

CBSE Class 12 Chemistry Question Paper 2020 with Solution PDF-Set 56-5-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) Question paper comprises four sections – A, B, C and D.
- (ii) There are **37** questions in the questions paper. **All** questions are compulsory.
- (iii) Section – A : Q. No. **1 to 20** are very short answer type questions carrying **one** mark each. Answer these questions in one word or one sentence.
- (iv) Section – B : Q. No. **21 to 27** are short answer type questions carrying **two** marks each.
- (v) Section – C : Q. No. **28 to 34** are long answer type-I questions carrying **three** marks each.
- (vi) Section – D : Q. No. **35 to 37** are long answer type-II questions carrying **five** marks each.
- (vii) There is NO overall choice in the question paper. However, an internal choice has been provided in **2** questions of **two** marks, **2** questions of **three** marks and all the **3** questions of **five** marks. You have to **attempt only one of the choices** in such questions.
- (viii) However, separate instructions are given with each section and question, wherever necessary.
- (ix) Use of calculators and log tables is NOT permitted.

Section A (20 marks)

1. Read the given passage and answer the questions 1 to 5 that follow:

The halogens have the smallest atomic radii in their respective periods. The atomic radius of fluorine is extremely small. All halogens exhibit -1 oxidation state. They are strong oxidising agents and have maximum negative electron gain enthalpy. Among halogens, fluorine shows anomalous behaviour in many properties. For example electro negativity and ionisation enthalpy are higher for fluorine than expected whereas bond dissociation enthalpy, m.p. and b.p. and electron gain enthalpy are quite lower than expected. Halogens react with hydrogen to give hydrogen halides (HX) and combine amongst themselves to form a number of compounds of the type XX' , XX'_3 , XX'_5 and XX'_7 called inter-halogens.

Why halogens have maximum negative electron gain enthalpy?

[1 mark]

Solution:

Concept:

- Electron gain enthalpy is the enthalpy change when an isolated gaseous atom accepts an electron:
 $X(g) + e^- \rightarrow X^-(g)$.
- Halogens have valence-shell configuration ns^2np^5 , one electron short of a filled shell.

Step 1: Identify the electronic requirement An incoming electron completes the halogen atom's valence shell, changing ns^2np^5 into the stable noble-gas configuration ns^2np^6 . Thus halogens have a strong tendency to accept an electron.

Step 2: Relate attraction to energy release Their small atomic sizes and high effective nuclear charge produce strong attraction for the added electron. Electron addition therefore releases considerable energy, giving a highly negative electron gain enthalpy. This explains the general behaviour of halogens among the elements of a period.

Step 3: Conclusion Halogens have highly negative electron gain enthalpy because accepting one electron gives a stable noble-gas configuration, with strong nuclear attraction for the added electron.

Quick Tip to Solve: Link the negative sign to energy release on completing the np^6 shell.

2. Why fluorine shows anomalous behaviour as compared to other halogens?

[1 mark]

Solution:

Concept:

- The first member of a group can differ because its valence electrons occupy a much smaller shell.
- Fluorine has a very small size, very high electronegativity and no vacant d orbitals in its valence shell.

Step 1: Identify the size and electronic factors Fluorine is much smaller than the other halogens. Consequently, it has very high electronegativity and ionisation enthalpy. Its compact $2p$ orbitals also cause strong electron-electron repulsions when another electron enters.

Step 2: Connect these factors to its unusual behaviour Crowding of lone pairs in the small fluorine

Quick Tip to Solve: Remember fluorine through small size, strong electron attraction and a weak F – F bond.

atoms weakens the F – F bond. Also, the second shell has no vacant *d* orbitals. These features distinguish fluorine from the heavier halogens and account for its anomalous properties.

Step 3: Conclusion Fluorine behaves anomalously because of its exceptionally small size, high electronegativity, low F – F bond dissociation enthalpy and absence of vacant valence-shell *d* orbitals.

Quick Tip to Solve: Remember fluorine through small size, strong electron attraction and a weak F – F bond.

3. Arrange the hydrogen halides (HF to HI) in the decreasing order of their reducing character.

[1 mark]

Solution:

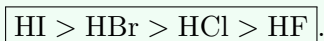
Concept:

- A reducing agent donates electrons and is itself oxidised.
- For hydrogen halides, reducing action involves oxidation of halide ions: $2X^- \longrightarrow X_2 + 2e^-$.

Step 1: Compare ease of oxidation Down the halogen group the halide ion becomes larger, so its outer electrons are less strongly held. Hence iodide loses electrons most readily, followed by bromide and chloride; fluoride is the most difficult to oxidise.

Step 2: Apply the trend to the hydrogen halides The H – X bond also becomes weaker from HF to HI. Thus reducing character increases down this series. Reversing the increasing trend gives the decreasing order asked in the question.

Step 3: Conclusion The decreasing order of reducing character is



Quick Tip to Solve: For reducing power, ask which halide loses electrons most easily: iodide comes first.

4. Why fluorine is a stronger oxidizing agent than chlorine?

[1 mark]

Solution:

Concept:

- An oxidising agent accepts electrons; a larger positive standard reduction potential indicates stronger oxidising power.
- For a halogen in water, reduction is $X_2(g) + 2e^- \longrightarrow 2X^-(aq)$; bond breaking, electron gain and hydration all contribute.

Step 1: Compare the energy contributions Although chlorine has a more negative electron gain enthalpy than fluorine, that factor alone does not decide oxidising strength in aqueous solution. The F – F bond has a low dissociation enthalpy, so relatively little energy is needed to split fluorine molecules.

Step 2: Include hydration of the ions The very small F^- ion has a very high magnitude of hydration

Quick Tip to Solve: Compare the complete aqueous reduction process; electron gain enthalpy alone gives the wrong prediction.

enthalpy: its hydration releases much energy. Together with the weak $F - F$ bond, this makes the overall reduction of fluorine more favourable than that of chlorine.

Step 3: Conclusion Fluorine is the stronger oxidising agent because its low bond dissociation enthalpy and highly exothermic hydration of F^- favour its reduction more strongly.

Quick Tip to Solve: Compare the complete aqueous reduction process; electron gain enthalpy alone gives the wrong prediction.

5. What are the sizes of X and X' in the interhalogen compounds?

[1 mark]

Solution:

Concept:

- Interhalogen compounds contain two different halogens and have formulae such as XX' , XX'_3 , XX'_5 and XX'_7 .
- The central halogen is generally larger and less electronegative than the surrounding halogen.

Step 1: Identify the central atom In the conventional formula XX'_n , X denotes the larger halogen atom. Its larger size permits smaller halogen atoms to surround it, particularly in compounds containing several terminal atoms.

Step 2: Identify the terminal atom The halogen represented by X' is smaller and more electronegative. For example, in IF_7 , iodine is the larger central atom and fluorine is the smaller terminal atom, illustrating the notation used in the passage.

Step 3: Conclusion X is the larger halogen atom, whereas X' is the smaller halogen atom.

Quick Tip to Solve: Use IF_7 as a memory aid: large iodine at the centre, small fluorine outside.

6. A hydrocarbon C_5H_{12} gives only one monochloride on photochemical chlorination. Identify the compound.

[1 mark]

Solution:

Concept:

- Photochemical chlorination replaces a hydrogen atom by chlorine through a free-radical substitution.
- Only one monochlorinated product forms when all hydrogen atoms of the hydrocarbon are equivalent by symmetry.

Step 1: Apply the single-product condition For C_5H_{12} , the possible carbon skeletons are straight-chain pentane, 2-methylbutane and 2,2-dimethylpropane. The first two have different types of hydrogen positions and therefore can give more than one monochloride.

Step 2: Select the symmetrical skeleton In 2,2-dimethylpropane, $C(CH_3)_4$, four identical methyl groups surround the central carbon. The central carbon has no hydrogen, and all twelve methyl hydrogens are equivalent. Replacing any one gives the same constitutional monochloride.

Quick Tip to Solve: One monochloride means one kind of hydrogen; look for the most symmetrical pentane isomer.

Step 3: Conclusion The compound is neopentane (2,2-dimethylpropane), $C(CH_3)_4$.

Quick Tip to Solve: One monochloride means one kind of hydrogen; look for the most symmetrical pentane isomer.

7. Out of $(CH_3)_3N$ and $(CH_3)_2NH$, which one is more basic in aqueous solution?

[1 mark]

Solution:

Concept:

- An amine acts as a base by accepting a proton at its nitrogen lone pair.
- Basicity in water depends on electron donation by alkyl groups and stabilisation of the protonated ion by hydration.

Step 1: Consider the alkyl-group effect Methyl groups donate electron density to nitrogen by the positive inductive effect. On this basis alone, the tertiary amine might seem the stronger base. In aqueous solution, however, hydration of the conjugate acid must also be considered.

Step 2: Compare hydration in water The dimethylammonium ion, $(CH_3)_2NH_2^+$, is hydrated more effectively than the more crowded trimethylammonium ion, $(CH_3)_3NH^+$. This greater stabilisation favours protonation of dimethylamine and outweighs the extra methyl-group effect in trimethylamine.

Step 3: Conclusion $(CH_3)_2NH$ (dimethylamine) is more basic in aqueous solution.

Quick Tip to Solve: For aqueous methylamines, include hydration of the conjugate acid before ranking basicity.

8. Out of $cis-[Pt(en)_2Cl_2]^{2+}$ and $trans-[Pt(en)_2Cl_2]^{2+}$, which one is optically active?

[1 mark]

Solution:

Concept:

- Optical isomerism occurs when a complex and its mirror image cannot be superimposed.
- Ethylenediamine, en, is a neutral bidentate ligand; two en ligands and two chloride ligands give an octahedral coordination sphere.

Step 1: Examine the cis arrangement In $cis-[Pt(en)_2Cl_2]^{2+}$, the two chloride ligands occupy adjacent positions. The two chelate rings can be arranged with opposite handedness. These arrangements are non-superimposable mirror images and form a pair of optical isomers.

Step 2: Compare the trans arrangement In the trans isomer the chloride ligands occupy opposite positions. This arrangement has symmetry that makes its mirror image superimposable on the original complex, so the trans isomer does not show optical activity.

Step 3: Conclusion $cis-[Pt(en)_2Cl_2]^{2+}$ is optically active.

Quick Tip to Solve: For an octahedral complex with two identical bidentate ligands and two identical monodentate ligands, check the cis form for a pair of mirror-image arrangements.

9. Name the method of refining used to obtain semiconductor of very high purity.

[1 mark]

Solution:

Concept:

- Semiconductors require extremely high purity because small amounts of impurities strongly affect their electrical properties.
- Zone refining uses the greater solubility of impurities in the molten metal than in the solid metal.

Step 1: Use selective distribution of impurities A narrow region of an impure semiconductor rod is melted using a moving heater. Impurities preferentially remain dissolved in this molten zone rather than entering the solid that forms behind it.

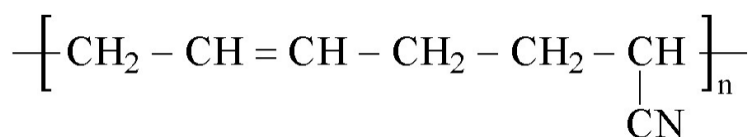
Step 2: Obtain the purified material As the heater moves along the rod, the molten zone carries impurities towards one end. Repeated passes concentrate impurities at that end, which is removed, leaving material of very high purity. This method is used for semiconductors such as silicon and germanium.

Step 3: Conclusion The method is zone refining.

Quick Tip to Solve: Associate very pure silicon and germanium with zone refining: a moving molten zone sweeps impurities to one end of the rod.

10. Is $[-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{CN})-]_n$ a homopolymer or copolymer?

[1 mark]



Solution:

Concept:

- A homopolymer is formed from only one kind of monomer; a copolymer is formed from two or more different monomers.
- Identify the parent monomers from chemically distinct segments in the polymer chain rather than from the presence of a repeating bracket alone.

Step 1: Identify the diene-derived segment The segment $-\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2-$ comes from 1,3-butadiene, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$, by addition polymerisation. One double bond remains in this segment of the chain.

Step 2: Identify the nitrile-containing segment The segment $-\text{CH}_2 - \text{CH}(\text{CN})-$ comes from acrylonitrile, $\text{CH}_2 = \text{CH} - \text{CN}$. Thus the chain contains units derived from two different monomer species, butadiene and acrylonitrile. This combination gives the rubber Buna-N.

Step 3: Conclusion The given polymer is a copolymer, formed from 1,3-butadiene and acrylonitrile.

Quick Tip to Solve: Split this chain into the four-carbon unsaturated unit and the two-carbon CN-bearing unit to recognise its two parent monomers.

11. The amount of electricity required to produce one mole of Zn from ZnSO_4 solution will be :

[1 mark]

- (A) 3F
- (B) 2F
- (C) 1F
- (D) 4F

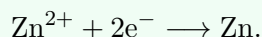
Correct Answer: (B) 2F

Solution:

Concept:

- One faraday, F , is the charge carried by one mole of electrons, approximately 96485 C mol^{-1} of electrons.
- The required number of moles of electrons is fixed by the balanced electrode half-reaction.

Step 1: Balance reduction of zinc ions In ZnSO_4 , zinc is present as Zn^{2+} . Its cathodic reduction is



Each zinc ion must gain two electrons to become a neutral zinc atom.

Step 2: Convert electron requirement to charge For one mole of zinc, two moles of electrons are needed. Hence $Q = nF = 2F$. Option (C), $1F$, would provide only half the required electrons. Options (A) and (D), $3F$ and $4F$, exceed the stoichiometric charge needed for one mole of zinc.

Step 3: Conclusion The required electricity is $2F$, so the correct option is (B).

Quick Tip to Solve: Write the metal-ion reduction first: the magnitude of its charge gives the number of faradays needed per mole of deposited metal.

12. Zinc is coated over iron to prevent rusting of iron because

[1 mark]

- (A) $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Fe}^{2+}/\text{Fe}}$
- (B) $E^\circ_{\text{Zn}^{2+}/\text{Zn}} < E^\circ_{\text{Fe}^{2+}/\text{Fe}}$
- (C) $E^\circ_{\text{Zn}^{2+}/\text{Zn}} > E^\circ_{\text{Fe}^{2+}/\text{Fe}}$
- (D) None of these

Correct Answer: (B) $E^\circ_{\text{Zn}^{2+}/\text{Zn}} < E^\circ_{\text{Fe}^{2+}/\text{Fe}}$

Solution:

Concept:

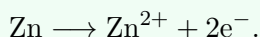
- A metal with a more negative standard reduction potential has a greater tendency to undergo oxidation.
- In galvanisation, zinc serves as a sacrificial anode and protects iron from oxidation, including when the coating is scratched.

Step 1: Compare the reduction potentials The standard reduction potentials are approximately

Quick Tip to Solve: For sacrificial protection, choose the coating metal with the more negative reduction potential: that metal is oxidised first.

$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ and $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$. Therefore the zinc reduction potential is smaller, or more negative, than that of iron.

Step 2: Connect the inequality to protection Zinc consequently oxidises preferentially:



It supplies electrons and protects iron against oxidation to iron ions. Equal potentials in (A) would not express this preferential oxidation; the reversed inequality in (C) would give the wrong relative tendency. Thus (D) is also excluded.

Step 3: Conclusion $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} < E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}$. The correct option is (B).

Quick Tip to Solve: For sacrificial protection, choose the coating metal with the more negative reduction potential: that metal is oxidised first.

13. The unit of rate constant depends upon the

[1 mark]

- (A) molecularity of the reaction
- (B) activation energy of the reaction
- (C) order of the reaction
- (D) temperature of the reaction

Correct Answer: (C) order of the reaction

Solution:

Concept:

- For a reaction of overall order n , the rate law can be written as $r = k[A]^n$ for dimensional analysis.
- Rate has units of concentration per time, so the units of k are $(\text{concentration})^{1-n}(\text{time})^{-1}$.

Step 1: Derive the dimensions Rearranging the rate law gives $k = r/[A]^n$. If concentration is expressed in mol L^{-1} and time in seconds,

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

The power of concentration therefore changes when the overall reaction order changes.

Step 2: Assess the alternatives For example, a first-order rate constant has units s^{-1} , whereas a second-order rate constant has units $\text{L mol}^{-1} \text{s}^{-1}$. Molecularity does not determine the units of a general experimental rate law. Activation energy and temperature affect the numerical value of the rate constant, but do not set its dimensions for a fixed order.

Step 3: Conclusion The units depend upon the order of the reaction. The correct option is (C).

Quick Tip to Solve: Use units of rate divided by units of concentration raised to the overall order; temperature changes the value of k , not this dimensional rule.

14. The formula of the complex triamminetri(nitrito-O)Cobalt (III) is

[1 mark]

- (A) $[\text{Co}(\text{ONO})_3(\text{NH}_3)_3]$
- (B) $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$
- (C) $[\text{Co}(\text{ONO}_2)_3(\text{NH}_3)_3]$
- (D) $[\text{Co}(\text{NO}_2)(\text{NH}_3)_3]$

Correct Answer: (A) $[\text{Co}(\text{ONO})_3(\text{NH}_3)_3]$

Solution:

Concept:

- NH_3 , named ammine, is a neutral ligand; nitrito-O is ONO^- , coordinated through oxygen.
- The prefixes triammine and trinitrito specify three ammine ligands and three nitrito ligands respectively.

Step 1: Translate the ligand names Triammine supplies three NH_3 ligands, while tri(nitrito-O) supplies three ONO^- ligands. Writing ONO next to cobalt identifies oxygen as the donor atom. Writing NO_2 next to cobalt, as in option (B), instead denotes bonding through nitrogen.

Step 2: Check composition and charge Cobalt(III) has oxidation state +3, the three nitrito ligands contribute -3 , and the ammine ligands contribute zero charge. The complex is therefore neutral. Option (C) contains ONO_2 , the wrong ligand composition; option (D) contains only one nitrite ligand and does not satisfy the prefix tri.

Step 3: Conclusion The formula is $[\text{Co}(\text{ONO})_3(\text{NH}_3)_3]$. The correct option is (A).

Quick Tip to Solve: Read the donor suffix first: nitrito-O binds through O and is written ONO beside the metal; then count ligands using the numerical prefixes.

15. Which of the following is a disaccharide?

[1 mark]

- (A) Glucose
- (B) Starch
- (C) Cellulose
- (D) Lactose

Correct Answer: (D) Lactose

Solution:

Concept:

- A disaccharide is a carbohydrate that gives two monosaccharide units on hydrolysis.
- Lactose contains one glucose unit and one galactose unit joined by a glycosidic linkage.

Step 1: Classify lactose Lactose is a disaccharide because hydrolysis of its glycosidic bond produces two monosaccharides, glucose and galactose. Both units are hexoses; the linkage in lactose is a β -(1 $\rightarrow$ 4) glycosidic linkage.

Step 2: Eliminate the other carbohydrates Glucose is itself a monosaccharide, so option (A) does

Quick Tip to Solve: Count the sugar units: glucose has one, lactose has two, while starch and cellulose are long glucose polymers.

not meet the definition. Starch and cellulose contain many glucose units and are polysaccharides, excluding options (B) and (C). Their hydrolysis yields many monosaccharide molecules rather than just two.

Step 3: Conclusion Lactose is the disaccharide. Hence, the correct option is (D).

Quick Tip to Solve: Count the sugar units: glucose has one, lactose has two, while starch and cellulose are long glucose polymers.

16. For Q16-Q20, choose the correct option:

(A) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is correct, but Reason (R) is wrong statement.

(D) Assertion (A) is wrong, but Reason (R) is correct statement.

Assertion (A): An ideal solution obeys Henry's law.

Reason (R): In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interaction.

[1 mark]

(A) A

(B) B

(C) C

(D) D

Correct Answer: (A) A

Solution:

Concept:

- Raoult's law for component i of an ideal solution is $p_i = x_i p_i^\circ$, where x_i is its liquid-phase mole fraction.
- Henry's law is $p_i = K_H x_i$; K_H is the Henry constant for that component.

Step 1: Evaluate the assertion An ideal solution obeys Raoult's law throughout its composition range. This is a linear relation between partial vapour pressure and mole fraction, and has Henry's-law form with $K_H = p_i^\circ$. The assertion is therefore correct.

Step 2: Evaluate the reason In an ideal solution, interactions between unlike molecules are similar to those between like molecules. Mixing therefore does not introduce an appreciable change in intermolecular attraction; $\Delta H_{\text{mix}} = 0$. The stated reason is correct.

Step 3: Connect the reason to the assertion The similarity of intermolecular interactions makes the escaping tendency of each component proportional to its mole fraction. Thus it accounts for ideal, linear vapour-pressure behaviour and explains why the solution obeys Henry's-law form. Option (B) wrongly denies this explanatory connection; (C) and (D) wrongly reject one statement.

Step 4: Conclusion Both statements are correct, and the reason correctly explains the assertion.

Quick Tip to Solve: Compare $p_i = x_i p_i^\circ$ with $p_i = K_H x_i$: for an ideal solution, $K_H = p_i^\circ$.

Hence, the correct option is (A).

Quick Tip to Solve: Compare $p_i = x_i p_i^\circ$ with $p_i = K_H x_i$: for an ideal solution, $K_H = p_i^\circ$.

17. Assertion (A): Conductivity of an electrolyte increases with decrease in concentration.

Reason (R): Number of ions per unit volume decreases on dilution.

[1 mark]

(A) A

(B) B

(C) C

(D) D

Correct Answer: (D) D

Solution:

Concept:

- Conductivity κ measures the conductance of a solution of unit length and unit cross-sectional area.
- Conductivity depends on the number of mobile charge carriers per unit volume; molar conductivity refers instead to a mole of electrolyte.

Step 1: Evaluate the assertion On dilution, the concentration of an electrolyte decreases and its conductivity generally decreases because there are fewer ions in a given volume to carry current. The assertion claims an increase in conductivity and is therefore false.

Step 2: Evaluate the reason Adding solvent increases solution volume. Consequently, the number of ions per unit volume decreases on dilution, even though dilution can increase the degree of dissociation of a weak electrolyte. The reason is correct.

Step 3: Select the statement combination The true reason accounts for the actual decrease in κ , rather than supporting the false assertion. Molar conductivity normally increases on dilution, but substituting that quantity for conductivity would change the question. Options (A), (B) and (C) all require the assertion to be true and are excluded.

Step 4: Conclusion The assertion is wrong and the reason is correct. Hence, the correct option is (D).

Quick Tip to Solve: On dilution distinguish κ from Λ_m : conductivity decreases, whereas molar conductivity increases.

18. Assertion (A): Benzaldehyde is less reactive than ethanal towards nucleophilic addition reactions.

Reason (R): Ethanal is more sterically hindered.

[1 mark]

- (A) A
- (B) B
- (C) C
- (D) D

Correct Answer: (C) C

Solution:

Concept:

- Nucleophilic addition begins with attack on the electrophilic carbon atom of the carbonyl group.
- Conjugation of a carbonyl group with a benzene ring reduces the positive character of its carbonyl carbon; steric crowding also hinders attack.

Step 1: Evaluate the assertion In benzaldehyde, the carbonyl group is conjugated with the phenyl ring. Resonance donation from the ring reduces the electrophilic character of the carbonyl carbon compared with ethanal. The bulky phenyl group further obstructs nucleophilic approach. Thus benzaldehyde is less reactive and the assertion is true.

Step 2: Evaluate the reason Ethanal, CH_3CHO , has a methyl group and a hydrogen attached to the carbonyl carbon. Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has the larger phenyl group. Ethanal is less sterically hindered, so the printed reason is false.

Step 3: Apply the code Since the reason reverses the steric comparison, it cannot explain the true assertion. Options (A) and (B) incorrectly treat the reason as true, and option (D) incorrectly treats the assertion as false.

Step 4: Conclusion The assertion is correct but the reason is wrong. Hence, the correct option is (C).

Quick Tip to Solve: For aromatic aldehydes check both effects: phenyl conjugation reduces electrophilicity and phenyl bulk hinders attack.

19. Assertion (A): Low spin tetrahedral complexes are rarely observed.

Reason (R): Crystal field splitting energy is less than pairing energy for tetrahedral complexes.

[1 mark]

- (A) A
- (B) B
- (C) C
- (D) D

Correct Answer: (A) A

Solution:

Concept:

- In a tetrahedral field the lower set is e and the higher set is t_2 ; their separation is Δ_t .

Quick Tip to Solve: Compare Δ_t with P : small tetrahedral splitting makes occupation of higher orbitals cheaper than pairing.

- Electron pairing competes with promotion: pairing is favoured only if crystal-field splitting exceeds the pairing energy P .

Step 1: Evaluate the assertion Tetrahedral splitting is usually small, so electrons generally occupy different orbitals with parallel spins before pairing. Tetrahedral complexes are consequently normally high spin; low spin tetrahedral complexes are rarely observed. The assertion is true.

Step 2: Evaluate the reason For ordinary tetrahedral complexes, $\Delta_t < P$. It costs less energy to occupy an available higher t_2 orbital than to pair electrons in the lower e orbitals. The reason correctly states this energy comparison.

Step 3: Test the explanatory link The inequality $\Delta_t < P$ directly favours unpaired electrons and hence high spin arrangements, explaining the rarity of low spin tetrahedral complexes. Option (B) incorrectly denies this connection; options (C) and (D) incorrectly reject one of the true statements.

Step 4: Conclusion Both statements are correct, and the reason correctly explains the assertion. Hence, the correct option is (A).

Quick Tip to Solve: Compare Δ_t with P : small tetrahedral splitting makes occupation of higher orbitals cheaper than pairing.

20. Assertion (A): The C-O-C bond angle in ethers is slightly less than tetrahedral angle.

Reason (R): Due to the repulsive interaction between the two alkyl groups in ethers.

[1 mark]

- (A) A
(B) B
(C) C
(D) D

Correct Answer: (D) D

Solution:

Concept:

- The oxygen atom in an ether has two bond pairs and two lone pairs, giving approximately tetrahedral electron-pair geometry.
- Repulsive interaction between the two attached alkyl groups tends to open the carbon-oxygen-carbon bond angle.

Step 1: Evaluate the assertion The C-O-C bond angle in ethers is slightly greater than the tetrahedral angle, not slightly less. For example, the angle in dimethyl ether is approximately 111.7° , compared with 109.5° for the tetrahedral angle. The assertion is false.

Step 2: Evaluate the reason The two alkyl groups attached to oxygen repel one another. This interaction tends to increase their separation by widening the angle at oxygen. The reason gives the relevant repulsive interaction and is correct.

Step 3: Apply the code to the printed assertion The stated repulsion supports an increase in bond angle, so it contradicts the direction claimed in the assertion. It does not make the assertion true. Options (A), (B) and (C), each of which requires a true assertion, are therefore eliminated.

Quick Tip to Solve: For ethers remember that alkyl-group repulsion opens the C-O-C angle slightly beyond 109.5° .

Step 4: Conclusion The assertion is wrong and the reason is correct. Hence, the correct option is (D).

Quick Tip to Solve: For ethers remember that alkyl-group repulsion opens the C–O–C angle slightly beyond 109.5° .

Section B (14 marks)

21. (a) Write the IUPAC name and hybridisation of the complex $[\text{Fe}(\text{CN})_6]^{3-}$. (Given: Atomic number of Fe = 26)

(b) What is the difference between an ambidentate ligand and a chelating ligand?

[2 marks]

Solution:

Concept:

- In coordination nomenclature, determine the metal oxidation state from the overall charge and the ligand charges. Each cyanido ligand, CN^- , carries charge -1 .
- Ambidentate ligands have alternative donor atoms but bind through only one at a time; chelating ligands use at least two donor atoms simultaneously to the same metal.

Step 1: Find the oxidation state and name For the given anion $[\text{Fe}(\text{CN})_6]^{3-}$, let the iron oxidation state be x . Charge balance gives

$$x + 6(-1) = -3 \Rightarrow x = +3.$$

Six cyanido ligands give the prefix hexacyanido, and an anionic iron complex uses the metal name ferrate. Its IUPAC name is **hexacyanidoferrate(III) ion**.

Step 2: Determine the hybridisation Iron has atomic number 26, and Fe^{3+} has configuration $[\text{Ar}]3d^5$. Cyanide is a strong-field ligand, giving the low spin octahedral arrangement $t_{2g}^5 e_g^0$, with one unpaired electron. In valence-bond terms, pairing leaves two inner $3d$ orbitals available; these combine with one $4s$ and three $4p$ orbitals to give $d^2 sp^3$ hybridisation.

Step 3: Distinguish the ligand types An ambidentate ligand can coordinate through either of two different donor atoms, but through only one in a given linkage, for example NO_2^- through nitrogen or oxygen. A chelating ligand coordinates through two or more donor atoms to the same metal at once, forming a ring; ethane-1,2-diamine (en) binds through both nitrogen atoms. Thus alternative binding sites differ from simultaneous multidentate attachment.

Step 4: Conclusion (a) $[\text{Fe}(\text{CN})_6]^{3-}$ is hexacyanidoferrate(III) ion, with $d^2 sp^3$ hybridisation. (b) An ambidentate ligand uses one of its alternative donor atoms; a chelating ligand binds simultaneously through multiple donor atoms and forms a ring.

Quick Tip to Solve: Use the overall complex charge before assigning the metal state: six cyanido ligands contribute a total charge of -6 .

22. Draw the structures of the following:

(i) HClO_4

(ii) XeOF_4

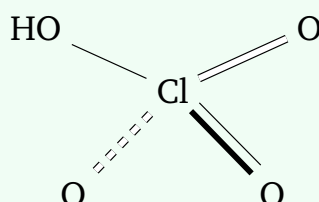
[2 marks]

Solution:

Concept:

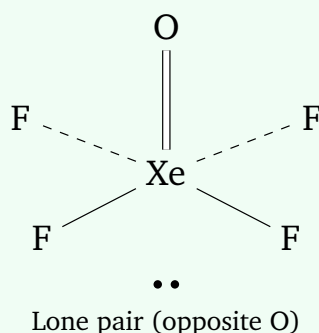
- In VSEPR theory, each single or multiple bond is one electron domain; lone pairs also occupy domains and determine molecular shape.
- In an oxyacid, the acidic hydrogen is attached to oxygen. In XeOF_4 , six domains around xenon give an octahedral electron-pair arrangement.

Step 1: Draw the structure of perchloric acid (i) Place chlorine at the centre and connect it to four oxygen atoms. Three are doubly bonded oxygen atoms, while the fourth is the oxygen of an -OH group. Thus the connectivity is $\text{HO}-\text{Cl}(=\text{O})_3$. The four bonding domains around chlorine are arranged tetrahedrally; hydrogen is bonded to oxygen, not directly to chlorine. The solid and dashed bonds show bonds projecting out of and behind the plane.



Perchloric acid: tetrahedral arrangement about chlorine

Step 2: Draw the structure of xenon oxytetrafluoride (ii) Xenon has four single $\text{Xe}-\text{F}$ bonds, one double $\text{Xe}=\text{O}$ bond and one lone pair. There are therefore five bonding domains and one lone-pair domain. The four fluorine atoms occupy a square base, oxygen occupies the apex, and the lone pair lies opposite oxygen. Removing the lone pair from the octahedral domain arrangement leaves a square-pyramidal molecular shape.



Xenon oxytetrafluoride: square-pyramidal structure

Step 3: Conclusion HClO_4 has tetrahedral coordination about chlorine with three $\text{Cl}=\text{O}$ bonds and one $\text{Cl}-\text{OH}$ bond. XeOF_4 is square pyramidal, with the xenon lone pair opposite oxygen, as drawn.

Quick Tip to Solve: Count a double bond as one VSEPR domain: five bonds plus one lone pair in xenon oxytetrafluoride give a square pyramid.

23(a). Write the role of

(a) Dilute NaCN in the extraction of Gold.

(b) CO in the extraction of Iron.

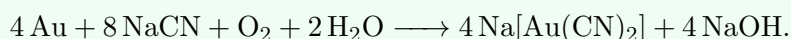
[2 marks]

Solution:

Concept:

- Leaching selectively dissolves the desired metal from its ore through formation of a soluble compound or complex.
- A reducing agent removes oxygen from a metal oxide and is itself oxidised during the reaction.

Step 1: State the role of dilute sodium cyanide (a) Dilute aqueous NaCN is a leaching agent in the extraction of gold. In the presence of air or oxygen, gold forms the soluble dicyanidoaurate(I) complex, $[\text{Au}(\text{CN})_2]^-$, leaving insoluble impurities behind:



Gold is subsequently recovered from this solution by displacement with zinc; sodium cyanide's role is complex formation and selective dissolution.

Step 2: State the role of carbon monoxide (b) Carbon monoxide acts as a reducing agent during iron extraction in the blast furnace. It reduces iron oxides to iron and is oxidised to carbon dioxide. The overall reduction of haematite can be represented as



Iron is reduced from oxidation state +3 to 0, while carbon in carbon monoxide is oxidised from +2 to +4.

Step 3: Conclusion Dilute NaCN leaches gold by forming a soluble cyanide complex; CO reduces iron oxides to iron in the blast furnace.

Quick Tip to Solve: Associate cyanide with soluble metal-complex formation and carbon monoxide with removal of oxygen from iron oxides.

OR

23(b). How is leaching carried out in the case of low grade copper ores? Name the method used for refining of copper metal.

[2 marks]

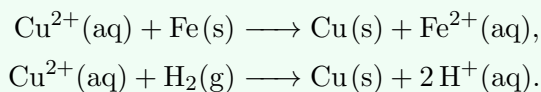
Solution:

Concept:

- Leaching brings the metal in an ore into solution. A more electropositive metal can then displace dissolved copper from its salt solution.
- Electrolytic refining transfers copper from an impure anode to a pure cathode through a suitable copper-ion electrolyte.

Quick Tip to Solve: Keep the stages distinct: leaching puts copper into solution, displacement recovers metal, and electrolysis refines it.

Step 1: Explain leaching of low-grade copper ore Low-grade copper ores are leached using acid, or bacteria. The treatment brings copper into solution as Cu^{2+} ions, while much of the gangue remains undissolved. Copper is then obtained from the leach liquor by displacement with scrap iron or with hydrogen:



This concentration in solution makes recovery possible even when the ore contains only a small proportion of copper.

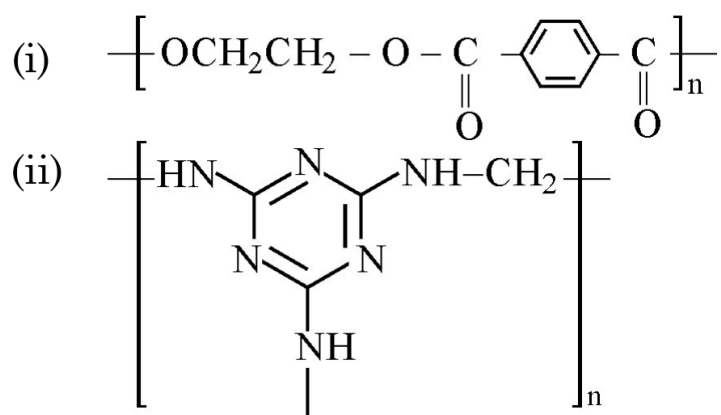
Step 2: Name the refining method Copper metal is purified by electrolytic refining. Impure copper is made the anode, a thin sheet of pure copper the cathode, and acidified copper sulphate solution the electrolyte. Copper dissolves from the anode as Cu^{2+} and deposits as pure copper at the cathode. Insoluble noble-metal impurities collect below the anode as anode mud.

Step 3: Conclusion Low-grade copper ores are leached using acid or bacteria, and copper is recovered from the solution by displacement. The refining method is electrolytic refining.

Quick Tip to Solve: Keep the stages distinct: leaching puts copper into solution, displacement recovers metal, and electrolysis refines it.

24. Identify the monomers in the following polymers:

[2 marks]



Solution:

Concept:

- A polyester is formed by condensation of a diol with a dicarboxylic acid. Splitting its ester linkages identifies the two monomers.
- An amino resin forms when an amino compound reacts with formaldehyde, producing methylene links between nitrogen-containing units.

Step 1: Identify the monomers of polymer (i) The first repeat unit contains the glycol residue $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ and the para-substituted aromatic dicarboxylate residue $-\text{CO}-\text{C}_6\text{H}_4-\text{CO}-$. Restoring hydroxyl groups at the ester links gives the monomers ethylene glycol (ethane-1,2-diol), $\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$, and terephthalic acid (benzene-1,4-dicarboxylic acid), $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$.

Quick Tip to Solve: Cut polyester ester links to recover the diol and diacid; in the triazine resin, trace the methylene bridges back to formaldehyde.

The two carboxyl groups are at the 1,4-positions, as shown in the printed ring; this distinguishes terephthalic acid from its positional isomers.

Step 2: Identify the monomers of polymer (ii) The second polymer contains a triazine ring bearing nitrogen links joined through methylene groups, $-\text{NH}-\text{CH}_2-\text{NH}-$. The ring-containing starting compound is melamine, $\text{C}_3\text{N}_3(\text{NH}_2)_3$, also called 2,4,6-triamino-1,3,5-triazine. Formaldehyde (methanal), HCHO , supplies the methylene links when it condenses with the amino groups of melamine to form the resin.

Step 3: Conclusion (i) Ethylene glycol and terephthalic acid. (ii) Melamine and formaldehyde.

Quick Tip to Solve: Cut polyester ester links to recover the diol and diacid; in the triazine resin, trace the methylene bridges back to formaldehyde.

25(a). Define adsorption with an example. What is the role of adsorption in heterogeneous catalysis?

[2 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon: molecules of a gas or solute accumulate on the surface of a solid or liquid, producing a higher concentration there than in the bulk.
- In heterogeneous catalysis, the catalyst and reactants are in different phases; the solid catalyst provides active surface sites for adsorption.

Step 1: Define adsorption with an example Adsorption is the accumulation of molecular species at a surface rather than throughout the bulk. For example, activated charcoal adsorbs gases on its large surface. Here charcoal is the adsorbent and the gas is the adsorbate. This differs from absorption, in which the substance enters the bulk of the material.

Step 2: Explain the catalytic role of adsorption Reactant molecules first adsorb at active sites on the solid catalyst. Adsorption brings the reactants close together and can weaken their bonds, allowing reaction through a pathway with lower activation energy. The adsorbed species react on the surface. Products then desorb, freeing the active sites for fresh reactant molecules. Thus, adsorption helps the surface reaction proceed repeatedly and increases its rate.

Step 3: Conclusion Adsorption is surface accumulation, exemplified by gas adsorption on charcoal. In heterogeneous catalysis it concentrates and activates reactants on the catalyst surface before the products desorb.

Quick Tip to Solve: For a surface catalyst, remember the sequence: adsorption, surface reaction, then desorption.

25(b). Define Brownian movement. What is the cause of Brownian movement in colloidal particles? How is it responsible for the stability of Colloidal Sol? [2 marks]

Solution:

Concept:

- Brownian movement is the continuous, irregular zigzag motion of colloidal particles suspended in a dispersion medium.
- Unequal molecular impacts from the dispersion medium keep colloidal particles moving and oppose their settling under gravity.

Step 1: Define the motion and state its cause Brownian movement is the ceaseless, random zigzag motion of colloidal particles in the dispersion medium. Molecules of the medium are themselves in thermal motion and strike each colloidal particle from all sides. At any instant, the impacts on different sides are unequal. The resulting unbalanced force changes in direction continuously, giving the particle its irregular path.

Step 2: Relate the motion to stability of the sol The continual random motion keeps colloidal particles dispersed and counteracts their tendency to settle under gravity. Consequently, they remain suspended for long periods, contributing to the stability of the colloidal sol. This kinetic contribution should be distinguished from the electrical contribution: like charges on particles also help stability by discouraging their aggregation.

Step 3: Conclusion Brownian movement is random zigzag motion caused by unequal collisions with molecules of the medium. It helps stabilise a sol by keeping its particles suspended against gravitational settling.

Quick Tip to Solve: Connect Brownian motion to unequal solvent impacts and resistance to settling; charge explains resistance to aggregation.

26. State Raoult's law for a solution containing volatile components. What is the similarity between Raoult's law and Henry's law? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal solution is $p_i = x_i p_i^\circ$, where p_i is the partial vapour pressure, x_i the liquid-phase mole fraction, and p_i° the vapour pressure of pure component i at the same temperature.
- Henry's law is $p = K_H x$, where p is gas partial pressure, x its mole fraction in solution, and K_H Henry's law constant at that temperature.

Step 1: State Raoult's law For a solution containing volatile components, the partial vapour pressure of each component is directly proportional to its mole fraction in the solution. The proportionality constant is its pure-component vapour pressure at the same temperature:

$$p_i = x_i p_i^\circ.$$

Quick Tip to Solve: Compare partial pressure with liquid mole fraction in both laws; do not confuse partial pressure with total pressure.

For a binary ideal solution, Dalton's law then gives the total vapour pressure as

$$p_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ.$$

Step 2: Identify the similarity Both laws express a linear proportionality between the partial pressure of a species above the solution and its mole fraction in the solution at fixed temperature. Their forms are $p = x \times \text{constant}$. The constant is p_i° in Raoult's law and K_H in Henry's law. Thus Raoult's law has the same mathematical form as Henry's law, with $K_H = p_i^\circ$ for that form.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^\circ$. Its similarity to Henry's law, $p = K_H x$, is that partial pressure is directly proportional to mole fraction at a fixed temperature.

Quick Tip to Solve: Compare partial pressure with liquid mole fraction in both laws; do not confuse partial pressure with total pressure.

27. Define the following terms with a suitable example in each:

(i) Bacteriocidal antibiotics

(ii) Food preservatives.

[2 marks]

Solution:

Concept:

- Bacteriocidal antibiotics kill bacteria, whereas bacteriostatic antibiotics inhibit bacterial growth.
- Food preservatives are substances added to food to prevent or retard spoilage and extend its usable life.

Step 1: Define bacteriocidal antibiotics and give an example Bacteriocidal antibiotics are antibiotics that kill susceptible bacteria. Penicillin is an example; it interferes with bacterial cell-wall synthesis, leading to death of susceptible growing bacterial cells. The essential point in the definition is that the bacteria are killed. An antibiotic that merely inhibits their growth is described as bacteriostatic instead.

Step 2: Define food preservatives and give an example Food preservatives are substances added to food to prevent or delay its spoilage, especially by inhibiting the growth of microorganisms. Sodium benzoate is a suitable example and is used to preserve acidic foods such as fruit juices and squashes. By restricting microbial growth, it helps the food retain its quality for a longer period. The role of a preservative is therefore distinct from that of a flavouring or colouring agent.

Step 3: Conclusion Bacteriocidal antibiotics kill bacteria; penicillin is an example. Food preservatives retard food spoilage; sodium benzoate is an example.

Quick Tip to Solve: Pair each definition immediately with its own example: penicillin kills bacteria; sodium benzoate preserves food.

Section C (21 marks)

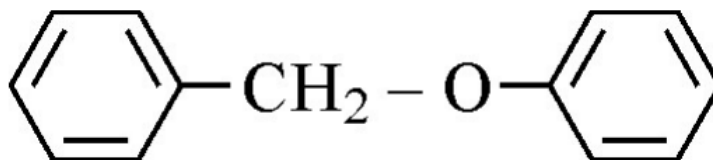
28(a). Give the structures of final products expected from the following reactions:

(i) Hydroboration of propene followed by oxidation with H_2O_2 in alkaline medium.

(ii) Dehydration of $(\text{CH}_3)_3\text{C}-\text{OH}$ by heating it with 20% H_3PO_4 at 358 K.

(iii) Heating of $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$ with HI.

[3 marks]

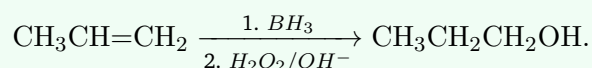


Solution:

Concept:

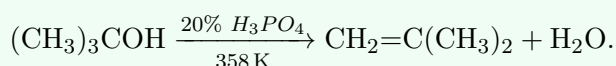
- Hydroboration followed by alkaline peroxide oxidation adds water across an alkene in the anti-Markovnikov orientation: the OH group enters the less substituted carbon.
- Acid-catalysed dehydration removes water from an alcohol to produce an alkene. HI cleaves an alkyl aryl ether at the alkyl-oxygen bond, leaving the aryl-oxygen bond intact.

Step 1: (i) Hydroboration and oxidation of propene Boron attaches preferentially to the terminal carbon of propene. Oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond with a carbon-oxygen bond without changing the carbon skeleton:



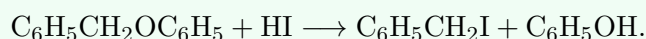
Thus the alcohol has its hydroxyl group at carbon 1; the product is propan-1-ol.

Step 2: (ii) Dehydration of the tertiary alcohol On heating with 20% phosphoric acid at 358 K, tert-butyl alcohol loses the OH group and a hydrogen atom from an adjacent methyl group as water:



All three methyl groups are equivalent, so elimination gives the same alkene, 2-methylpropene.

Step 3: (iii) Cleavage of benzyl phenyl ether Protonation of the ether oxygen makes cleavage possible. The benzyl-oxygen bond breaks, and iodide forms benzyl iodide; the phenyl-oxygen bond is resistant to substitution because it has partial double-bond character and involves an aromatic carbon:



Phenol does not undergo further replacement of its OH group by iodide under these conditions.

Step 4: Conclusion The final products are (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, (ii) $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and (iii) $\text{C}_6\text{H}_5\text{CH}_2\text{I}$ together with $\text{C}_6\text{H}_5\text{OH}$.

Quick Tip to Solve: In an aryl alkyl ether, retain the aryl-O bond and put iodine on the alkyl fragment; hydroboration puts OH on the less substituted alkene carbon.

28(b). How can you convert the following?

(i) Phenol to o-hydroxybenzaldehyde.

(ii) Methanal to ethanol.

(iii) Phenol to phenyl ethanoate.

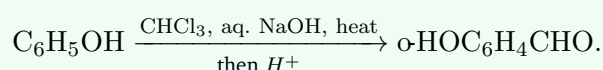
[3 marks]

Solution:

Concept:

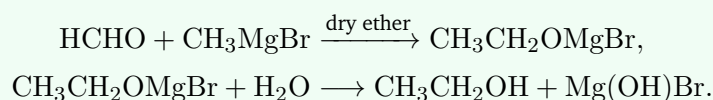
- The Reimer–Tiemann reaction introduces a formyl group, $-\text{CHO}$, predominantly ortho to the hydroxyl group of phenol using chloroform and aqueous alkali followed by acidification.
- A Grignard reagent adds an alkyl group to methanal; hydrolysis of the magnesium alkoxide gives a primary alcohol with one more carbon than the alkyl group.
- Acylation replaces the hydrogen of a phenolic OH group by an acyl group, forming an ester while retaining the phenyl–oxygen bond.

Step 1: (i) Phenol to o-hydroxybenzaldehyde Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. This is the Reimer–Tiemann reaction:



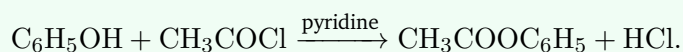
The formyl group enters the ring next to the existing OH group. The isolated ortho product is 2-hydroxybenzaldehyde, also called salicylaldehyde; the original hydroxyl group remains present.

Step 2: (ii) Methanal to ethanol Add methylmagnesium bromide to methanal in dry ether, then hydrolyse the magnesium alkoxide with dilute acid:



The methyl reagent supplies the extra carbon. Ether must be dry during the addition because water destroys the Grignard reagent before it can react with methanal.

Step 3: (iii) Phenol to phenyl ethanoate Treat phenol with ethanoyl chloride in the presence of pyridine, which removes the hydrogen chloride formed:



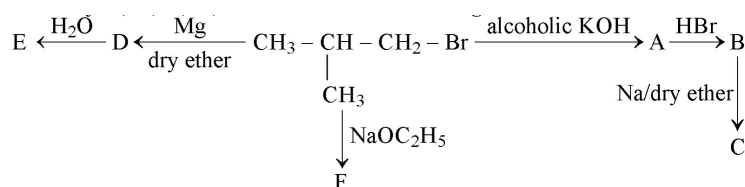
The ethanoate group is attached through oxygen. The ester is therefore phenyl ethanoate, with structure $\text{C}_6\text{H}_5\text{OCOCH}_3$.

Step 4: Conclusion Use (i) $\text{CHCl}_3/\text{aq. NaOH}$, heat, then H^+ ; (ii) CH_3MgBr in dry ether, then hydrolysis; and (iii) CH_3COCl with pyridine, respectively.

Quick Tip to Solve: To make ethanol from methanal, add exactly one carbon using methylmagnesium bromide; for phenyl ethanoate, acylate the phenolic oxygen.

29. Identify A, B, C, D, E and F in the following:

[3 marks]

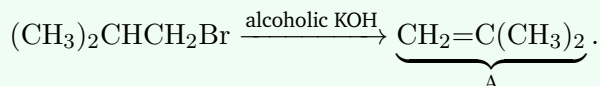


Solution:

Concept:

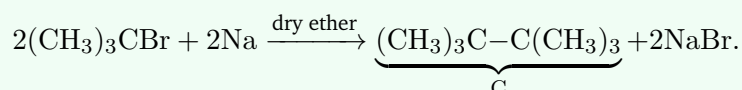
- Alcoholic KOH promotes beta-elimination of HBr. HBr adds to an unsymmetrical alkene according to Markovnikov's rule when no peroxide is specified.
- Magnesium in dry ether converts an alkyl bromide into a Grignard reagent, RMgBr; hydrolysis gives RH. Sodium in dry ether couples two alkyl halide molecules in the Wurtz reaction.
- An alkoxide substitutes the halogen of a primary alkyl halide to form an ether by Williamson ether synthesis.

Step 1: Identify A and B by elimination followed by addition The starting halide is 1-bromo-2-methylpropane, $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$. Alcoholic KOH removes H from the adjacent carbon and Br from the terminal carbon:



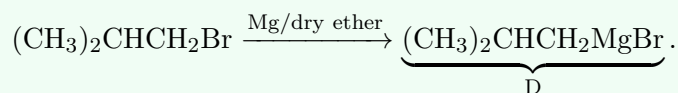
Addition of HBr puts H on the terminal carbon, giving the more stable tertiary carbocation before bromide attacks. Therefore B is $(\text{CH}_3)_3\text{CBr}$, 2-bromo-2-methylpropane.

Step 2: Identify C from the B branch Follow the arrow from B, rather than from the original halide. Its Wurtz coupling joins two tert-butyl groups:

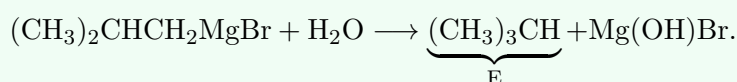


Hence the coupling product is 2,2,3,3-tetramethylbutane. This is the formal Wurtz product represented by the reaction scheme; tertiary halides can also undergo competing elimination in practice.

Step 3: Identify D and E from Grignard formation and hydrolysis Magnesium inserts into the carbon-bromine bond of the starting compound without changing its carbon skeleton:



Hydrolysis replaces the magnesium bromide group with hydrogen:

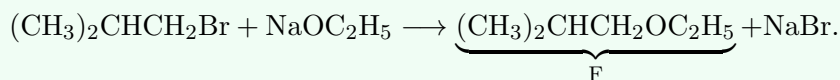


D is 2-methylpropylmagnesium bromide and E is 2-methylpropane.

Step 4: Identify F by Williamson ether synthesis The reagent on the downward arrow is sodium

Quick Tip to Solve: Trace every arrow from its own starting compound: C comes from B, whereas D and F come from the original primary bromide.

ethoxide, NaOC_2H_5 . Ethoxide replaces Br on the primary carbon:



F is 1-ethoxy-2-methylpropane; the oxygen remains bonded to the ethyl group supplied by the alkoxide.

Step 5: Conclusion A = $\text{CH}_2=\text{C}(\text{CH}_3)_2$; B = $(\text{CH}_3)_3\text{CBr}$.

C = $(\text{CH}_3)_3\text{C}-\text{C}(\text{CH}_3)_3$; D = $(\text{CH}_3)_2\text{CHCH}_2\text{MgBr}$.

E = $(\text{CH}_3)_3\text{CH}$; F = $(\text{CH}_3)_2\text{CHCH}_2\text{OC}_2\text{H}_5$.

Quick Tip to Solve: Trace every arrow from its own starting compound: C comes from B, whereas D and F come from the original primary bromide.

30. A 0.01 m aqueous solution of AlCl_3 freezes at -0.068°C . Calculate the percentage of dissociation. [Given: K_f for Water = $1.86 \text{ K kg mol}^{-1}$] [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality.
- If one formula unit dissociates into n ions with degree of dissociation α , the number of solute particles per initial formula unit is $(1 - \alpha) + n\alpha$; hence $i = 1 + (n - 1)\alpha$.

Step 1: Calculate the observed van't Hoff factor Pure water freezes at 0°C . Therefore the positive depression in freezing point is

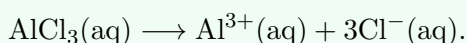
$$\Delta T_f = 0 - (-0.068) = 0.068 \text{ K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. Using the given molality directly,

$$i = \frac{\Delta T_f}{K_fm} = \frac{0.068}{1.86 \times 0.01} = 3.6559.$$

The value exceeds unity because dissociation increases the number of dissolved particles.

Step 2: Relate the factor to dissociation of aluminium chloride The dissociation equation is



Thus one dissociated formula unit produces four ions. Starting with one mole, the undissociated salt contributes $1 - \alpha$ mole of particles and the ions contribute 4α mole. Consequently,

$$i = 1 + 3\alpha, \quad \alpha = \frac{3.6559 - 1}{3} = 0.8853.$$

Multiplication by 100 converts this fraction into the required percentage. As a check, $1 < i < 4$ gives

Quick Tip to Solve: Count all four ions from AlCl_3 before using $\alpha = (i - 1)/3$; the freezing-point depression is positive.

a physically allowed dissociation fraction between zero and one.

Step 3: Conclusion The percentage dissociation of AlCl_3 is $0.8853 \times 100 = 88.5\%$ (approximately).

Quick Tip to Solve: Count all four ions from AlCl_3 before using $\alpha = (i - 1)/3$; the freezing-point depression is positive.

31. (i) What are the hydrolysis products of DNA?

(ii) What happens when D-glucose is treated with Bromine water?

(iii) What is the effect of denaturation on the structure of proteins?

[3 marks]

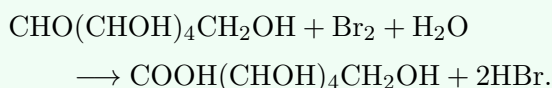
Solution:

Concept:

- DNA is a polynucleotide built from a pentose sugar, phosphate groups and nitrogenous bases. Complete hydrolysis separates these constituents.
- Bromine water is a mild oxidising agent that converts an aldehyde group into a carboxylic acid group.
- A protein's primary structure is its amino-acid sequence joined by peptide bonds; its secondary and tertiary structures depend on interactions that maintain folding.

Step 1: (i) Identify the products of complete DNA hydrolysis Complete hydrolysis of DNA yields the pentose sugar 2-deoxy-D-ribose, phosphoric acid and the nitrogenous bases adenine, guanine, cytosine and thymine. DNA contains deoxyribose rather than ribose; thymine is its characteristic pyrimidine base in place of uracil. These products account respectively for the sugar, phosphate and base components of its nucleotide units.

Step 2: (ii) Describe the action of bromine water on D-glucose Bromine water oxidises the aldehyde group of D-glucose to a carboxylic acid group, forming D-gluconic acid. The terminal primary alcohol group remains unchanged under these mild conditions:



Bromine water is decolourised as bromine is consumed. This reaction provides evidence for an aldehydic group in the open-chain form of glucose.

Step 3: (iii) Explain the structural change on protein denaturation Denaturation disrupts the interactions responsible for the secondary and tertiary structures, so the folded protein loses its native shape and biological activity. For example, hydrogen-bond disruption can unfold an ordered chain. The primary structure remains intact because ordinary denaturation does not hydrolyse the peptide bonds or change the amino-acid sequence. Thus loss of folding should be distinguished from breaking the chain into amino acids.

Step 4: Conclusion (i) DNA gives 2-deoxy-D-ribose, phosphoric acid, adenine, guanine, cytosine and thymine. (ii) D-glucose gives D-gluconic acid with bromine water. (iii) Denaturation destroys secondary and tertiary structures while retaining primary structure.

Quick Tip to Solve: Link DNA to deoxyribose and thymine; for denaturation, distinguish loss of folding from cleavage of peptide bonds.

32. When a steady current of 2A was passed through two electrolytic cells A and B containing electrolytes ZnSO_4 and CuSO_4 connected in series, 2 g of Cu were deposited at the cathode of cell B. How long did the current flow? What mass of Zn was deposited at cathode of cell A?

[Atomic mass: $\text{Cu} = 63.5 \text{ g mol}^{-1}$, $\text{Zn} = 65 \text{ g mol}^{-1}$; $1F = 96500 \text{ C mol}^{-1}$]

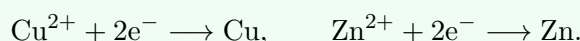
[3 marks]

Solution:

Concept:

- Faraday's first law gives $m = MQ/(zF)$, where m is deposited mass, M molar mass, $Q = It$ the charge, z electrons required per metal ion and $F = 96500 \text{ C mol}^{-1}$.
- Electrolytic cells connected in series receive the same charge. For this common charge, deposited masses are proportional to the equivalent masses M/z .

Step 1: Find the charge required for the copper deposit The cathode reactions are



Thus $z = 2$ for each metal. In cell B, 2 g of copper corresponds to $2/63.5$ mole of copper and twice this number of moles of electrons. Hence

$$Q = \frac{m_{\text{Cu}} z F}{M_{\text{Cu}}} = \frac{2 \times 2 \times 96500}{63.5} = 6078.74 \text{ C}.$$

Step 2: Calculate the time of current flow The steady current is $I = 2 \text{ A} = 2 \text{ C s}^{-1}$. Since $Q = It$,

$$t = \frac{Q}{I} = \frac{6078.74}{2} = 3039.37 \text{ s} = 50.66 \text{ min}.$$

The time is the same for both cells because they are in the same series circuit.

Step 3: Calculate the zinc deposited by the same charge Equal charge passes through both electrolytes; it is not divided between the cells. Applying Faraday's second law,

$$\frac{m_{\text{Zn}}}{m_{\text{Cu}}} = \frac{M_{\text{Zn}}/2}{M_{\text{Cu}}/2} = \frac{65}{63.5}.$$

Therefore

$$m_{\text{Zn}} = 2 \times \frac{65}{63.5} = 2.0472 \text{ g}.$$

Zinc has a slightly greater equivalent mass than copper, so its deposited mass is correspondingly slightly greater.

Step 4: Conclusion The current flowed for $3.04 \times 10^3 \text{ s}$ (about 50.7 min), depositing 2.05 g of zinc in cell A.

Quick Tip to Solve: In series, use the same charge in both cells; since both ions are divalent, their deposited masses follow their molar-mass ratio.

33(a). Write three differences between lyophobic sol and lyophilic sol.

[3 marks]

Solution:

Concept:

- A lyophilic sol has a strong affinity between its dispersed phase and dispersion medium; a lyophobic sol has little affinity between them.
- Solvation is the association of dispersion-medium molecules with dispersed particles. In water this association is called hydration and contributes to colloidal stability.

Step 1: Compare affinity and preparation Lyophilic sols form because the dispersed substance has a strong attraction for the medium. They can generally be prepared by directly mixing the substance with a suitable dispersion medium; starch or gum in water is an example. Lyophobic sols have little attraction for the medium and require special dispersion or condensation methods for preparation; a gold sol in water is an example. Thus, the first difference is strong versus weak affinity for the dispersion medium.

Step 2: Compare reversibility Lyophilic sols are reversible: after the dispersion medium is removed, the residue can again form a sol on adding the medium. Lyophobic sols are irreversible: once precipitated or coagulated, their particles do not readily form the original sol merely by adding the dispersion medium. This is a second independent difference.

Step 3: Compare stability towards electrolytes Lyophilic sols are relatively stable because their particles are strongly solvated; a comparatively large amount of electrolyte is needed to coagulate them. Lyophobic sols are less stable and are readily coagulated by small amounts of a suitable electrolyte, which neutralises the charge responsible for their stability. This provides the third difference.

Step 4: Conclusion The three differences are: lyophobic sols have little affinity for the medium, are irreversible and coagulate readily; lyophilic sols have strong affinity, are reversible and resist coagulation by small amounts of electrolyte.

Quick Tip to Solve: Organise the comparison under affinity, reversibility and electrolyte stability so that each of the three differences is independent.

OR

33(b). Define the following terms:

- (i) Protective colloid
- (ii) Zeta potential
- (iii) Emulsifying agent

[3 marks]

Solution:

Concept:

- Colloidal stability depends on interactions at the interface between dispersed particles and the surrounding medium, including solvation and electrical charge.

Quick Tip to Solve: Link each term to its function: protection against coagulation, electrical double-layer potential, and prevention of droplet coalescence.

- Emulsions contain two immiscible liquids: one forms dispersed droplets and the other is the dispersion medium. An interfacial stabiliser helps prevent the droplets from joining together.

Step 1: Define protective colloid A protective colloid is a lyophilic colloid which, when added to a lyophobic sol, protects it against coagulation by electrolytes. Its particles form a protective, solvated layer around the lyophobic particles and improve their stability. For example, gelatin can protect a gold sol. The protective effect is associated with the stabilising layer surrounding the dispersed particles.

Step 2: Define zeta potential Zeta potential, also called electrokinetic potential, is the potential difference between the fixed layer of charge associated with a colloidal particle and the diffuse layer of opposite charge surrounding it. The charged particle attracts counter-ions from the medium, producing an electrical double layer. Zeta potential thus describes the electrical potential difference associated with these layers, rather than the charge on the particle itself.

Step 3: Define emulsifying agent An emulsifying agent is a substance added to an emulsion to stabilise it. It forms an interfacial film between the two immiscible liquid phases and prevents the dispersed droplets from coalescing. Soap, detergent and gum are common examples. By keeping droplets from combining into larger drops, it helps prevent separation of the liquid phases.

Step 4: Conclusion A protective colloid protects a lyophobic sol from coagulation; zeta potential is the potential difference between the fixed and diffuse charge layers; an emulsifying agent stabilises an emulsion against coalescence.

Quick Tip to Solve: Link each term to its function: protection against coagulation, electrical double-layer potential, and prevention of droplet coalescence.

34. Give reasons:

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

(ii) Aromatic primary amines cannot be prepared by Gabriel's phthalimide synthesis.

(iii) Aliphatic amines are stronger bases than ammonia.

[3 marks]

Solution:

Concept:

- A Lewis acid accepts an electron pair. The nitrogen lone pair of an amine can coordinate to a Lewis acid or accept a proton, so its availability controls the amine's reactivity and basicity.
- Gabriel synthesis involves nucleophilic substitution of a halide by the phthalimide anion. Alkyl groups exert an electron-releasing inductive effect, denoted by $+I$.

Step 1: (i) Explain the behaviour of aniline in Friedel-Crafts reactions Aniline reacts with the Lewis-acid catalyst $AlCl_3$ through the lone pair on nitrogen, forming an aniline-aluminium chloride salt/complex. Nitrogen then acquires positive character and withdraws electron density from the benzene ring. The ring becomes strongly deactivated towards electrophilic substitution, so aniline does not undergo the usual Friedel-Crafts alkylation or acylation reaction.

Step 2: (ii) Explain the limitation of Gabriel synthesis In Gabriel's phthalimide synthesis, potassium

Quick Tip to Solve: For these three reasons, identify what controls the step: catalyst binding, aryl-halide substitution, and availability of the nitrogen lone pair.

phthalimide must displace halide by nucleophilic substitution. To prepare an aromatic primary amine, an aryl halide would be required. Aryl halides do not undergo the required nucleophilic substitution under the conditions of Gabriel synthesis: resonance gives the aryl carbon-halogen bond partial double-bond character and makes it difficult to break. Hence the required N-arylphthalimide intermediate is not formed by this route.

Step 3: (iii) Compare aliphatic amines with ammonia Alkyl groups attached to nitrogen donate electron density by their $+I$ effect. The nitrogen lone pair in an aliphatic amine is consequently more available for accepting a proton than the lone pair in ammonia. The alkyl group also helps stabilise the positive charge of the conjugate alkylammonium ion. Therefore, aliphatic amines are generally stronger bases than ammonia.

Step 4: Conclusion Aniline is deactivated by complex formation with $AlCl_3$; aryl halides resist the substitution required in Gabriel synthesis; and the electron-releasing $+I$ effect of alkyl groups makes aliphatic amines stronger bases than ammonia.

Quick Tip to Solve: For these three reasons, identify what controls the step: catalyst binding, aryl-halide substitution, and availability of the nitrogen lone pair.

Section D (15 marks)

35(a). Write the products formed when benzaldehyde reacts with the following reagents:

(i) CH_3CHO in presence of dilute NaOH

(ii) $\text{H}_2\text{N}-\text{NH}-\text{C}_6\text{H}_5$ (phenylhydrazine)

(iii) Conc. NaOH

(b) Distinguish between following:

(i) $\text{CH}_3-\text{CH}=\text{CH}-\text{CO}-\text{CH}_3$ and $\text{CH}_3-\text{CH}_2-\text{CO}-\text{CH}=\text{CH}_2$

(ii) Benzaldehyde and Benzoic acid.

[5 marks]

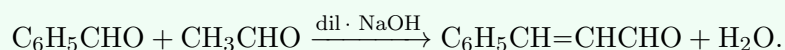


Solution:

Concept:

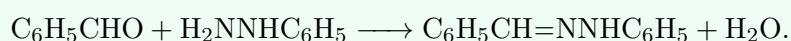
- Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no α -hydrogen. It undergoes crossed aldol condensation with an aldehyde having α -hydrogens, but undergoes Cannizzaro disproportionation in concentrated alkali.
- Phenylhydrazine condenses with the carbonyl group to form a phenylhydrazone, with elimination of water.
- The iodoform test identifies the methyl ketone group, $-\text{COCH}_3$. Carboxylic acids liberate CO_2 from aqueous sodium hydrogen carbonate; aldehydes do not.

Step 1: (a)(i) Carry out crossed aldol condensation Ethanal has α -hydrogens and forms an enolate in dilute NaOH . This attacks the carbonyl carbon of benzaldehyde, which cannot itself form an enolate. The initial β -hydroxy aldehyde loses water to give cinnamaldehyde (3-phenylprop-2-enal):



The new carbon-carbon bond joins the ethanal α -carbon to the original carbonyl carbon of benzaldehyde; the aldehyde group in the final product comes from ethanal.

Step 2: (a)(ii) Form the phenylhydrazone The terminal $-\text{NH}_2$ group of phenylhydrazine reacts with the carbonyl group. Addition followed by loss of water replaces $\text{C}=\text{O}$ by $\text{C}=\text{N}-\text{NHC}_6\text{H}_5$:



Quick Tip to Solve: Look directly beside the carbonyl carbon for $-\text{CH}_3$ before choosing the iodoform test. For benzaldehyde, dilute alkali with ethanal gives crossed aldol condensation, whereas concentrated alkali alone gives Cannizzaro products.

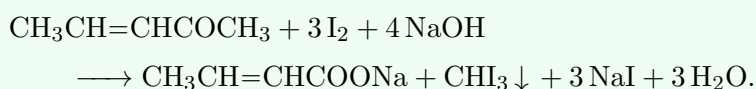
The product is benzaldehyde phenylhydrazone. The hydrogen originally attached to the aldehyde carbon remains on that carbon.

Step 3: (a)(iii) Apply the Cannizzaro reaction In concentrated NaOH, two molecules of benzaldehyde undergo disproportionation. One is reduced to benzyl alcohol and the other is oxidised to sodium benzoate:



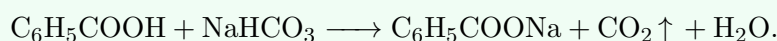
Sodium benzoate, rather than free benzoic acid, is formed because the reaction medium is strongly alkaline.

Step 4: (b)(i) Distinguish the two ketones by the iodoform test Warm separate samples with iodine and aqueous NaOH. The compound $\text{CH}_3\text{CH}=\text{CHCOCH}_3$ contains a methyl ketone group and gives a yellow precipitate of iodoform, CHI_3 :



The compound $\text{CH}_3\text{CH}_2\text{COCH}=\text{CH}_2$ has no $-\text{COCH}_3$ group, so it gives no yellow iodoform precipitate. Both compounds contain a carbon-carbon double bond, so a test for unsaturation does not distinguish them.

Step 5: (b)(ii) Test with sodium hydrogen carbonate Add aqueous NaHCO_3 separately to the samples. Benzoic acid gives brisk effervescence of carbon dioxide:

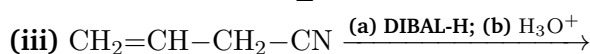
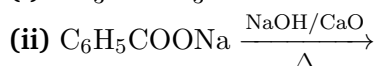
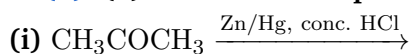


Benzaldehyde gives no such effervescence because it has no carboxylic acid group. The evolved gas can be confirmed by its turning limewater milky.

Step 6: Conclusion (a) The products are (i) cinnamaldehyde, $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$; (ii) benzaldehyde phenylhydrazone, $\text{C}_6\text{H}_5\text{CH}=\text{NNHC}_6\text{H}_5$; and (iii) benzyl alcohol plus sodium benzoate. (b) The first ketone alone gives yellow iodoform; benzoic acid alone effervesces with aqueous NaHCO_3 .

Quick Tip to Solve: Look directly beside the carbonyl carbon for $-\text{CH}_3$ before choosing the iodoform test. For benzaldehyde, dilute alkali with ethanal gives crossed aldol condensation, whereas concentrated alkali alone gives Cannizzaro products.

35(b). (a) Write the final products in the following:



(b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:



(c) Draw the structure of 2,4-DNP derivative of acetaldehyde.

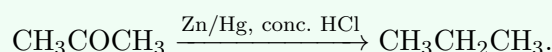
[5 marks]

Solution:

Concept:

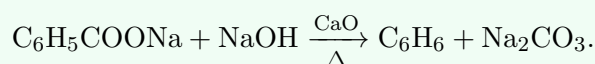
- Clemmensen reduction, using zinc amalgam and concentrated hydrochloric acid, converts the carbonyl group of an aldehyde or ketone into a methylene group without changing the carbon skeleton.
- Heating a sodium carboxylate with soda lime removes its carboxyl carbon as carbonate. DIBAL-H reduces a nitrile to an intermediate which gives an aldehyde on acidic hydrolysis.
- Nucleophilic addition is favoured by a more electrophilic, less crowded carbonyl carbon. Alkyl donation, steric hindrance and conjugation with a phenyl ring reduce reactivity.
- 2,4-Dinitrophenylhydrazine reacts through its terminal amino group with a carbonyl compound, eliminating water to form a 2,4-dinitrophenylhydrazone.

Step 1: (a)(i) Reduce acetone by the Clemmensen method The ketone carbonyl group $>\text{C}=\text{O}$ is reduced to $>\text{CH}_2$. Both methyl groups remain attached to the same central carbon:



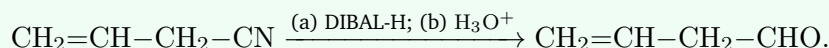
The product is propane; Clemmensen reduction does not stop at the secondary alcohol.

Step 2: (a)(ii) Decarboxylate sodium benzoate Soda lime is a mixture of sodium hydroxide and calcium oxide. On heating, the carboxylate group is replaced by hydrogen, giving a hydrocarbon with one carbon atom fewer:



Thus the organic product is benzene. The aromatic ring remains intact.

Step 3: (a)(iii) Convert the nitrile into an aldehyde DIBAL-H selectively reduces the nitrile group; subsequent acidic hydrolysis gives the aldehyde. The nitrile carbon becomes the aldehyde carbon, and the carbon-carbon double bond remains:



The product is but-3-enal. This partial reduction gives an aldehyde rather than the primary amine

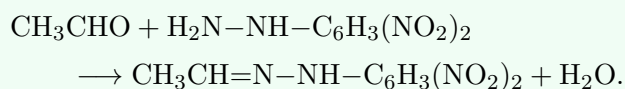
Quick Tip to Solve: Track the functional-group carbon: Clemmensen retains it as methylene, soda lime removes it, and DIBAL-H retains the nitrile carbon as the aldehyde carbon.

obtained on complete reduction of a nitrile.

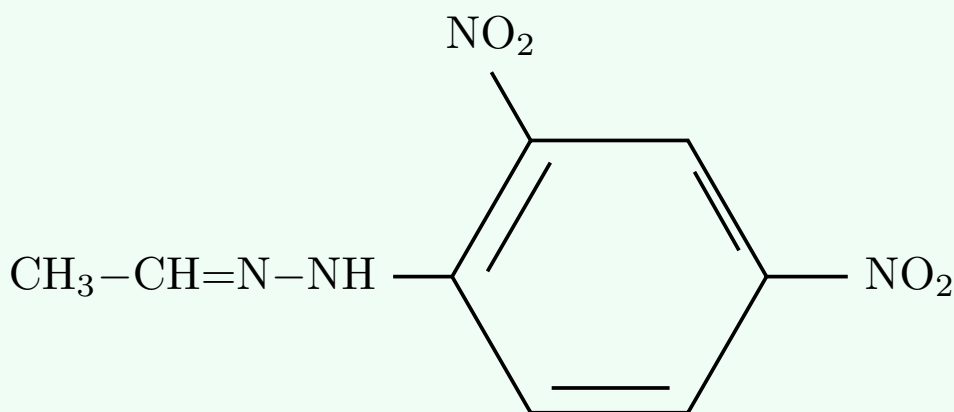
Step 4: (b) Compare carbonyl electrophilicity and crowding Formaldehyde has no electron-donating alkyl group and offers the least steric hindrance, so it is the most reactive. Acetaldehyde has one methyl group, whereas acetone has two; the second methyl group both donates electron density and hinders the approaching nucleophile. In acetophenone, conjugation of the carbonyl group with the phenyl ring further lowers the electrophilicity of its carbonyl carbon. Hence the increasing order is



Step 5: (c) Form the 2,4-DNP derivative of acetaldehyde Acetaldehyde condenses with 2,4-dinitrophenylhydrazine to give acetaldehyde 2,4-dinitrophenylhydrazone. The carbonyl oxygen and two hydrogens from the terminal amino group leave as water:



In the structure below, the nitro groups occupy positions 2 and 4 relative to the ring carbon bonded to the hydrazone nitrogen. The original aldehydic hydrogen remains on the carbon of the C=N bond.



Acetaldehyde 2,4-dinitrophenylhydrazone

Step 6: Conclusion (a) The products are (i) propane, $\text{CH}_3\text{CH}_2\text{CH}_3$; (ii) benzene, C_6H_6 ; and (iii) but-3-enal, $\text{CH}_2=\text{CHCH}_2\text{CHO}$. (b) Increasing reactivity: $\text{C}_6\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}$. (c) The derivative is $\text{CH}_3\text{CH}=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$, with nitro groups at positions 2 and 4.

Quick Tip to Solve: Track the functional-group carbon: Clemmensen retains it as methylene, soda lime removes it, and DIBAL-H retains the nitrile carbon as the aldehyde carbon.

36(a). A first order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% completed?

(b) Define order of reaction. Write the condition under which a bimolecular reaction follows first order kinetics. [5 marks]

Solution:

Concept:

- For a first order reaction, the rate is proportional to the concentration of one reactant: $r = k[A]$. Its integrated equation is $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the initial and remaining concentrations.
- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law. Molecularity counts the reacting species in an elementary step and need not equal the observed order.
- A bimolecular reaction can show pseudo first order kinetics when one reactant is present in such large excess that its concentration remains practically constant during the reaction.

Step 1: (a) Determine the fraction remaining after 40 minutes Completion of 25% means that 75% of the initial reactant remains. Thus $[A]_t = 0.75[A]_0$, so the concentration ratio in the integrated equation is $1/0.75 = 4/3$, rather than 4. Substituting the given time,

$$\begin{aligned}k &= \frac{2.303}{40} \log \frac{4}{3} \\&= \frac{2.303}{40} (0.6021 - 0.4771) \\&= 7.20 \times 10^{-3} \text{ min}^{-1}.\end{aligned}$$

A first order rate constant has units of inverse time; since the time was entered in minutes, its unit here is min^{-1} .

Step 2: (a) Calculate the total time for 80 percent completion At 80% completion only 20% remains, giving $[A]_0/[A]_t = 5$. The rate constant is unchanged at the same temperature, and therefore

$$\begin{aligned}t_{80} &= \frac{2.303}{k} \log 5 \\&= 40 \frac{\log 5}{\log(4/3)} \\&= 40 \frac{0.6991}{0.1250} \\&\simeq 223.7 \text{ min}.\end{aligned}$$

This is the time measured from the start of the reaction. It exceeds 40 minutes because progressively less reactant is available and the instantaneous rate decreases as the reaction proceeds.

Step 3: (b) Define order and explain the pseudo first order condition If the experimental rate law is $r = k[A]^m[B]^n$, the order of reaction is $m + n$, the sum of the concentration exponents in that rate law. It is obtained experimentally and cannot generally be read from the balanced overall chemical equation.

Quick Tip to Solve: Always convert percent completion to percent remaining before substituting into the first order logarithm; use a ratio of times to cancel the rate constant.

For a bimolecular reaction with rate law $r = k[A][B]$, take B in large excess. Its fractional consumption is then negligible, so $[B] \simeq [B]_0$ throughout the measurement. Hence

$$r = k[B]_0[A] = k_{\text{obs}}[A], \quad k_{\text{obs}} = k[B]_0.$$

The observed rate now depends only on the first power of the changing concentration $[A]$. Acid hydrolysis of an ester in a large excess of water is a standard example at constant acid concentration.

Step 4: Conclusion (a) $k \simeq 7.20 \times 10^{-3} \text{ min}^{-1}$ and $t_{80} \simeq 224 \text{ min}$. (b) Order is the sum of concentration powers in the experimental rate law. A bimolecular reaction exhibits pseudo first order kinetics when one reactant is in sufficiently large excess that its concentration is effectively constant.

Quick Tip to Solve: Always convert percent completion to percent remaining before substituting into the first order logarithm; use a ratio of times to cancel the rate constant.

OR

36(b). (a) A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(b) Write the two conditions for collisions to be effective collisions.

(c) How order of reaction and molecularity differ towards a complex reaction?

[Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$, $\log 5 = 0.6991$]

[5 marks]

Solution:

Concept:

- For a first order reaction, $t_{1/2} = \ln 2/k$. Thus, at different temperatures, rate constants are inversely proportional to the corresponding half-lives.
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$. At two temperatures it gives $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$, where E_a is activation energy and R is the gas constant.
- An effective collision requires sufficient energy to overcome the activation barrier and an orientation suitable for the required bond rearrangement.

Step 1: (a) **Obtain the rate constant ratio from the half-lives** A reaction is half complete when 50% of its reactant has reacted, so the stated times are half-lives. For the two temperatures,

$$\begin{aligned} T_1 &= 300 \text{ K}, & t_{1/2,1} &= 30 \text{ min}, \\ T_2 &= 320 \text{ K}, & t_{1/2,2} &= 10 \text{ min}. \end{aligned}$$

Using $k = 0.693/t_{1/2}$, we obtain $k_1 = 0.0231 \text{ min}^{-1}$ and $k_2 = 0.0693 \text{ min}^{-1}$. Equivalently, their ratio follows directly:

$$\frac{k_2}{k_1} = \frac{t_{1/2,1}}{t_{1/2,2}} = \frac{30}{10} = 3.$$

This ratio is dimensionless; no conversion of minutes to seconds is needed because both rate constants use the same time unit.

Quick Tip to Solve: When a first order reaction is 50 percent complete, use the time directly as its half-life; the rate constant ratio is the inverse half-life ratio.

Step 2: (a) Apply the two-temperature Arrhenius equation Rearranging the Arrhenius relation and substituting $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$,

$$\begin{aligned} E_a &= \frac{2.303R \log(k_2/k_1)}{1/T_1 - 1/T_2} \\ &= \frac{2.303(8.314)(0.4771)}{1/300 - 1/320} \\ &= 2.303(8.314)(0.4771) \frac{300 \times 320}{20} \\ &\simeq 4.385 \times 10^4 \text{ J mol}^{-1} \\ &= 43.85 \text{ kJ mol}^{-1}. \end{aligned}$$

The sign is positive: $k_2 > k_1$ and $1/T_1 - 1/T_2 > 0$, consistent with a faster reaction at the higher temperature.

Step 3: (b) State both requirements for effective collisions First, the colliding molecules must possess sufficient kinetic energy to cross the activation energy barrier; collisions below the required threshold cannot form products. Second, the molecules must collide with the proper orientation so that the required bonds can break and new bonds can form. An energetic collision with unsuitable orientation can therefore still be ineffective.

Step 4: (c) Distinguish order and molecularity for a complex reaction The order of a complex reaction is defined for the overall experimentally determined rate law as the sum of its concentration powers. It reflects the reaction mechanism and its rate-controlling steps, and may be zero, integral or fractional. Molecularity is the number of reacting species participating in a single elementary step. A complex reaction consists of several elementary steps, each with its own molecularity. Molecularity is therefore not assigned to the overall complex reaction; it is meaningful only for its individual elementary steps and is always a positive integer. The coefficients of the overall equation do not determine its observed order.

Step 5: Conclusion (a) $E_a = 43.85 \text{ kJ mol}^{-1}$. (b) Effective collisions require sufficient collision energy and proper molecular orientation. (c) Overall order is experimentally defined for a complex reaction, whereas molecularity is defined only for its individual elementary steps.

Quick Tip to Solve: When a first order reaction is 50 percent complete, use the time directly as its half-life; the rate constant ratio is the inverse half-life ratio.

37(a). Give reasons:

- (i) Transition metals and their compounds show catalytic activities.
- (ii) Separation of a mixture of Lanthanoid elements is difficult.
- (iii) Zn, Cd and Hg are soft and have low melting point.

(b) Write the preparation of the following:

- (i) $\text{Na}_2\text{Cr}_2\text{O}_7$ from Na_2CrO_4
- (ii) K_2MnO_4 from MnO_2

[5 marks]

Solution:

Concept:

- Transition metals can exhibit variable oxidation states and form intermediate complexes, providing reaction pathways with lower activation energy.
- Lanthanoids predominantly form tripositive ions with very similar ionic radii; the resulting similarity of chemical properties makes separation difficult.
- Metallic bond strength depends on the electrons available for bonding. The filled d^{10} subshells of Zn, Cd and Hg contribute little to metallic bonding.
- Acidification converts chromate into dichromate, whereas oxidative fusion of manganese dioxide with alkali produces manganate.

Step 1: (a)(i) Explain catalytic activity Transition metals and their compounds can change oxidation state during a reaction and form intermediate complexes with reactants. These intermediates provide an alternative pathway of lower activation energy; the catalyst is regenerated at the end. Finely divided metals also adsorb reactants on their surfaces, increasing contact and weakening bonds in the adsorbed molecules. For example, iron catalyses ammonia synthesis and V_2O_5 catalyses oxidation of SO_2 to SO_3 .

Step 2: (a)(ii) Explain the difficulty of lanthanoid separation Lanthanoids generally occur together as +3 ions. Successive ionic sizes decrease only slightly because of lanthanoid contraction. Consequently, their ionic radii and chemical properties, including basicity and solubility behaviour, are very similar. Ordinary chemical separation therefore distinguishes them only weakly, so separating a mixture is difficult.

Step 3: (a)(iii) Relate softness to weak metallic bonding The configurations of Zn, Cd and Hg contain completely filled d^{10} subshells. There are no unpaired d electrons to strengthen the metallic bond, unlike many other transition-series metals. Their relatively weak interatomic metallic bonding accounts for their softness and low melting points; mercury is liquid at room temperature.

Step 4: (b)(i) Acidify sodium chromate Treat an aqueous solution of sodium chromate with dilute sulphuric acid. Yellow chromate is converted into orange dichromate:

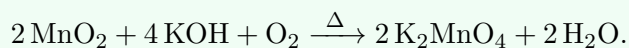


The ionic equilibrium is $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$. Increasing the hydrogen ion concentration shifts it towards dichromate. Concentrating the solution allows sodium dichromate to crystallise, commonly as its dihydrate.

Step 5: (b)(ii) Oxidise manganese dioxide in molten alkali Fuse MnO_2 with potassium hydroxide in

Quick Tip to Solve: Distinguish the two preparations: add acid to chromate for dichromate, but use hot alkali and an oxidant for green manganate.

the presence of air or oxygen. The manganese oxidation state rises from +4 to +6, producing green potassium manganate:



Oxygen supplies the oxidising action and the strongly alkaline medium stabilises manganate. The product here is manganate, K_2MnO_4 , rather than permanganate.

Step 6: Conclusion Catalysis follows from variable oxidation states, intermediate formation and adsorption; lanthanoid separation is difficult because their tripositive ions have similar sizes; weak metallic bonding explains the softness and low melting points of Zn, Cd and Hg. Acidification prepares $\text{Na}_2\text{Cr}_2\text{O}_7$ from chromate, and oxidative fusion of MnO_2 with KOH prepares K_2MnO_4 .

Quick Tip to Solve: Distinguish the two preparations: add acid to chromate for dichromate, but use hot alkali and an oxidant for green manganate.

OR

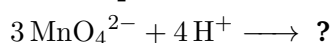
37(b). (a) Account for the following:

(i) Ti^{3+} is coloured whereas Sc^{3+} is colourless in aqueous solution.

(ii) Cr^{2+} is a strong reducing agent.

(b) Write two similarities between chemistry of lanthanoids and actinoids.

(c) Complete the following ionic equation:



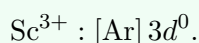
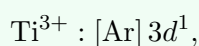
[5 marks]

Solution:

Concept:

- In aqueous transition-metal ions, ligands split the d -orbital energies. Absorption of visible light can produce a $d-d$ transition when a suitable d electron is present.
- A reducing agent loses an electron and is oxidised. Formation of the relatively stable d^3 configuration favours oxidation of Cr^{2+} to Cr^{3+} .
- Lanthanoids and actinoids are inner-transition series involving filling of $4f$ and $5f$ subshells respectively; both commonly show the +3 oxidation state and contraction across their series.
- Disproportionation converts one oxidation state into both a higher and a lower oxidation state, with equal numbers of electrons lost and gained.

Step 1: (a)(i) Compare the electronic configurations Titanium has atomic number 22 and scandium has atomic number 21. Removing the $4s$ electrons before the $3d$ electrons gives

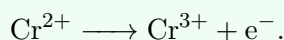


In hydrated Ti^{3+} , the single d electron can absorb visible light and move between the ligand-field-split d levels. The transmitted light therefore appears coloured. Hydrated Sc^{3+} has no d electron, so a $d-d$

Quick Tip to Solve: For manganate disproportionation, use two manganese atoms going from +6 to +7 for each one going from +6 to +4; then balance oxygen with water and hydrogen with acid.

transition is impossible and the ion is colourless.

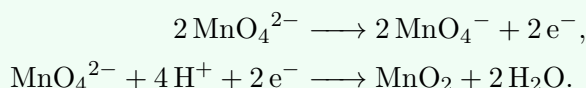
Step 2: (a)(ii) Explain the reducing action of chromium(II) The configurations of Cr^{2+} and Cr^{3+} are $[\text{Ar}] 3d^4$ and $[\text{Ar}] 3d^3$, respectively. In an octahedral aqueous complex, the d^3 ion has the stable t_{2g}^3 arrangement. Chromium(II) readily loses an electron to form this more stable chromium(III) state:



By donating this electron to another species, Cr^{2+} reduces that species; thus it acts as a strong reducing agent.

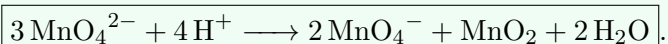
Step 3: (b) State two similarities of the two inner-transition series First, both lanthanoids and actinoids commonly exhibit the +3 oxidation state, although actinoids also show a wider range of other oxidation states. Second, both series show a progressive decrease in atomic and ionic radii as atomic number increases: lanthanoid contraction in the $4f$ series and actinoid contraction in the $5f$ series. Poor shielding by the added f electrons allows the increasing nuclear charge to attract the outer electrons more strongly.

Step 4: (c) Balance the disproportionation of manganate In MnO_4^{2-} , manganese is in oxidation state +6. In acidic medium it disproportionates into permanganate, containing manganese in +7, and manganese dioxide, containing manganese in +4. Two manganese atoms each lose one electron, while a third gains two electrons. The half-equations are



On adding them, electrons cancel. There are three manganese atoms, twelve oxygen atoms and four hydrogen atoms on each side, and both sides have total charge -2 .

Step 5: Conclusion Ti^{3+} is coloured because its d^1 configuration permits $d-d$ transitions; Sc^{3+} is d^0 and colourless. Cr^{2+} reduces other species while forming stable Cr^{3+} . Both inner-transition series commonly show +3 and a contraction in size. The completed equation is



Quick Tip to Solve: For manganate disproportionation, use two manganese atoms going from +6 to +7 for each one going from +6 to +4; then balance oxygen with water and hydrogen with acid.