

CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/1/2 - Compartment



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Questions number 1 to 8 are very short-answer questions and carry 1 mark each.
- (iii) Questions number 9 to 18 are short-answer questions and carry 2 marks each.
- (iv) Questions number 19 to 27 are also short-answer questions and carry 3 marks each.
- (v) Questions number 28 to 30 are long-answer questions and carry 5 marks each.
- (vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. What type of stoichiometric defect is shown by NaCl?

[1 mark]

Solution:

Concept:

- A stoichiometric defect preserves the ratio of cations to anions and the electrical neutrality of the crystal.
- In a Schottky defect, equal numbers of cations and anions are absent from their normal lattice sites.

Step 1: Identify the vacancy defect NaCl is an ionic crystal in which both Na^+ and Cl^- can be missing from their respective lattice sites. The vacancies occur in equal numbers, so the ratio $\text{Na}^+ : \text{Cl}^- = 1 : 1$ is maintained.

Step 2: Check the consequences The removal of one positive ion together with one negative ion preserves electrical neutrality. Since some ions are missing while the crystal volume remains nearly unchanged, its density decreases. This distinguishes this vacancy defect from a Frenkel defect, in which an ion occupies an interstitial site.

Step 3: Conclusion NaCl shows a **Schottky defect**.

Quick Tip to Solve: Equal cation and anion vacancies with decreased density identify a Schottky defect.

2. Define 'Emulsions'.

[1 mark]

Solution:

Concept:

- A colloid consists of a dispersed phase distributed throughout a dispersion medium.
- For an emulsion, both the dispersed phase and the dispersion medium are liquids that are immiscible with one another.

Step 1: Identify the two phases In an emulsion, fine droplets of one liquid form the dispersed phase, while another liquid forms the continuous dispersion medium. The liquids do not dissolve uniformly in one another; one is dispersed as colloidal droplets in the other.

Step 2: Illustrate the definition For example, milk is an oil-in-water emulsion: fat droplets are dispersed in an aqueous medium. Emulsions may also be water-in-oil, where water droplets are dispersed in an oily continuous phase. Thus, the essential classification is liquid dispersed in liquid.

Step 3: Conclusion Emulsions are colloidal dispersions of one liquid in another immiscible liquid.

Quick Tip to Solve: For an emulsion, identify both phases as liquids; one exists as droplets in the other.

3. Draw the structure of XeF₄.

[1 mark]

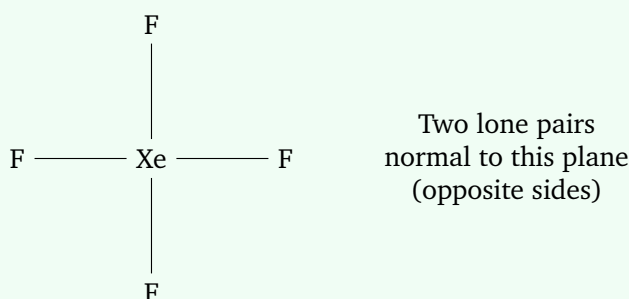
Solution:

Concept:

- VSEPR theory predicts geometry by minimising repulsion between electron pairs around a central atom.
- In XeF₄, xenon has four bonding pairs and two lone pairs: the electron-pair arrangement is octahedral.

Step 1: Count electron pairs around xenon Xenon has eight valence electrons. Four electrons participate in four single Xe – F bonds, leaving four electrons as two lone pairs. Hence, there are six electron-pair regions around Xe, corresponding to AX₄E₂.

Step 2: Place the atoms and lone pairs The two lone pairs occupy opposite positions in the octahedral arrangement to minimise their mutual repulsion. The four fluorine atoms therefore lie in one plane, at the corners of a square centred on xenon. Adjacent F – Xe – F angles are 90°, and opposite fluorine atoms subtend 180°.



Square-planar XeF₄; the two lone pairs lie above and below the plane.

Step 3: Conclusion XeF₄ has a **square-planar structure**, with its two lone pairs trans to one another above and below the molecular plane.

Quick Tip to Solve: For XeF₄, start with six electron regions and place the two lone pairs opposite each other.

4. What role is played by CO₂ in getting pure alumina (Al₂O₃) in the extraction of aluminium?

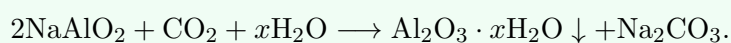
[1 mark]

Solution:

Concept:

- In the Bayer process, alumina dissolves in aqueous sodium hydroxide as soluble sodium aluminate.
- Passing carbon dioxide through sodium aluminate solution precipitates hydrated alumina, which yields pure alumina on heating.

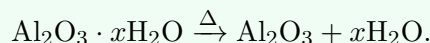
Step 1: Precipitate hydrated alumina Carbon dioxide neutralises the alkaline sodium aluminate solution and brings down hydrated alumina as a precipitate. A conventional representation is



Quick Tip to Solve: Connect CO₂ with precipitation of hydrated alumina, then calcination to the pure oxide.

The hydrated alumina is separated from the solution.

Step 2: Obtain the pure oxide The precipitated hydrated alumina is filtered, washed and heated. Calcination removes its water, giving pure aluminium oxide:



Thus, carbon dioxide enables recovery of alumina from its soluble aluminate form.

Step 3: Conclusion CO_2 precipitates hydrated alumina from sodium aluminate solution; heating the precipitate gives pure Al_2O_3 .

Quick Tip to Solve: Connect CO_2 with precipitation of hydrated alumina, then calcination to the pure oxide.

5. Draw the structure of 2-bromopentane.

[1 mark]

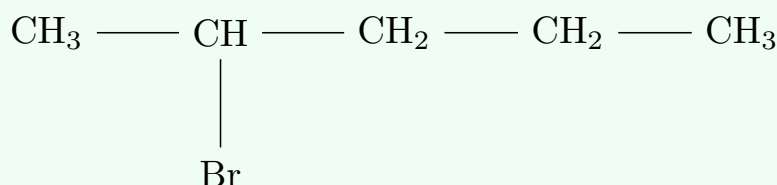
Solution:

Concept:

- The parent name pentane specifies an open chain of five carbon atoms joined by single bonds.
- The locant 2 in 2-bromopentane places the bromine substituent on carbon 2 of that chain.

Step 1: Build and number the parent chain Write a chain of five carbon atoms and number it from the end nearer the substituent. The parent skeleton is pentane, so it contains no carbon-carbon double or triple bonds. The bromine-bearing carbon must have locant 2, rather than 4.

Step 2: Attach bromine and complete valencies Attach Br to the second carbon. This carbon bonds to its two neighbouring carbons, one hydrogen and bromine. The terminal carbons are CH_3 groups, and the third and fourth carbons are CH_2 groups. This gives five carbons and a single bromine substituent, with molecular formula $\text{C}_5\text{H}_{11}\text{Br}$.



Structural formula of 2-bromopentane.

Step 3: Conclusion The structure is $\boxed{\text{CH}_3 - \text{CH}(\text{Br}) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3}$.

Quick Tip to Solve: Write the five-carbon chain first, then replace one hydrogen on carbon 2 by bromine.

6. Why do transition elements show variable oxidation states?

[1 mark]

Solution:

Concept:

- Transition elements have valence electrons in both the outer ns and inner $(n-1)d$ subshells.
- The small energy difference between these subshells allows different numbers of electrons to participate in bonding.

Step 1: Compare the valence subshells The ns and $(n-1)d$ orbitals are close in energy. Thus the outer s electrons and a variable number of d electrons can be used in bond formation or removed during oxidation.

Step 2: Relate electron participation to oxidation state Different numbers of valence electrons can therefore be involved in different compounds. For example, iron exhibits +2 and +3 oxidation states, corresponding to different extents of electron loss.

Step 3: Conclusion Transition elements show variable oxidation states because their ns and $(n-1)d$ electrons have similar energies and can participate in bonding in different numbers.

Quick Tip to Solve: Link variable oxidation states to the small energy gap between ns and $(n-1)d$ orbitals.

7. Out of $\text{CH}_3\text{--NH}_2$ and $(\text{CH}_3)_3\text{N}$, which one has higher boiling point?

[1 mark]

Solution:

Concept:

- Boiling point depends on the total intermolecular attraction, including hydrogen bonding and London dispersion forces.
- A hydrogen-bond comparison alone is reliable only when molecular size and other factors are comparable.

Step 1: Compare hydrogen bonding Methylamine, CH_3NH_2 , has N--H bonds and can form intermolecular hydrogen bonds. Trimethylamine, $(\text{CH}_3)_3\text{N}$, lacks an N--H bond, so its pure liquid cannot form such hydrogen bonds.

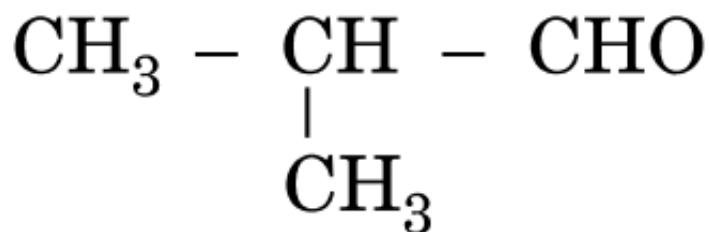
Step 2: Compare the actual pair Trimethylamine has a larger electron cloud and greater molar mass, giving stronger dispersion attractions. For this pair these effects outweigh methylamine's hydrogen bonding. The normal boiling points are approximately 3°C for trimethylamine and -6°C for methylamine.

Step 3: Conclusion $(\text{CH}_3)_3\text{N}$, trimethylamine, has the higher normal boiling point.

Quick Tip to Solve: Check molecular size as well as N-H bonds: these two amines are not isomers.

8. Write the IUPAC name of the following compound.

[1 mark]



Solution:

Concept:

- For an aldehyde, select the longest carbon chain containing the $-\text{CHO}$ carbon; that carbon receives position 1.
- Use the suffix $-\text{al}$ for the parent aldehyde and state the position of each alkyl substituent.

Step 1: Choose and number the parent chain The longest continuous chain containing the aldehyde carbon has three carbon atoms: $\text{CHO} - \text{CH} - \text{CH}_3$. Numbering starts at CHO , so the parent compound is propanal.

Step 2: Locate the substituent The middle carbon, numbered 2, carries the remaining CH_3 group as a methyl substituent. Combining its locant and name with the parent gives 2-methylpropanal.

Step 3: Conclusion The IUPAC name is 2-methylpropanal.

Quick Tip to Solve: Count the CHO carbon in the parent chain and always assign it position 1.

9. Differentiate between molarity and molality of a solution. How can we change the molality value of a solution into the molarity value?

[2 marks]

Solution:

Concept:

- Molarity M is moles of solute per litre of solution; molality m is moles of solute per kilogram of solvent.
- To convert between them, use the solution density d in g mL^{-1} and solute molar mass M_s in g mol^{-1} .

Step 1: Distinguish the two concentrations

$$M = \frac{n_{\text{solute}}}{V_{\text{solution in litres}}}, \quad m = \frac{n_{\text{solute}}}{w_{\text{solvent in kilograms}}}$$

Their units are mol L^{-1} and mol kg^{-1} , respectively. Molarity changes with temperature because solution volume changes; molality is temperature independent because it uses mass.

Step 2: Convert using a mass basis Take 1 kg of solvent. There are m moles of solute, of mass mM_s grams. The solution mass is $(1000 + mM_s)$ grams and its volume is $(1000 + mM_s)/(1000d)$ litres.

Quick Tip to Solve: Choose 1 kg of solvent, then add the solute mass before using density to find solution volume.

Therefore,

$$M = \frac{1000dm}{1000 + mM_s}.$$

Density must be taken at the temperature at which the molarity is required.

Step 3: Conclusion Molarity uses solution volume; molality uses solvent mass. Their conversion is $M = 1000dm/(1000 + mM_s)$, with the units defined above.

Quick Tip to Solve: Choose 1 kg of solvent, then add the solute mass before using density to find solution volume.

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

(b) Write the unit of rate constant 'k' for the first order reaction.

[2 marks]

Solution:

Concept:

- The overall order is the sum of concentration exponents in the experimentally determined rate law.
- For a first order reaction, $\text{Rate} = k[A]$; rate has units $\text{mol L}^{-1} \text{s}^{-1}$.

Step 1: Part (a): add the rate-law powers The given expression is $\text{Rate} = k[A]^1[B]^2$. It is first order with respect to A and second order with respect to B . Thus the overall reaction order is

$$n = 1 + 2 = 3.$$

Reaction order follows the stated rate law, not the stoichiometric coefficients in the reaction equation.

Step 2: Part (b): derive the unit for first order For a separate first order reaction, $k = \text{Rate}/[A]$. Hence

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

The concentration units cancel completely. This unit applies to the first order reaction asked about in part (b), rather than to the third order rate law in part (a).

Step 3: Conclusion (a) The order is $\boxed{3}$. (b) The first order rate constant has unit $\boxed{\text{s}^{-1}}$.

Quick Tip to Solve: Keep the two parts separate: part (b) explicitly asks for a first order rate constant.

11. Describe the underlying principles of the following processes:

(i) Froth floatation process of concentration of ores

(ii) Vapour phase refining of metals

[2 marks]

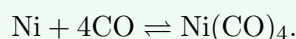
Solution:

Concept:

- Froth floatation separates particles according to their different wetting behaviour towards oil and water.
- Vapour phase refining forms a volatile metal compound that can be separated and decomposed to recover pure metal.

Step 1: Part (i): froth floatation The principle is preferential wetting: sulphide ore particles are wetted by oil, while gangue particles are wetted by water. Finely powdered ore is mixed with water and a suitable frothing agent such as pine oil. Air is blown through the mixture; oil-wetted ore particles attach to air bubbles and rise with the froth. Water-wetted gangue remains behind. The froth is skimmed off to obtain concentrated ore.

Step 2: Part (ii): vapour phase refining The impure metal is converted selectively into a volatile compound using a suitable reagent. This vapour separates from nonvolatile impurities and is then decomposed under suitable conditions to deposit pure metal. Thus the compound must form readily, be volatile, and decompose readily to yield the metal. For example, in Mond refining,



Volatile nickel carbonyl is formed and subsequently heated to recover pure nickel.

Step 3: Conclusion (i) Froth floatation uses differential wetting by oil and water. (ii) Vapour phase refining uses formation and decomposition of a volatile metal compound.

Quick Tip to Solve: For floatation state which material each liquid wets; for refining state both formation and decomposition.

12. Draw the structures of the following compounds:

(i) H_2SO_3

(ii) N_2O_5

[2 marks]

Solution:

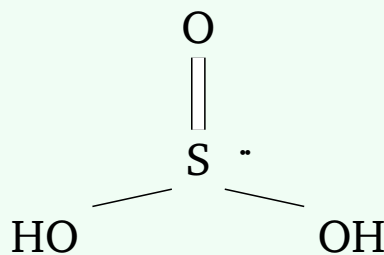
Concept:

- In an oxoacid, acidic hydrogen atoms are attached to oxygen. Thus sulphurous acid has two hydroxyl groups, rather than direct S–H bonds.
- In molecular dinitrogen pentoxide, two nitrogen centres are joined through a bridging oxygen. Formal charges allow each nitrogen to obey the octet rule.

Step 1: (i) Sulphurous acid The structure is $\text{HO} - \text{S}(=\text{O}) - \text{OH}$. Sulphur is the central atom, bonded to two hydroxyl oxygen atoms by single bonds and to one oxygen atom by a double bond. It also has

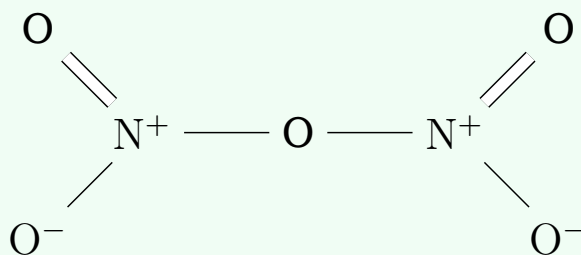
Quick Tip to Solve: Attach both hydrogens of sulphurous acid to oxygen; use an oxygen bridge between the two nitrogen atoms in dinitrogen pentoxide.

one lone pair, so the arrangement of the three oxygen atoms around sulphur is pyramidal.



Sulphurous acid

Step 2: (ii) Dinitrogen pentoxide The molecular structure is $\text{O}_2\text{N} - \text{O} - \text{NO}_2$. Each nitrogen has one terminal double-bonded oxygen, one terminal single-bonded oxygen and a bond to the central bridging oxygen. Each nitrogen carries formal charge +1, and each singly bonded terminal oxygen carries -1. Resonance interchanges the two terminal N-O bonds in each group; the molecule is electrically neutral.



Molecular dinitrogen pentoxide (one resonance form)

Step 3: Conclusion The required structures are $\text{HO} - \text{S}(=\text{O}) - \text{OH}$ and molecular $\text{O}_2\text{N} - \text{O} - \text{NO}_2$, as drawn.

Quick Tip to Solve: Attach both hydrogens of sulphurous acid to oxygen; use an oxygen bridge between the two nitrogen atoms in dinitrogen pentoxide.

13(a). Assign a reason for each of the following observations:

- The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
- The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly.

[2 marks]

Solution:

Concept:

- The strength of metallic bonding depends on the number of valence electrons participating in bonding, including the $(n - 1)d$ and ns electrons.
- Ionisation enthalpy is the energy required to remove an electron from a gaseous atom or ion. Nuclear attraction and the stability of the initial and final electronic configurations both affect it.

Quick Tip to Solve: For physical strength discuss metallic bonding; for irregular ionisation energies compare the configurations before and after electron removal.

Step 1: (i) Hardness and high melting and boiling points Transition metals generally have several unpaired d electrons as well as outer s electrons available for strong metallic bonding. Their high enthalpies of atomisation reflect this strong cohesion, making them hard and requiring much energy to melt or boil. Zn, Cd and Hg have filled d^{10} subshells and weaker metallic bonding, so they are exceptions.

Step 2: (ii) Irregular ionisation enthalpies Across the first transition series, increasing nuclear charge tends to increase ionisation enthalpy, but changes in shielding and electron-electron repulsion oppose a uniform trend. The extra stability of half-filled d^5 and completely filled d^{10} configurations also affects the energy of removal. Removing an electron may destroy or produce such a stable configuration. These competing effects cause irregular first and second ionisation enthalpies.

Step 3: Conclusion Strong metallic bonding explains the hardness and high melting and boiling points; changing d-electron configurations and their relative stabilities explain the irregular ionisation enthalpies.

Quick Tip to Solve: For physical strength discuss metallic bonding; for irregular ionisation energies compare the configurations before and after electron removal.

OR

13(b). What is lanthanoid contraction? Write a consequence of lanthanoid contraction.

[2 marks]

Solution:

Concept:

- Across the lanthanoid series, electrons enter the inner 4f subshell while the nuclear charge increases.
- The 4f electrons shield the nuclear charge poorly. Consequently the effective nuclear attraction on the electron cloud increases across the series.

Step 1: Define lanthanoid contraction and its cause Lanthanoid contraction is the gradual decrease in atomic and ionic radii of the lanthanoids with increasing atomic number, from lanthanum to lutetium. In particular, the radii of the corresponding Ln^{3+} ions decrease steadily. Added 4f electrons do not adequately screen the additional nuclear charge, so the outer electron cloud is drawn closer to the nucleus.

Step 2: State a consequence One consequence is the very similar radii of corresponding second- and third-row transition elements, for example zirconium and hafnium. The increase in size expected on adding a new shell in hafnium is largely offset by the preceding lanthanoid contraction. Thus Zr and Hf have very similar chemical properties and are difficult to separate.

Step 3: Conclusion Lanthanoid contraction is the gradual decrease in lanthanoid atomic and ionic radii; a consequence is the almost equal sizes and closely similar chemistry of Zr and Hf.

Quick Tip to Solve: Link poor shielding by 4f electrons to increasing effective nuclear charge, then cite the Zr–Hf similarity as a consequence.

14. Assign reason for each of the following:

(i) Transition elements exhibit paramagnetic behaviour.

(ii) Co^{2+} is easily oxidised in the presence of a strong ligand.

[2 marks]

Solution:

Concept:

- An unpaired electron has a magnetic moment. Species with one or more unpaired electrons are attracted into an applied magnetic field and are paramagnetic.
- Strong-field ligands produce a large splitting of d-orbital energies; the resulting crystal-field stabilisation can favour one oxidation state over another.

Step 1: (i) Paramagnetism of transition elements Transition elements and many of their ions have incompletely filled d subshells containing unpaired electrons. The magnetic moments of these electrons account for their paramagnetic behaviour. The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton. A species with no unpaired electrons is diamagnetic.

Step 2: (ii) Oxidation of cobalt(II) with a strong ligand Co^{2+} has a $3d^7$ configuration, whereas Co^{3+} has $3d^6$. In an octahedral strong-field complex, cobalt(III) forms the particularly stable low-spin configuration $t_{2g}^6 e_g^0$, with all electrons in the lower-energy set. The large crystal-field stabilisation of this cobalt(III) complex favours oxidation of cobalt(II) to cobalt(III) in the presence of a suitable oxidant. The strong ligand stabilises the product; it need not itself be the oxidant.

Step 3: Conclusion Unpaired d electrons cause paramagnetism. Strong ligands stabilise low-spin Co^{3+} , t_{2g}^6 , favouring oxidation of Co^{2+} .

Quick Tip to Solve: Count unpaired electrons for magnetism; compare d7 cobalt(II) with the stable low-spin d6 cobalt(III) complex for oxidation.

15. Enumerate the reactions of glucose which cannot be explained by its open chain structure.

[2 marks]

Solution:

Concept:

- An open-chain glucose molecule, $\text{CHO}(\text{CHOH})_4\text{CH}_2\text{OH}$, contains a free aldehyde group and five hydroxyl groups.
- A free aldehyde group should show characteristic carbonyl addition reactions; the observed exceptions support a cyclic hemiacetal structure.

Step 1: List the missing aldehyde reactions Despite containing an aldehyde group in its proposed open-chain formula, glucose does not give Schiff's test and does not form the usual addition product with sodium hydrogen sulphite, NaHSO_3 . Thus it does not behave as a simple freely available aldehyde in these reactions.

Step 2: Examine the pentaacetate reaction Glucose pentaacetate does not react with hydroxylamine, NH_2OH , to form an oxime. If a free $-\text{CHO}$ group remained in the pentaacetate, oxime formation

Quick Tip to Solve: Distinguish glucose from its pentaacetate: the hydroxylamine exception belongs specifically to the pentaacetate.

would be expected. Its failure indicates that the carbonyl group is not free in this derivative.

Step 3: Conclusion The unexplained observations are: absence of Schiff's test, absence of a NaHSO_3 addition product, and failure of glucose pentaacetate to form an oxime with hydroxylamine.

Quick Tip to Solve: Distinguish glucose from its pentaacetate: the hydroxylamine exception belongs specifically to the pentaacetate.

16. Write the equations involved in the following reactions:

(i) Williamson ether synthesis

(ii) Kolbe's reaction

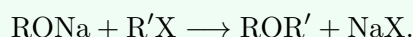
[2 marks]

Solution:

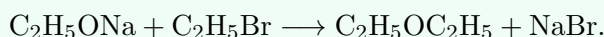
Concept:

- Williamson synthesis prepares an ether by the S_N2 reaction of a sodium alkoxide with an alkyl halide.
- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure; acidification gives salicylic acid.

Step 1: (i) Williamson ether synthesis The general equation is

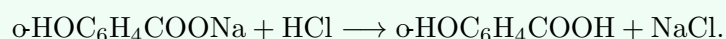
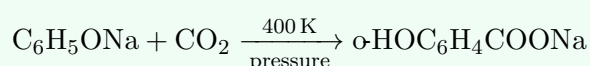


For example, sodium ethoxide reacts with ethyl bromide to give ethoxyethane:



A primary alkyl halide is preferred because it undergoes substitution readily.

Step 2: (ii) Kolbe reaction Sodium phenoxide is heated with carbon dioxide at about 400 K under 4–7 atm pressure, producing sodium salicylate. Acidification liberates salicylic acid:



The carboxyl group is introduced mainly ortho to the phenolic hydroxyl group.

Step 3: Conclusion Williamson synthesis yields an ether, while Kolbe's reaction of sodium phenoxide followed by acidification yields salicylic acid (2-hydroxybenzoic acid).

Quick Tip to Solve: In the phenols chapter, Kolbe reaction means carboxylation of sodium phenoxide; show the acidification step.

17. Answer the following questions:

(i) Why are vitamin A and vitamin C essential for us?

(ii) What is the difference between a nucleoside and a nucleotide?

[2 marks]

Solution:

Concept:

- Vitamins are organic micronutrients needed for normal physiological functions; their deficiency produces characteristic disorders.
- A nucleoside contains a nitrogenous base linked to a pentose sugar. Adding a phosphate group gives a nucleotide.

Step 1: (i) Importance of vitamins A and C Vitamin A is essential for normal vision, particularly vision in dim light, and for maintaining healthy epithelial tissues. Its deficiency can cause night blindness and xerophthalmia. Vitamin C (ascorbic acid) is essential for collagen formation, healthy gums and wound healing; it also acts as an antioxidant. Its deficiency causes scurvy, associated with bleeding gums and poor healing.

Step 2: (ii) Compare the molecular components A nucleoside consists of a nitrogenous base joined to ribose or deoxyribose through an N-glycosidic linkage. A nucleotide contains these same two components plus a phosphate group attached to the sugar, usually at its 5' hydroxyl group. Thus adenosine is a nucleoside, whereas adenosine monophosphate (AMP) is a nucleotide. Nucleotides are the building units of nucleic acids.

Step 3: Conclusion Vitamin A supports vision and epithelial health; vitamin C supports collagen formation and healing. Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.

Quick Tip to Solve: Use phosphate as the deciding feature: its presence distinguishes a nucleotide from a nucleoside.

18. How are the following conversions carried out?

(i) Propene to Propan-2-ol

(ii) Ethyl chloride to Ethanal

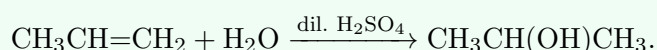
[2 marks]

Solution:

Concept:

- Acid-catalysed hydration of an unsymmetrical alkene follows Markovnikov addition, putting hydroxyl on the more substituted carbon.
- Aqueous alkali replaces chlorine in a primary chloroalkane by hydroxyl. Controlled oxidation of the resulting primary alcohol gives an aldehyde.

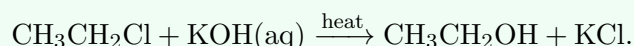
Step 1: (i) Convert propene into propan-2-ol Add water to propene in the presence of dilute sulphuric acid. Hydrogen adds to the terminal carbon and hydroxyl to the middle carbon:



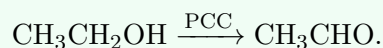
Quick Tip to Solve: For ethyl chloride to ethanal, insert ethanol as the intermediate and choose a reagent that stops at the aldehyde.

This gives the required secondary alcohol, propan-2-ol, in accordance with Markovnikov's rule.

Step 2: (ii) Convert ethyl chloride into ethanal First heat ethyl chloride with aqueous potassium hydroxide to obtain ethanol:



Then oxidise ethanol with pyridinium chlorochromate (PCC), which stops the oxidation at the aldehyde stage:



Aqueous alkali is used for substitution; alcoholic alkali would favour elimination to ethene. Avoid excess strong aqueous oxidant, which can oxidise ethanal further to ethanoic acid.

Step 3: Conclusion Propene $\xrightarrow{\text{H}_2\text{O}/\text{H}^+}$ propan-2-ol; ethyl chloride $\xrightarrow{\text{aq. KOH}}$ ethanol $\xrightarrow{\text{PCC}}$ ethanal.

Quick Tip to Solve: For ethyl chloride to ethanal, insert ethanol as the intermediate and choose a reagent that stops at the aldehyde.

19. Hydrogen peroxide, H_2O_2 (aq) decomposes to H_2O (l) and O_2 (g) in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3} \text{ min}^{-1}$.

(i) How long will it take for 15% of a sample of H_2O_2 to decompose?

(ii) How long will it take for 85% of the sample to decompose?

[3 marks]

Solution:

Concept:

- For a first-order decomposition, the integrated rate equation is $kt = \ln([A]_0/[A]_t)$, where $[A]_0$ is the initial concentration and $[A]_t$ is the concentration remaining after time t .
- The fraction remaining is one minus the fraction decomposed. Since the rate constant is $k = 1.06 \times 10^{-3} \text{ min}^{-1}$, a time calculated with this value will be in minutes.

Step 1: Establish the concentration ratio Take the initial amount of hydrogen peroxide as 100 units. For a fixed sample volume, the ratio of concentrations equals the ratio of amounts. Thus, if $x\%$ decomposes, the remaining amount is $100 - x$ units, and

$$t = \frac{1}{1.06 \times 10^{-3}} \ln \left(\frac{100}{100 - x} \right).$$

The equation must use peroxide remaining, rather than peroxide consumed.

Step 2: Calculate the time for 15 percent decomposition Here, 85 percent of the original peroxide remains. Substituting this ratio into the first-order equation gives

$$t_{15} = \frac{\ln(100/85)}{1.06 \times 10^{-3}} = \frac{0.162519}{1.06 \times 10^{-3}} = 153.32 \text{ min}.$$

This time is less than the half-life, as expected because less than half of the sample has reacted.

Quick Tip to Solve: Convert the percentage decomposed to percentage remaining before inserting it into the logarithm.

Step 3: Calculate the time for 85 percent decomposition Here, only 15 percent remains. Hence

$$t_{85} = \frac{\ln(100/15)}{1.06 \times 10^{-3}} = \frac{1.897120}{1.06 \times 10^{-3}} = 1789.74 \text{ min.}$$

The much longer time is consistent with first-order kinetics: the reaction rate decreases as hydrogen peroxide is consumed, so equal additional percentages of the initial sample take progressively longer to decompose.

Step 4: Conclusion (i) The time for 15 percent decomposition is 1.53×10^2 min. (ii) The time for 85 percent decomposition is 1.79×10^3 min.

Quick Tip to Solve: Convert the percentage decomposed to percentage remaining before inserting it into the logarithm.

20. Some ethylene glycol, $\text{HOCH}_2\text{CH}_2\text{OH}$, is added to your car's cooling system along with 5 kg of water. If the freezing point of the water-glycol solution is -15.0°C , what is the boiling point of the solution?

($K_b = 0.52 \text{ K kg mol}^{-1}$ and $K_f = 1.86 \text{ K kg mol}^{-1}$ for water)

[3 marks]

Solution:

Concept:

- For a nonvolatile solute, freezing-point depression is $\Delta T_f = K_f m$ and boiling-point elevation is $\Delta T_b = K_b m$, where m is molality in mol kg^{-1} .
- Ethylene glycol is a molecular nonelectrolyte, so its van't Hoff factor is $i = 1$. The same solution molality determines both temperature changes.

Step 1: Find the freezing-point depression At normal atmospheric pressure, pure water freezes at 0.0°C . The solution freezes at -15.0°C , so the depression is the positive difference

$$\Delta T_f = 0.0 - (-15.0) = 15.0 \text{ K.}$$

A temperature difference has the same numerical value in kelvin and degrees Celsius.

Step 2: Use the depression to obtain the solution molality Using the given cryoscopic constant,

$$m = \frac{\Delta T_f}{K_f} = \frac{15.0 \text{ K}}{1.86 \text{ K kg mol}^{-1}} = 8.0645 \text{ mol kg}^{-1}.$$

Although the system contains 5 kg of water, that mass need not be used separately: the measured freezing point already fixes the number of solute moles per kilogram of water. Multiplying by 5 would find the total moles, but would not change the molality.

Step 3: Calculate the boiling-point elevation and boiling point The same molality gives

$$\Delta T_b = K_b m = 0.52 \times 8.0645 = 4.1935 \text{ K.}$$

Equivalently, the molality can be eliminated to give $\Delta T_b = (K_b/K_f)\Delta T_f$. Taking the normal boiling

Quick Tip to Solve: Eliminate molality directly: multiply the freezing-point depression by the ratio K_b/K_f .

point of pure water as 100.0°C , the solution boiling point is

$$T_b = 100.0 + 4.1935 = 104.1935^{\circ}\text{C}.$$

The boiling point increases because dissolved nonvolatile glycol lowers the vapour pressure of water.

Step 4: Conclusion The boiling point of the water–ethylene glycol solution is approximately 104.2°C at normal atmospheric pressure.

Quick Tip to Solve: Eliminate molality directly: multiply the freezing-point depression by the ratio K_b/K_f .

21. The density of copper is 8.95 g cm^{-3} . It has a face centred cubic structure. What is the radius of copper atom?

(Atomic mass Cu = 63.5 g mol^{-1} , $N_A = 6.02 \times 10^{23}\text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- An fcc unit cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms. Its density is $\rho = ZM/(N_A a^3)$, where M is molar mass, N_A is the Avogadro constant and a is the cube edge.
- In an fcc structure, atoms touch along a face diagonal. Thus $4r = \sqrt{2}a$, or $r = a/(2\sqrt{2})$, where r is the atomic radius.

Step 1: Calculate the mass of one fcc unit cell The eight corner atoms contribute one atom in total and the six face-centred atoms contribute three atoms, giving four copper atoms per cell. Hence the mass of one cell is

$$m_{\text{cell}} = \frac{4M}{N_A} = \frac{4 \times 63.5}{6.02 \times 10^{23}}\text{ g} = 4.2193 \times 10^{-22}\text{ g}.$$

Dividing the molar mass by the Avogadro constant first gives the mass of a single atom.

Step 2: Obtain the edge length from the density Since density is mass divided by volume, the cubic cell volume is

$$a^3 = \frac{m_{\text{cell}}}{\rho} = \frac{4 \times 63.5}{8.95 \times 6.02 \times 10^{23}}\text{ cm}^3 = 4.7143 \times 10^{-23}\text{ cm}^3.$$

Taking its cube root gives

$$a = 3.6125 \times 10^{-8}\text{ cm}.$$

The use of density in grams per cubic centimetre and molar mass in grams per mole makes the resulting edge length a length in centimetres.

Step 3: Use contact along the face diagonal A face diagonal joins a corner atom, a face-centred atom and the opposite corner atom. Its length contains four atomic radii, so

$$r = \frac{a}{2\sqrt{2}} = \frac{3.6125 \times 10^{-8}}{2\sqrt{2}}\text{ cm} = 1.2772 \times 10^{-8}\text{ cm}.$$

Using $1\text{ cm} = 10^{10}\text{ pm}$, this is 127.72 pm . The radius is smaller than half the cell edge, consistent with contact occurring along the longer face diagonal.

Step 4: Conclusion The radius of a copper atom is approximately $1.28 \times 10^{-8}\text{ cm} = 1.28 \times 10^{-10}\text{ m} =$

Quick Tip to Solve: For fcc, use four atoms per cell and face-diagonal contact: $r = a/(2\sqrt{2})$.

128 pm.

Quick Tip to Solve: For fcc, use four atoms per cell and face-diagonal contact: $r = a/(2\sqrt{2})$.

22. Define the following terms:

(i) Sorption

(ii) Tyndall effect

(iii) Electrophoresis

[3 marks]

Solution:

Concept:

- Adsorption is accumulation at a surface, whereas absorption involves entry into the bulk of a substance.
- Colloidal particles scatter visible light and normally carry a net electrical charge; these properties distinguish a colloidal sol from a true solution.

Step 1: (i) Sorption Sorption is the process in which adsorption and absorption occur simultaneously. The substance is taken up both at the surface and within the bulk of the material. For example, when a dye is taken up by cotton fibres, surface adsorption and penetration into the fibres can occur together. The combined uptake is called sorption.

Step 2: (ii) Tyndall effect The Tyndall effect is the scattering of light by colloidal particles, which makes the path of a beam passing through a colloidal sol visible. The illuminated path appears as a bright cone, called the Tyndall cone. A true solution does not show this effect appreciably because its dissolved particles are too small to scatter visible light in the same way.

Step 3: (iii) Electrophoresis Electrophoresis is the movement of colloidal particles towards an oppositely charged electrode when an electric field is applied. Positively charged particles move towards the cathode, whereas negatively charged particles move towards the anode. This motion provides evidence that the dispersed particles possess an electrical charge.

Step 4: Conclusion Sorption combines surface adsorption and bulk absorption; the Tyndall effect is light scattering by colloidal particles; electrophoresis is their motion under an applied electric field.

Quick Tip to Solve: Distinguish the three terms by asking: where is matter taken up, what happens to light, and what moves in an electric field?

23. Account for the following:

- (i) Aniline does not give Friedel-Crafts reaction.
(ii) Ethylamine is soluble in water whereas aniline is not.
(iii) pK_b of methylamine is less than that of aniline.

[3 marks]

Solution:

Concept:

- The nitrogen lone pair gives amines their Lewis basic character and allows hydrogen bonding with water.
- For a base, $pK_b = -\log K_b$; a larger K_b , and hence a smaller pK_b , means a stronger base.

Step 1: (i) Aniline and Friedel–Crafts reaction Aniline coordinates through its nitrogen lone pair with the Lewis acid catalyst, anhydrous $AlCl_3$, to form a salt-like complex. This removes the activating influence of the free amino group and strongly deactivates the aromatic ring towards electrophilic substitution. Consequently, aniline does not undergo the usual Friedel–Crafts alkylation or acylation under these conditions.

Step 2: (ii) Solubility in water Ethylamine forms hydrogen bonds with water through its $-NH_2$ group. Its ethyl group is small, so hydration adequately compensates for the nonpolar part and ethylamine is soluble in water. Aniline can also form hydrogen bonds, but its much larger hydrophobic phenyl group reduces its affinity for water. Thus aniline is only sparingly soluble, described as insoluble in the question.

Step 3: (iii) Relative basic strengths In methylamine, the electron-releasing inductive effect of CH_3 increases electron density on nitrogen, making its lone pair more available for protonation. In aniline, the lone pair is delocalised into the benzene ring by resonance and is less available to accept a proton. Therefore $K_b(CH_3NH_2) > K_b(C_6H_5NH_2)$, so methylamine has the smaller pK_b .

Step 4: Conclusion Aniline complexes with $AlCl_3$; its phenyl group limits water solubility; and resonance makes it a weaker base than methylamine.

Quick Tip to Solve: Compare lone-pair availability for basicity, but compare the hydrophobic group size for aqueous solubility.

24. (a) Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH$ group?

(i) CH_3Br or CH_3I

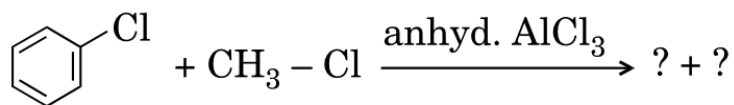
(ii) $(CH_3)_3CCl$ or CH_3Cl

(b) Write the product of the following reactions:

(i) $CH_3-Cl + KCN \rightarrow ?$

(ii) Chlorobenzene + $CH_3-Cl \xrightarrow{\text{anhyd. } AlCl_3} ? + ?$

[3 marks]



Solution:

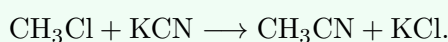
Concept:

- An S_N2 reaction proceeds by concerted backside attack. A better leaving group and lower steric hindrance increase its rate.
- CN^- from ionic KCN attacks mainly through carbon. Chlorine deactivates a benzene ring but directs electrophilic substitution to the ortho and para positions.

Step 1: (a)(i) Compare the leaving groups CH_3I reacts faster than CH_3Br with OH^- . Both substrates are methyl halides and have comparable steric accessibility. The weaker $C-I$ bond breaks more readily than the $C-Br$ bond, and iodide is a better leaving group than bromide.

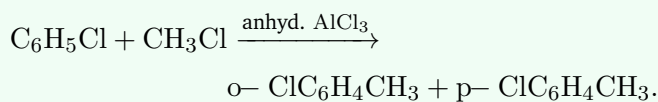
Step 2: (a)(ii) Compare steric hindrance CH_3Cl reacts faster than $(CH_3)_3CCl$. Hydroxide can readily approach the methyl carbon from the side opposite chlorine. In tert-butyl chloride, three methyl groups crowd the reacting carbon and strongly obstruct backside attack, making the S_N2 pathway unfavourable.

Step 3: (b)(i) Reaction with potassium cyanide KCN supplies cyanide ions whose carbon end attacks methyl chloride, replacing chloride to form ethanenitrile (acetonitrile):



The nitrile contains one more carbon atom than the starting haloalkane; methyl isocyanide is not the product with KCN.

Step 4: (b)(ii) Friedel-Crafts methylation In the presence of anhydrous $AlCl_3$, chlorobenzene gives the ortho and para methyl-substitution products requested:



These are 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene, respectively. Chlorine directs substitution to these positions by resonance; the para product is favoured because it has less steric crowding.

Step 5: Conclusion (a) Faster substrates: (i) CH_3I , (ii) CH_3Cl . (b) Products: (i) CH_3CN ; (ii) ortho-chlorotoluene and para-chlorotoluene.

Quick Tip to Solve: For S_N2 , compare steric crowding first, then leaving groups; remember that KCN adds a carbon to the product chain.

25(a). Write down the IUPAC name for each of the following complexes:



[3 marks]

Solution:

Concept:

- Name ligands alphabetically before the metal. Neutral NH_3 is ammine; Cl^- is chlorido and CN^- is cyanido. Prefixes give the number of each ligand.
- The oxidation state of the metal follows its name as a Roman numeral. An anionic coordination entity takes a metal name ending in -ate; the cation is named before the anion in a salt.

Step 1: (i) Name the cobalt salt The two chloride ions outside the square brackets require the complex cation to have charge +2. If the cobalt oxidation state is x , then $x + 5(0) - 1 = +2$, so $x = +3$. Five ammine ligands precede one chlorido ligand alphabetically. The name is **pentaamminechloridocobalt(III) chloride**. The external chloride is named separately and does not count among the coordinated ligands.

Step 2: (ii) Name the iron salt Three potassium ions balance a complex ion of charge -3 . Thus $x + 6(-1) = -3$, giving iron oxidation state +3. There are six cyanido ligands. Because the coordination entity is anionic, iron becomes ferrate. The complete name is **potassium hexacyanidoferrate(III)**.

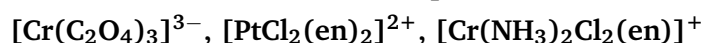
Step 3: (iii) Name the nickel complex ion For the complex anion, $x + 4(-1) = -2$, hence nickel is in oxidation state +2. Four chlorido ligands give tetrachlorido, and the anionic metal name is nickelate. Its name is **tetrachloridonickelate(II) ion**.

Step 4: Conclusion The names are (i) pentaamminechloridocobalt(III) chloride, (ii) potassium hexacyanidoferrate(III), and (iii) tetrachloridonickelate(II) ion.

Quick Tip to Solve: First calculate the charge inside the brackets; only an anionic coordination entity changes the metal name to -ate.

OR

25(b). Draw the structures of optical isomers of each of the following complex ions:



[3 marks]

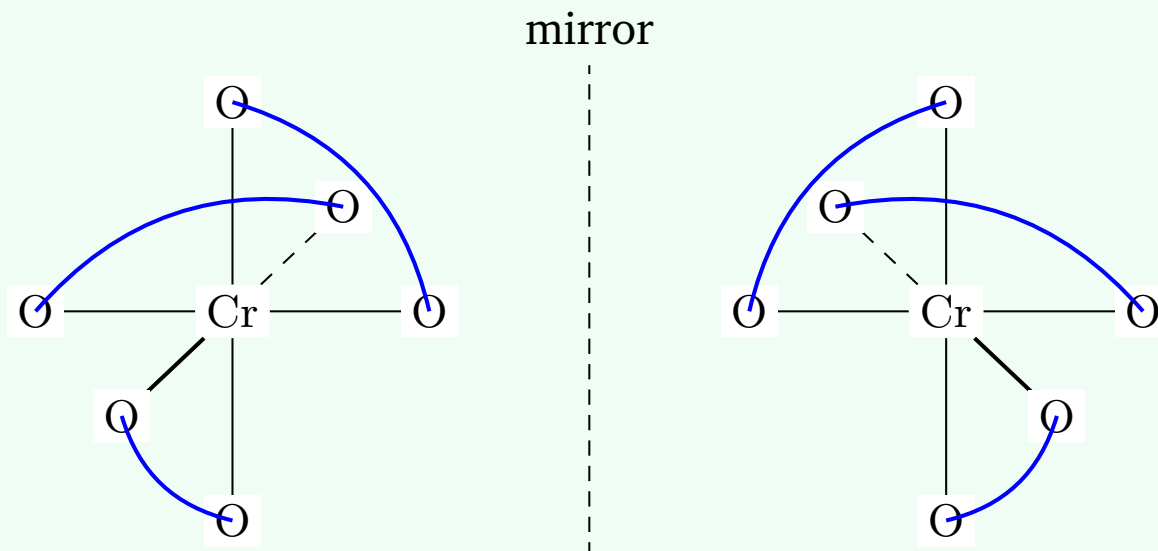
Solution:

Concept:

- Optical isomers are non-superimposable mirror images. All three ions have six donor atoms around the central metal and are represented as octahedral complexes.
- Oxalate and ethane-1,2-diamine (en) are bidentate ligands: their two donor atoms occupy adjacent coordination sites. The curved links in the figures indicate the donor atoms belonging to the same chelating ligand.

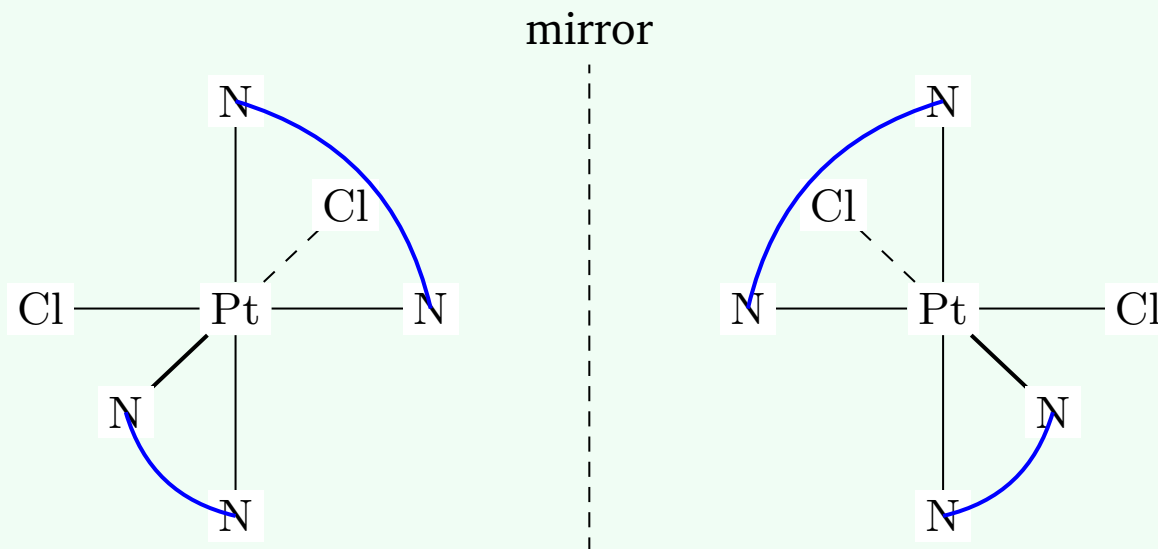
Quick Tip to Solve: Keep the two ends of every chelating ligand adjacent, then reflect the complete octahedral arrangement to obtain its optical partner.

Step 1: (i) Tris(oxalato)chromate(III) Each $\text{C}_2\text{O}_4^{2-}$ ligand supplies two O donors. Three oxalate chelate rings twist around chromium in either of two opposite senses, conventionally designated Δ and Λ . The structures below are mirror images with identical ligand connections. No rotation superposes all three chelate rings of one on the other.



Mirror-image tris(oxalato) pair. Each curved blue link joins the two O donors of one oxalate ligand.

Step 2: (ii) Dichloridobis(ethane-1,2-diamine)platinum(IV) The optically active form is the cis arrangement of $[\text{PtCl}_2(\text{en})_2]^{2+}$. Its two chloride ligands occupy adjacent sites, while two en ligands each join adjacent N donor positions. Reflection reverses the handed arrangement of the chelate rings, giving the two structures below. The trans form has a symmetry element that makes it optically inactive and is therefore not the pair requested.

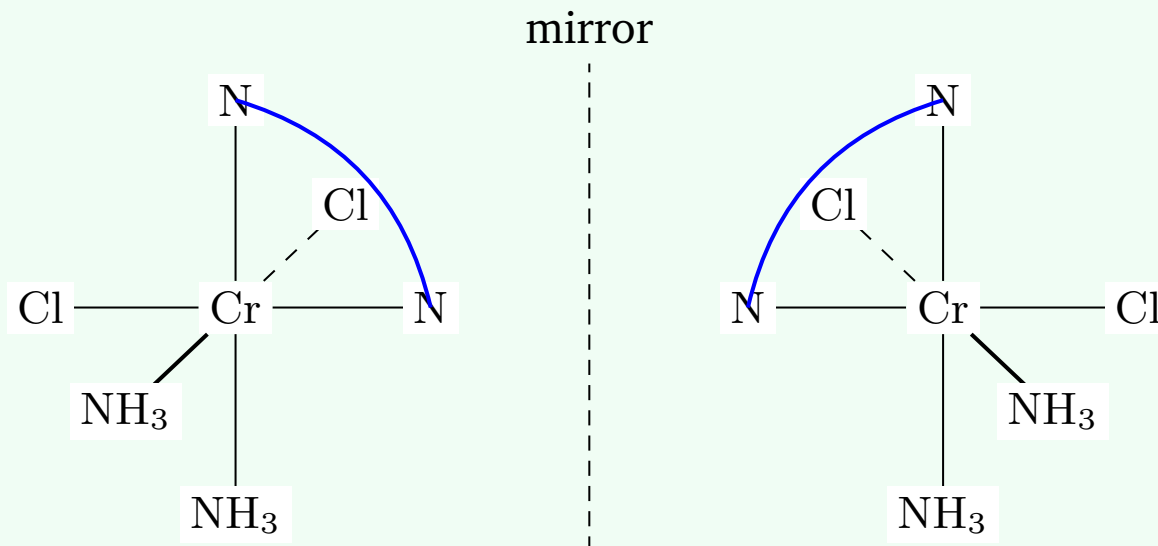


Optical pair of cis- $[\text{PtCl}_2(\text{en})_2]^{2+}$. Each blue link represents one ethane-1,2-diamine ligand.

Step 3: (iii) Diammine dichlorido(ethane-1,2-diamine)chromium(III) For $[\text{Cr}(\text{NH}_3)_2\text{Cl}_2(\text{en})]^+$, choose

Quick Tip to Solve: Keep the two ends of every chelating ligand adjacent, then reflect the complete octahedral arrangement to obtain its optical partner.

the cis-cis form: the two ammonia ligands are adjacent and the two chloride ligands are also adjacent. The en ligand occupies the remaining adjacent sites. This arrangement and its reflection form a non-superimposable pair. In each projection below, the vertical sites are opposite, the horizontal sites are opposite, and the two diagonal sites are opposite. Solid diagonal bonds project towards the viewer and dashed ones project away.



Optical pair with both like monodentate ligand pairs cis. The blue link joins the N donors of en.

Step 4: Conclusion The drawings show the optical pairs of the tris(oxalato) ion, cis dichloridobis(en) ion, and cis-cis diammine dichlorido(en) ion respectively.

Quick Tip to Solve: Keep the two ends of every chelating ligand adjacent, then reflect the complete octahedral arrangement to obtain its optical partner.

26. What are the following? Give one example of each.

- (i) Sweetening agents
- (ii) Food preservatives
- (iii) Antibiotics

[3 marks]

Solution:

Concept:

- Food additives are classified by their function: a sweetener supplies a sweet taste, whereas a preservative delays spoilage.
- Antibiotics act against susceptible microorganisms by inhibiting their growth or destroying them; they are used in treating microbial infections.

Step 1: (i) Sweetening agents Sweetening agents are substances added to food or beverages to impart a sweet taste. Artificial sweeteners can replace sugar when sweetness with a small calorific contribution is required. An example is saccharin, which is much sweeter than sucrose and is used

Quick Tip to Solve: Distinguish the three functions in order: impart sweetness, prevent food spoilage, and inhibit or kill susceptible microorganisms.

in small amounts. Its purpose is to sweeten the preparation, rather than to prevent microbial spoilage.

Step 2: (ii) Food preservatives Food preservatives are substances added to food to retard its spoilage, particularly spoilage caused by microorganisms, and thereby increase its usable storage life. An example is **sodium benzoate**, commonly used for preserving acidic food preparations such as fruit products. Preventing deterioration is the defining role of this class; a preservative need not provide sweetness.

Step 3: (iii) Antibiotics Antibiotics are chemical substances originally obtained from microorganisms, and also produced synthetically or semisynthetically, which at low concentrations inhibit the growth of or destroy other susceptible microorganisms. An example is **penicillin**, an antibiotic used against susceptible bacteria. Antibiotics do not serve as general cures for viral infections; their action depends on the organism and its susceptibility.

Step 4: Conclusion Examples: sweetening agent—saccharin; food preservative—sodium benzoate; antibiotic—penicillin.

Quick Tip to Solve: Distinguish the three functions in order: impart sweetness, prevent food spoilage, and inhibit or kill susceptible microorganisms.

27. Give the names of the monomers of the following polymers:

(i) Neoprene

(ii) Polystyrene

(iii) Polypropene

[3 marks]

Solution:

Concept:

- A monomer is the small molecule whose repeated addition forms a polymer chain. In addition polymerisation, carbon-carbon double bonds open to form bonds along the chain.
- The substituents on a monomer remain attached to the polymer backbone. To identify a monomer, restore the double bond without removing its phenyl, methyl or chlorine substituent.

Step 1: Identify the monomer of neoprene Neoprene is formed by polymerisation of chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its structure is $\text{CH}_2 = \text{C}(\text{Cl}) - \text{CH} = \text{CH}_2$. The chlorine substituent distinguishes it from buta-1,3-diene, which gives polybutadiene. Chloroprene is a conjugated diene, containing two alternating carbon-carbon double bonds.

Step 2: Identify the monomer of polystyrene Polystyrene is formed from styrene, also called phenylethene, $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$. The vinyl double bond opens during addition polymerisation; the phenyl group remains attached to every alternate carbon of the polymer chain. Thus its monomer is styrene, rather than benzene.

Step 3: Identify the monomer of polypropene Polypropene is formed from propene, $\text{CH}_2 = \text{CH} - \text{CH}_3$. Opening the double bond gives the repeating unit $[-\text{CH}_2 - \text{CH}(\text{CH}_3)-]_n$, retaining the methyl group as a side group on the chain.

Step 4: Conclusion (i) Neoprene: chloroprene (2-chlorobuta-1,3-diene); (ii) polystyrene: styrene

Quick Tip to Solve: Remember the chlorine-bearing diene for neoprene; restore a double bond while retaining the phenyl or methyl group for the other two polymers.

(phenylethene); (iii) polypropene: propene.

Quick Tip to Solve: Remember the chlorine-bearing diene for neoprene; restore a double bond while retaining the phenyl or methyl group for the other two polymers.

28(a). Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature.

(b) The measured resistance of a conductivity cell was 100 ohm. Calculate (i) the specific conductance and (ii) the molar conductance of the solution.

(Molar mass of KCl = 74.5 g mol^{-1} and cell constant = 1.25 cm^{-1})

[5 marks]

Solution:

Concept:

- Conductance is $G = 1/R$. Conductivity κ is the conductance of a solution between electrodes of unit area separated by unit distance: $\kappa = G(l/A)$, where l/A is the cell constant.
- Molar conductivity Λ_m is the conductance of the volume of solution containing one mole of electrolyte, placed between electrodes at unit separation. For c in mol L^{-1} , $\Lambda_m = 1000\kappa/c$ when κ is in S cm^{-1} .

Step 1: (a) Define conductivity and molar conductivity Conductivity measures the ability of a unit geometric volume of electrolyte solution to conduct current. Its SI unit is S m^{-1} ; the commonly used unit here is S cm^{-1} . Molar conductivity measures the conducting ability associated with one mole of dissolved electrolyte, including the ions produced by that mole. Its SI unit is $\text{S m}^2 \text{ mol}^{-1}$, or $\text{S cm}^2 \text{ mol}^{-1}$ with centimetre-based units.

Step 2: Explain the temperature dependence For an electrolyte solution, both conductivity and molar conductivity generally increase as temperature rises. The viscosity of the solvent decreases, so the ions move more readily under an applied electric field. Increased ionic mobility raises conductance. For a weak electrolyte, an increase in its ionisation can additionally increase the number of charge carriers.

Step 3: (b)(i) Calculate specific conductance Specific conductance is another name for conductivity. Using the measured resistance $R = 100 \Omega$ and cell constant $l/A = 1.25 \text{ cm}^{-1}$,

$$G = \frac{1}{100} = 0.0100 \text{ S}, \quad \kappa = \frac{1.25}{100} = 0.0125 \text{ S cm}^{-1}.$$

The cell constant converts the conductance of this particular cell into the conductivity of its solution.

Step 4: (b)(ii) Express the molar conductance If the solution concentration is $c \text{ mol L}^{-1}$, then

$$\Lambda_m = \frac{1000(0.0125)}{c} = \frac{12.5}{c} \text{ S cm}^2 \text{ mol}^{-1}.$$

The printed question supplies no concentration or mass of KCl per solution volume. The molar mass alone cannot determine concentration. Therefore a unique numerical molar conductance cannot be calculated from the given data. If x is the concentration in g L^{-1} , then $c = x/74.5$ and $\Lambda_m = 931.25/x \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: First calculate conductivity from cell constant divided by resistance; calculate molar conductivity only after obtaining the solution concentration.

Step 5: Conclusion Both conductivity and molar conductivity increase with temperature. Specific conductance is 0.0125 S cm^{-1} . Molar conductance is $12.5/c \text{ S cm}^2 \text{ mol}^{-1}$, where c is in mol L^{-1} ; a numerical value requires the missing concentration.

Quick Tip to Solve: First calculate conductivity from cell constant divided by resistance; calculate molar conductivity only after obtaining the solution concentration.

OR

28(b). (a) Predict the products of electrolysis in each of the following:

(i) An aqueous solution of AgNO_3 with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes.

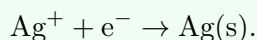
(b) Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C . The Gibbs energy change for the decomposition reaction $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$ is 960 kJ. ($F = 96500 \text{ C mol}^{-1}$) [5 marks]

Solution:

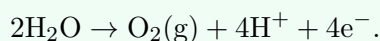
Concept:

- Reduction occurs at the cathode and oxidation at the anode. With inert platinum electrodes, the competing species are the dissolved ions and water.
- For an electrolytic reaction, the minimum external electrical work equals the positive Gibbs energy change: $E_{\min} = \Delta G/(nF)$, where n is the moles of electrons transferred for the reaction as written and F is the Faraday constant.

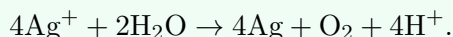
Step 1: (a)(i) Electrolysis of aqueous silver nitrate Silver ions are reduced preferentially to water, so silver metal is deposited on the platinum cathode:



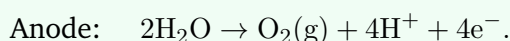
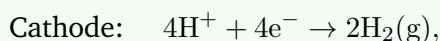
Nitrate ions are not oxidised under these conditions. Water is oxidised at the inert platinum anode, liberating oxygen:



Thus the cathode product is silver and the anode product is oxygen. The overall ionic equation is



Step 2: (a)(ii) Electrolysis of aqueous sulphuric acid Hydrogen ions gain electrons at the cathode, while water loses electrons at the anode. Sulphate ions remain in solution:



Adding gives $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$. Hydrogen is liberated at the cathode and oxygen at the anode, in the volume ratio 2 : 1 at the same temperature and pressure.

Quick Tip to Solve: Count electrons using the fractional reaction exactly as printed: $\frac{4}{3}$ mole of Al needs four moles of electrons, not six.

Step 3: (b) Find the electron transfer and required potential For the printed reaction $\frac{2}{3}\text{Al}_2\text{O}_3 \rightarrow \frac{4}{3}\text{Al} + \text{O}_2$, each aluminium ion gains three electrons. Therefore the production of $\frac{4}{3}$ mole of aluminium requires

$$n = \frac{4}{3} \times 3 = 4.$$

The Gibbs energy supplied is for this reaction, so it must be paired with this value of n , rather than six electrons for one mole of alumina. At 500°C ,

$$E_{\min} = \frac{960 \times 10^3}{4 \times 96500} = 2.487 \text{ V} \simeq 2.49 \text{ V}.$$

The cell potential for spontaneous operation in the decomposition direction would be negative, -2.49 V ; the external potential needed to drive it has positive magnitude 2.49 V . This is the thermodynamic minimum; losses increase the actual applied voltage.

Step 4: Conclusion Aqueous AgNO_3 : silver at the cathode and oxygen at the anode. Aqueous H_2SO_4 : hydrogen at the cathode and oxygen at the anode. The minimum applied potential for alumina decomposition is $\boxed{2.49 \text{ V}}$.

Quick Tip to Solve: Count electrons using the fractional reaction exactly as printed: $\frac{4}{3}$ mole of Al needs four moles of electrons, not six.

29(a). Describe:

(i) Aldol condensation

(ii) Cannizzaro reaction

(b) Describe a chemical test to distinguish between:

(i) Ethanal and Propanal

(ii) Benzaldehyde and Acetophenone

(iii) Propan-2-one and Propan-3-one

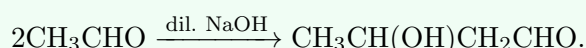
[5 marks]

Solution:

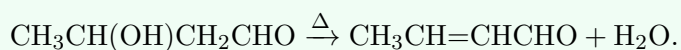
Concept:

- Aldehydes and ketones with an α -hydrogen undergo aldol condensation. Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation in concentrated alkali.
- The iodoform test detects the $\text{CH}_3\text{CO}-$ group and ethanal: iodine in alkali produces yellow CHI_3 . Tollens' reagent oxidises aldehydes but gives no silver mirror with ordinary ketones.

Step 1: (a)(i) Aldol condensation Two molecules of an aldehyde or ketone containing at least one α -hydrogen combine in dilute alkali to give a β -hydroxy aldehyde or ketone. On heating, this product loses water to form an α, β -unsaturated carbonyl compound. For example, ethanal forms 3-hydroxybutanal (aldol), then but-2-enal:

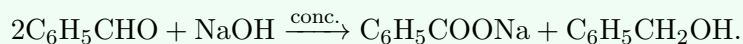


Quick Tip to Solve: Before choosing a carbonyl test, check the structure: ethanal gives iodoform, aldehydes give Tollens' test, and a ketone carbonyl cannot be terminal.



The α -hydrogen permits formation of an enolate, which attacks the carbonyl carbon of another molecule; dehydration gives the conjugated product.

Step 2: (a)(ii) Cannizzaro reaction An aldehyde lacking an α -hydrogen undergoes self-oxidation and reduction in concentrated alkali. One molecule becomes a carboxylate salt while another becomes a primary alcohol. Benzaldehyde illustrates the reaction:



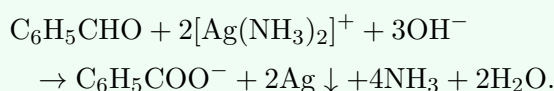
Sodium benzoate is the oxidation product and benzyl alcohol is the reduction product. The carboxylate gives benzoic acid on acidification.

Step 3: (b)(i) Distinguish ethanal and propanal Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform; propanal gives no yellow precipitate. Ethanal is the aldehyde that gives the iodoform test:



Tollens' reagent would not distinguish this pair, because both compounds are aldehydes and both reduce it.

Step 4: (b)(ii) Distinguish benzaldehyde and acetophenone Warm separate samples gently with freshly prepared Tollens' reagent. Benzaldehyde gives a silver mirror because its aldehyde group is oxidised to benzoate. Acetophenone, a ketone, gives no silver mirror:



Alternatively, acetophenone gives a positive iodoform test because it contains $\text{CH}_3\text{CO}-$, whereas benzaldehyde does not.

Step 5: (b)(iii) Examine the printed compound names The printed pair is propan-2-one and propan-3-one. Propan-2-one is acetone, CH_3COCH_3 , and gives yellow iodoform with iodine and alkali. However, propan-3-one is not a valid ketone: a ketonic carbonyl carbon must be bonded to two carbon atoms, whereas carbon 3 of a three-carbon chain is terminal. A terminal carbonyl with a hydrogen would instead be the aldehyde propanal. Therefore there is no distinct ketone named propan-3-one, and a chemical distinction between the literal printed pair cannot be made. If the terminal-carbonyl compound propanal is meant, Tollens' reagent gives it a silver mirror while propan-2-one gives none; this conditional test does not change the printed name.

Step 6: Conclusion Aldol condensation forms a β -hydroxy carbonyl compound followed by dehydration; Cannizzaro reaction gives an alcohol and a carboxylate. Use iodoform for ethanal/propanal and Tollens' reagent for benzaldehyde/acetophenone. Part (b)(iii), as printed, has no valid second ketone because propan-3-one is not a chemically valid name.

Quick Tip to Solve: Before choosing a carbonyl test, check the structure: ethanal gives iodoform, aldehydes give Tollens' test, and a ketone carbonyl cannot be terminal.

29(b). (a) Draw the structures of the following compounds:

(i) 4-Chloropentan-2-one

(ii) But-2-en-1-al

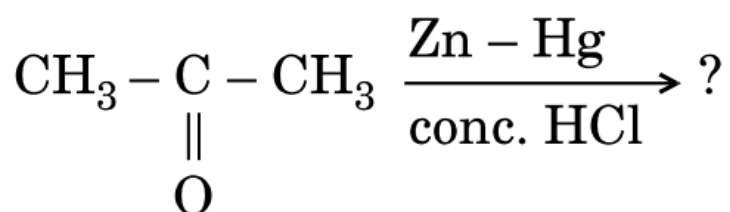
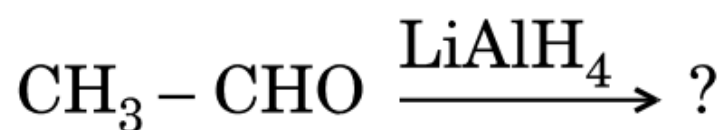
(b) Write the product(s) in the following:

(i) $\text{CH}_3\text{--COOH} \xrightarrow{\text{Br}_2/\text{P}} ?$

(ii) $\text{CH}_3\text{--CHO} \xrightarrow{\text{LiAlH}_4} ?$

(iii) $\text{CH}_3\text{--CO--CH}_3 \xrightarrow{\text{Zn--Hg / conc. HCl}} ?$

[5 marks]

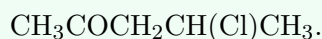


Solution:

Concept:

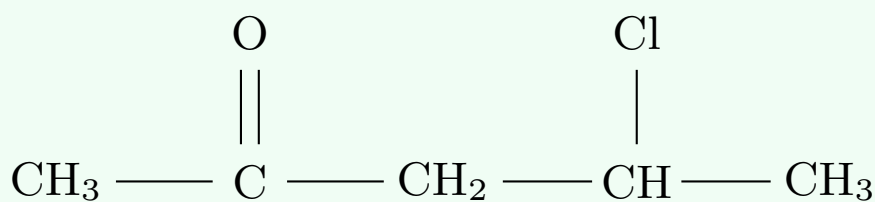
- In an aldehyde the terminal carbon of the --CHO group is numbered 1; in a ketone the chain is numbered to give the carbonyl carbon the lowest possible locant.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen. Lithium aluminium hydride reduces an aldehyde to a primary alcohol; Clemmensen reduction changes a carbonyl group into a methylene group.

Step 1: (a)(i) Structure of 4-chloropentan-2-one Take a five-carbon chain and place the ketone carbonyl at carbon 2. The chlorine substituent is attached to carbon 4, giving the following condensed structure:

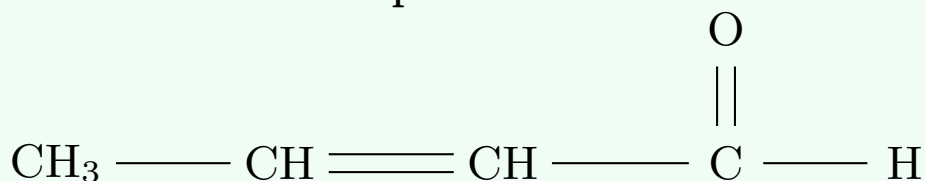


Numbering from the opposite end would assign the carbonyl locant 4, so it is not used. The labelled structural formula is drawn below.

Quick Tip to Solve: Number the aldehyde carbon as 1, then distinguish alpha bromination, hydride reduction to alcohol and Clemmensen reduction to alkane by the reagent.



4-chloropentan-2-one

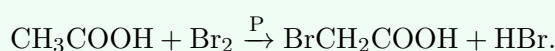


but-2-en-1-al

Structural formulae of the two named compounds

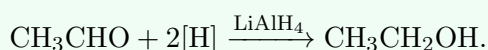
Step 2: (a)(ii) Structure of but-2-en-1-al The aldehyde carbon belongs to the four-carbon parent chain and is carbon 1. Place the double bond between carbons 2 and 3, giving $\text{CH}_3 - \text{CH} = \text{CH} - \text{CHO}$. Thus, numbering from the aldehyde end, the structure is $\text{O} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$; the carbonyl double bond does not count as the carbon-carbon double bond denoted by “en”.

Step 3: (b)(i) Bromination of ethanoic acid Ethanoic acid has alpha hydrogens on its methyl carbon. Bromine in the presence of phosphorus carries out alpha bromination (the Hell-Volhard-Zelinsky reaction), producing bromoethanoic acid:



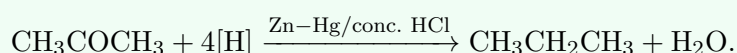
Bromine replaces a hydrogen adjacent to the carboxyl group; the carboxyl group itself is retained.

Step 4: (b)(ii) Reduction of ethanal Lithium aluminium hydride supplies hydride to the carbonyl carbon. Protonation during the usual work-up gives the primary alcohol ethanol:



The aldehyde carbon becomes the carbon of the $-\text{CH}_2\text{OH}$ group, with no change in the number of carbon atoms.

Step 5: (b)(iii) Clemmensen reduction of propanone Zinc amalgam and concentrated hydrochloric acid reduce the ketone carbonyl group completely to a methylene group:



The product is propane. Under these conditions the product is an alkane rather than the secondary alcohol obtained by ordinary hydride reduction of a ketone.

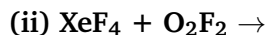
Step 6: Conclusion (a) The structures are $\text{CH}_3\text{COCH}_2\text{CH}(\text{Cl})\text{CH}_3$ and $\text{CH}_3\text{CH} = \text{CHCHO}$. (b)

Quick Tip to Solve: Number the aldehyde carbon as 1, then distinguish alpha bromination, hydride reduction to alcohol and Clemmensen reduction to alkane by the reagent.

The organic products are (i) bromoethanoic acid, BrCH_2COOH ; (ii) ethanol, $\text{CH}_3\text{CH}_2\text{OH}$; and (iii) propane, $\text{CH}_3\text{CH}_2\text{CH}_3$.

Quick Tip to Solve: Number the aldehyde carbon as 1, then distinguish alpha bromination, hydride reduction to alcohol and Clemmensen reduction to alkane by the reagent.

30(a). Complete the following chemical equations:



(b) How would you account for the following situations?

(i) The acidic strength of these compounds increases in the following order: $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$

(ii) The oxidising power of oxoacids of chlorine follows the order: $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$

(iii) In vapour state sulphur exhibits paramagnetic behaviour.

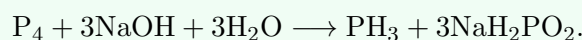
[5 marks]

Solution:

Concept:

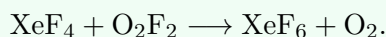
- Disproportionation is simultaneous oxidation and reduction of the same element; oxidation numbers and atom balance determine the products' coefficients.
- Across a period, increasing electronegativity strengthens the acidic character of covalent hydrides. Oxidising strength depends on ease of reduction, rather than oxidation number alone.
- Paramagnetism requires unpaired electrons in the molecular orbitals of the species present.

Step 1: (a)(i) Reaction of phosphorus with alkali White phosphorus reacts with hot aqueous sodium hydroxide to form phosphine and sodium hypophosphite:



Phosphorus changes from oxidation number zero to -3 in PH_3 and $+1$ in hypophosphite. One phosphorus atom gains three electrons while three each lose one, so this is disproportionation. Both sides contain four P, three Na, nine H and six O atoms.

Step 2: (a)(ii) Fluorination of xenon tetrafluoride Dioxygen difluoride is a strong fluorinating agent and converts xenon tetrafluoride into xenon hexafluoride:



Xenon is oxidised from $+4$ to $+6$, and the oxygen in O_2F_2 is reduced from $+1$ to zero. The equation balances one Xe atom, six F atoms and two O atoms on each side.

Step 3: (b)(i) Increasing acidity of the hydrides From P to S to Cl across the same period, electronegativity increases. The central atom attracts the bonding electrons more strongly, making the hydrogen increasingly positive and facilitating its release as H^+ . The conjugate anion is also better able to accommodate negative charge. Consequently, acidic character increases in the printed order $\text{PH}_3 < \text{H}_2\text{S} < \text{HCl}$.

Quick Tip to Solve: Balance phosphorus by pairing one P reduced to -3 with three P oxidised to $+1$; for sulphur vapour identify S_2 before counting unpaired electrons.

Step 4: (b)(ii) Oxidising strength of chlorine oxoacids As oxygen content increases, the oxoacid and its conjugate oxoanion acquire greater resonance stabilisation and become more resistant to reduction. Hypochlorous acid is readily reduced, whereas perchloric acid is much more stable under ordinary conditions. Thus the ease of reduction, and hence oxidising power, decreases from hypochlorous to perchloric acid, giving $\text{HClO}_4 < \text{HClO}_3 < \text{HClO}_2 < \text{HClO}$. A higher chlorine oxidation number alone therefore does not imply a stronger oxidising agent in this series.

Step 5: (b)(iii) Paramagnetism of sulphur vapour At high temperature, sulphur vapour contains diatomic S_2 molecules. Like O_2 , each S_2 molecule has two unpaired electrons occupying separate degenerate antibonding π^* molecular orbitals. These unpaired electrons cause attraction to a magnetic field and account for the paramagnetic behaviour of sulphur vapour.

Step 6: Conclusion The products are $\text{PH}_3 + 3\text{NaH}_2\text{PO}_2$ and $\text{XeF}_6 + \text{O}_2$, with the balanced reactants shown above. The trends follow increasing hydride polarity and decreasing ease of oxoacid reduction; sulphur vapour is paramagnetic because S_2 has two unpaired electrons.

Quick Tip to Solve: Balance phosphorus by pairing one P reduced to -3 with three P oxidised to +1; for sulphur vapour identify S_2 before counting unpaired electrons.

OR

30(b). (a) Using VSEPR theory predict the probable structures of the following:

(i) N_2O_3

(ii) BrF_3

(b) Arrange the following groups of substances in the order of the property indicated against each group:

(i) NH_3 , PH_3 , AsH_3 , SbH_3 – increasing order of boiling points.

(ii) O, S, Se, Te – increasing order of electron gain enthalpy with negative sign.

(iii) F_2 , Cl_2 , Br_2 , I_2 – increasing order of bond dissociation enthalpy.

[5 marks]

Solution:

Concept:

- VSEPR theory arranges electron domains to minimise repulsion; a multiple bond counts as one domain. Lone pairs affect molecular shape more strongly than bonding pairs.
- Hydride boiling points depend on intermolecular hydrogen bonding and dispersion forces. Electron gain enthalpy measures the enthalpy change when a gaseous atom gains an electron.
- Bond dissociation enthalpy is the energy needed to break one mole of gaseous diatomic molecules into gaseous atoms; both bond length and lone-pair repulsion matter.

Step 1: (a)(i) Structure of dinitrogen trioxide The molecular skeleton is $\text{O} = \text{N} - \text{NO}_2$, with a bond joining the two nitrogen atoms. A Lewis resonance form is $\text{O} = \text{N} - \text{N}^+(\equiv \text{O}) - \text{O}^-$, with the equivalent resonance form interchanging the two oxygen atoms of the NO_2 group. The nitrosyl nitrogen has an N–O bonding domain, an N–N bonding domain and a lone pair: three domains give a bent $\text{O} - \text{N} - \text{N}$ arrangement. The nitrogen of the NO_2 group has three bonding domains and a

Quick Tip to Solve: Remember the three exceptions: ammonia hydrogen-bonds, oxygen resists electron addition in compact 2p orbitals, and fluorine has strong lone-pair repulsion.

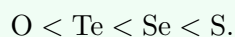
trigonal planar arrangement. The molecule is planar, with a bent nitrosyl end and a trigonal planar nitro end. It is not a linear chain of atoms.

Step 2: (a)(ii) Structure of bromine trifluoride Bromine has seven valence electrons. Three Br-F bonds leave two lone pairs on Br, giving five electron domains: AX_3E_2 . Their electron-pair geometry is trigonal bipyramidal. Both lone pairs occupy equatorial sites, where they experience fewer 90° interactions. The remaining fluorine atoms occupy two axial sites and one equatorial site, producing a T-shaped molecule. The axial-to-equatorial bond angles are slightly less than 90° owing to lone-pair repulsion.

Step 3: (b)(i) Increasing boiling points of the hydrides Among PH_3 , AsH_3 and SbH_3 , increasing size and polarisability strengthen dispersion forces, raising the boiling point down the group. Ammonia forms intermolecular hydrogen bonds, so it boils above phosphine and arsine. The strong dispersion forces in the much larger stibine molecule put its boiling point above ammonia. Hence:



Step 4: (b)(ii) Increasing electron gain enthalpy with negative sign Here the indicated property is the negative of electron gain enthalpy, $-\Delta_{eg}H$, so a larger value means more energy released on electron addition. Oxygen's compact $2p$ orbitals cause unusually strong electron-electron repulsion, making its electron gain enthalpy less negative than sulphur's. Below sulphur, increasing size reduces attraction for the added electron. Thus the increasing energy-release magnitude is:



For clarity, typical signed values of $\Delta_{eg}H$ are approximately $-141, -190, -195, -200 \text{ kJ mol}^{-1}$, respectively, in the displayed element order; their negatives increase in precisely that order.

Step 5: (b)(iii) Increasing bond dissociation enthalpy From chlorine to iodine, increasing bond length weakens the bond. Fluorine is anomalous: its short bond brings three lone pairs on each small atom very close together, causing substantial repulsion and lowering bond strength below bromine's. Typical values for I_2, F_2, Br_2, Cl_2 are about 151, 159, 193, 243 kJ mol^{-1} , respectively. Therefore:



Step 6: Conclusion N_2O_3 is planar with the $ON - NO_2$ skeleton; BrF_3 is T-shaped. The required increasing orders are $PH_3 < AsH_3 < NH_3 < SbH_3$, $O < Te < Se < S$ for $-\Delta_{eg}H$, and $I_2 < F_2 < Br_2 < Cl_2$.

Quick Tip to Solve: Remember the three exceptions: ammonia hydrogen-bonds, oxygen resists electron addition in compact $2p$ orbitals, and fluorine has strong lone-pair repulsion.