0591/n) \log K_c$. Here log is the base-ten logarithm.

Step 1: Determine the electron transfer Nickel loses two electrons and two silver ions accept them. The balanced half-reactions are



Therefore $n = 2$ for the reaction as written. The number of electrons is determined by the balanced reaction, rather than by the number of distinct chemical species present.

Step 2: Calculate standard Gibbs energy Using $E^\circ_{\text{cell}} = 1.05 \text{ V}$ and $F = 96500 \text{ C mol}^{-1}$,

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96500 \times 1.05 \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

The result refers to one mole of the balanced reaction. Its negative sign agrees with the positive standard emf: the forward cell reaction is spontaneous under standard conditions.

Step 3: Calculate the equilibrium logarithm Apply the standard 298 K relation between emf and equilibrium constant:

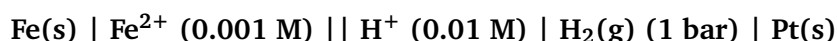
$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 1.05}{0.0591} = 35.53.$$

The equilibrium expression is $K_c = [\text{Ni}^{2+}]/[\text{Ag}^+]^2$. Pure solid nickel and silver have unit activity and are omitted. The large positive value of the logarithm indicates that the equilibrium strongly favours the products, consistent with the negative standard Gibbs energy.

Step 4: Conclusion $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$ and, at 298 K, $\log K_c \approx 35.53$.

Quick Tip to Solve: Count electrons using the half-reactions first; two silver ions mean $n = 2$, and a positive standard emf gives negative Gibbs energy and positive log K .

11(b). Calculate the e.m.f. of the following cell at 298 K:



Given that $E^\circ_{\text{cell}} = +0.44 \text{ V}$

$[\log 2 = 0.3010, \log 3 = 0.4771, \log 10 = 1]$

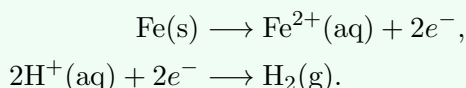
[3 marks]

Solution:

Concept:

- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n counts the electrons transferred and Q is the reaction quotient.
- Pure solids have unit activity. A gas at its standard pressure of 1 bar has unit relative pressure, while dilute aqueous ion activities are approximated by their molar concentrations relative to the standard concentration.

Step 1: Write the cell reaction In the given cell notation, the left electrode is the anode and the right electrode is the cathode. Iron is oxidised, while hydrogen ions are reduced on the inert platinum electrode:



Adding the half-reactions gives $\text{Fe(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_2(\text{g})$. Thus $n = 2$; platinum is only an electrical conductor and does not enter the reaction quotient.

Step 2: Evaluate the reaction quotient For the balanced reaction, hydrogen-ion concentration is squared because its stoichiometric coefficient is two. With the hydrogen gas at 1 bar, its relative pressure is one:

$$Q = \frac{[\text{Fe}^{2+}](p_{\text{H}_2}/p^\circ)}{[\text{H}^+]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

Here the numerical concentrations are taken relative to 1 mol L^{-1} , so Q is dimensionless. Consequently $\log Q = \log 10 = 1$; the other supplied logarithms are not needed.

Step 3: Apply the Nernst equation Substitute $E^\circ_{\text{cell}} = 0.44 \text{ V}$, $n = 2$, and $\log Q = 1$:

$$\begin{aligned}E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \times 1 \\ &= 0.44 - 0.02955 \\ &= 0.41045 \text{ V}.\end{aligned}$$

Because $Q > 1$, the Nernst correction reduces the emf below its standard value. The emf remains positive, so the reaction still proceeds spontaneously in the direction represented by the cell notation.

Step 4: Conclusion The cell emf at 298 K is $E_{\text{cell}} = 0.41045 \text{ V} \approx 0.410 \text{ V}$.

Quick Tip to Solve: Square the hydrogen-ion concentration in Q : forgetting the coefficient 2 changes both the reaction quotient and the direction of the Nernst correction.

Section C (5 marks)

12. Read the following passage and answer the questions that follow:

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law:

$$\text{Rate} = k[A]^x [B]^y$$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction. When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reactions are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. [5 marks]

12(a). What is the effect of temperature on the rate constant of a reaction?

[1 mark]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For a reaction with positive activation energy, heating increases the fraction of molecules having enough energy to react.

Step 1: Apply the temperature dependence In the Arrhenius equation, increasing T makes the exponent $-E_a/(RT)$ less negative. Consequently the exponential factor increases, assuming A and E_a remain approximately constant over the temperature interval.

Step 2: Connect this change with effective collisions A greater fraction of molecules can overcome the activation-energy barrier at the higher temperature. Thus successful collisions become more frequent. For many reactions, an increase of about 10 K approximately doubles the rate constant, although this is an empirical rule and not a universal exact factor.

Step 3: Conclusion The rate constant generally increases with increasing temperature.

Quick Tip to Solve: Use the Arrhenius exponent: a larger absolute temperature makes a negative exponent less negative.

12(b). For a reaction $A + B \rightarrow \text{Product}$, the rate law is given by, $\text{Rate} = k[A]^2[B]^{1/2}$. What is the order of the reaction?

[1 mark]

Solution:

Concept:

- The overall order is the sum of the exponents of reactant concentrations in the experimentally determined rate law.

Quick Tip to Solve: Read powers from the rate law, then add them; do not add coefficients from the reaction equation.

- Partial orders may be fractional; they need not equal the coefficients in the balanced chemical equation.

Step 1: Read the partial orders from the rate law The supplied law is $\text{Rate} = k[A]^2[B]^{1/2}$. Therefore the reaction is second order with respect to A and half order with respect to B . The rate constant k is not a concentration term and contributes no exponent to the order.

Step 2: Add the concentration exponents The overall order is calculated directly from these powers:

$$n = 2 + \frac{1}{2} = \frac{5}{2} = 2.5.$$

The coefficient of each reactant in $A + B \rightarrow \text{Product}$ is one, but adding those coefficients would give molecular counting rather than the order specified by this rate law.

Step 3: Conclusion The overall order of the reaction is $\boxed{5/2}$, i.e. 2.5.

Quick Tip to Solve: Read powers from the rate law, then add them; do not add coefficients from the reaction equation.

12(c). How order and molecularity are different for complex reactions?

[1 mark]

Solution:

Concept:

- Order is the sum of concentration exponents in the observed rate law and is determined experimentally.
- Molecularity counts the reacting species participating in a single elementary reaction step.

Step 1: Explain the order of a complex reaction A complex reaction proceeds through several elementary steps. Its observed rate law describes the overall dependence of the rate on reactant concentrations. The sum of its concentration exponents gives the overall order, which may be zero, an integer or a fraction.

Step 2: Explain where molecularity is meaningful Molecularity is defined separately for each elementary step and is a positive integer, since it counts the particles taking part in that step. An overall complex reaction has no single molecularity. Thus its overall order cannot be equated with the sum of reactant coefficients or with a supposed overall molecularity.

Step 3: Conclusion For a complex reaction, overall order is defined by its experimental rate law, whereas molecularity is defined only for the individual elementary steps.

Quick Tip to Solve: When several steps form a mechanism, distinguish the overall measured order from each step's particle count.

12(d). A first order reaction has a rate constant $2 \times 10^{-3} \text{ s}^{-1}$. How long will 6 g of this reactant take to reduce to 2 g? [2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \frac{2.303}{k} \log([A]_0/[A]_t)$, where k is the rate constant and the concentrations refer to the initial and remaining reactant.
- At unchanged volume, the concentration ratio equals the mass ratio for the same reactant; hence initial and remaining masses can be used directly.

Step 1: Identify the initial and remaining amounts Here $k = 2.0 \times 10^{-3} \text{ s}^{-1}$, the initial mass is 6 g and the remaining mass is 2 g. Therefore

$$\frac{[A]_0}{[A]_t} = \frac{m_0}{m_t} = \frac{6}{2} = 3.$$

The mass that has reacted is 4 g, but the denominator in the integrated rate law must be the remaining mass, not the mass consumed.

Step 2: Substitute in the integrated first-order law Using $\log 3 = 0.4771$,

$$\begin{aligned} t &= \frac{2.303}{2.0 \times 10^{-3}} \log 3 \\ &= 1151.5 \times 0.4771 \\ &= 549.38 \text{ s.} \end{aligned}$$

The time unit is seconds because k is given in reciprocal seconds. As a check, the half-life is $0.693/k = 346.5 \text{ s}$. Reaching one-third of the initial mass requires longer than one half-life, as the calculated time does.

Step 3: Conclusion The required time is $5.49 \times 10^2 \text{ s}$, approximately 549 s.

Quick Tip to Solve: Put the mass left, not the mass used up, in the denominator of the first-order logarithmic ratio.

OR

12(d). The half life for radioactive decay of ^{14}C is 6930 years. An archaeological artifact containing wood had only 75% of the ^{14}C found in a living tree. Find the age of the sample.

[$\log 4 = 0.6021$, $\log 3 = 0.4771$, $\log 2 = 0.3010$, $\log 10 = 1$]

[2 marks]

Solution:

Concept:

- Radioactive decay follows first-order kinetics: $kt = 2.303 \log(N_0/N)$, where N_0 is the original amount of radioactive carbon, N is its remaining amount after time t , and k is the decay constant.
- For a first-order decay, $k = 0.693/t_{1/2}$. The fraction remaining is measured relative to a living tree,

Quick Tip to Solve: Convert the percentage remaining to a fraction first: here $75\% = 3/4$, so use $\log(4/3)$, not $\log 4$.

which provides the initial radioactive-carbon reference.

Step 1: Determine the decay constant and the remaining fraction The half-life is $t_{1/2} = 6930$ years, hence

$$k = \frac{0.693}{6930} = 1.00 \times 10^{-4} \text{ year}^{-1}.$$

The wood contains 75% of its initial ^{14}C , so $N/N_0 = 75/100 = 3/4$. Therefore the ratio required in the integrated rate equation is $N_0/N = 4/3$. The amount lost is 25%, but the equation uses the amount remaining.

Step 2: Calculate the elapsed time Using the supplied common logarithms,

$$\log\left(\frac{4}{3}\right) = \log 4 - \log 3 = 0.6021 - 0.4771 = 0.1250.$$

Substitution in the first-order equation gives

$$t = \frac{2.303}{1.00 \times 10^{-4}}(0.1250) = 2878.75 \text{ years}.$$

Since more than half the carbon remains, this age is correctly less than one half-life.

Step 3: Conclusion The age of the archaeological wood sample is approximately 2.88×10^3 years, or about 2879 years.

Quick Tip to Solve: Convert the percentage remaining to a fraction first: here $75\% = 3/4$, so use $\log(4/3)$, not $\log 4$.