

CBSE Class 12 Chemistry Question Paper 2004 with Solution PDF-Set 56/1 (Outside Delhi)

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) Marks for each question are indicated against it.
- (iii) Question numbers **1 to 5** are very short-answer, carrying **1** mark each. Answer these in one word or about one-sentence each.
- (iv) Question numbers **6 to 12** are short-answer, carrying **2** marks each. Answer these in about **30** words each.
- (v) Question numbers **13 to 24** are short-answer questions of **3** marks each. Answer these in about **40** words each.
- (vi) Question numbers **25 and 27** are long-answer questions of **5** marks each. Answer these in about **70** words each.
- (vii) Use Log Tables, if necessary. Use of calculators is not permitted.

1. Define the term 'amorphous'.

[1 mark]

Solution:

Concept:

- The arrangement of constituent particles distinguishes crystalline solids from amorphous solids.
- Long-range order means a regular arrangement that repeats throughout the solid.

Step 1: Identify the structural feature In an amorphous solid, the constituent atoms, ions or molecules are not arranged in a regular repeating pattern over large distances. Only short-range order may be present among neighbouring particles.

Step 2: Relate this to the term The term amorphous means without a definite geometrical form. Glass is a familiar example: its particles lack the long-range periodic arrangement characteristic of a crystal.

Step 3: Conclusion An amorphous solid is a solid whose constituent particles lack long-range regular order and hence a definite crystalline geometrical form.

Quick Tip to Solve: Use the absence of long-range order as the defining feature; short-range order can still exist.

2. What is the sum of the mole fractions of all the components in a three component system?

[1 mark]

Solution:

Concept:

- The mole fraction of component i is $x_i = n_i/n_{\text{total}}$, where n_i is its amount in moles.
- For three components, $n_{\text{total}} = n_1 + n_2 + n_3$.

Step 1: Write each mole fraction The three mole fractions are $x_1 = n_1/(n_1 + n_2 + n_3)$, $x_2 = n_2/(n_1 + n_2 + n_3)$ and $x_3 = n_3/(n_1 + n_2 + n_3)$. Each uses the same total number of moles.

Step 2: Add the fractions

$$x_1 + x_2 + x_3 = \frac{n_1 + n_2 + n_3}{n_1 + n_2 + n_3} = 1.$$

The numerator accounts for all the components of the mixture, so it equals the denominator. Mole fraction has no unit.

Step 3: Conclusion The sum of the mole fractions is unity: $x_1 + x_2 + x_3 = 1$.

Quick Tip to Solve: Always use total moles of every component in the denominator of each mole fraction.

3. What is meant by an elementary reaction?

[1 mark]

Solution:

Concept:

- A reaction mechanism describes the sequence of individual events by which reactants form products.
- An elementary reaction is a single event in that mechanism and has no further reaction steps.

Step 1: Identify the single-step nature An elementary reaction proceeds in one step at the molecular level. The reactants participating in that event form the products of that step directly; the reaction is not a combination of several successive elementary steps.

Step 2: Distinguish it from an overall reaction An overall chemical equation may represent a multistep process and therefore need not be elementary. For an elementary step, molecularity is the number of reacting species taking part in that one event.

Step 3: Conclusion An elementary reaction is a reaction that takes place in a single step, without a sequence of intermediate reaction steps.

Quick Tip to Solve: Look for a single molecular event, rather than judging elementary character from a balanced overall equation.

4(a). Write the IUPAC name of the following:

[1 mark]



Solution:

Concept:

- An ionic compound is named by writing the organic cation first and the anion second.
- Protonation of an amine gives an ammonium ion; methyl groups attached directly to nitrogen are indicated by the locant *N*.

Step 1: Identify the cation The benzene ring is bonded to a positively charged nitrogen bearing one hydrogen and two methyl groups. Thus the cation is the protonated form of *N,N*-dimethylaniline, named *N,N*-dimethylbenzenaminium (also called *N,N*-dimethylanilinium).

Step 2: Identify the counter-ion The negatively charged oxygen belongs to CH_3COO^- , the ethanoate ion. It is the counter-ion to the organic cation, rather than an additional substituent on the benzene ring.

Step 3: Conclusion The IUPAC name is *N,N*-dimethylbenzenaminium ethanoate (*N,N*-dimethylanilinium ethanoate).

Quick Tip to Solve: Check the charge on nitrogen first: a protonated amine must be named as a salt with its counter-ion.

4(b). Write the IUPAC name of the following:

[1 mark]



Solution:

Concept:

- For this aromatic amine, the carbon bonded to NH_2 is carbon 1 of the aniline parent.
- The OCH_3 group is a methoxy substituent; opposite ring positions have locants 1 and 4.

Step 1: Choose the parent The structure contains a benzene ring bearing an amino group and a methoxy group. Use aniline as the retained parent name, with the amino-bearing carbon numbered 1. The oxygen links the methyl group to the ring, so the substituent is methoxy, not methyl.

Step 2: Locate the substituent The methoxy group is directly opposite the amino group on the ring. Numbering from the amino-bearing carbon places it at carbon 4 in either direction. Hence the methoxy prefix takes the locant 4; the common positional descriptor is para.

Step 3: Conclusion The IUPAC name is 4-methoxyaniline (also 4-methoxybenzenamine).

Quick Tip to Solve: Number the amino-bearing ring carbon as 1; the group directly opposite it is always at position 4.

5. Draw the structure of 4-methylpent-3-en-2-one.

[1 mark]

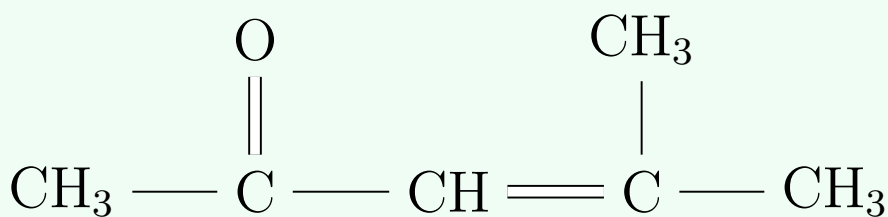
Solution:

Concept:

- The parent name pent denotes a five-carbon chain. The suffix -2-one places a ketone carbonyl at carbon 2.
- The locants 3-en and 4-methyl specify a double bond between carbons 3 and 4 and a methyl substituent on carbon 4.

Step 1: Build the parent chain Number the chain from the end nearer the ketone group. Its skeleton is $\text{C}_1 - \text{C}_2(=\text{O}) - \text{C}_3 = \text{C}_4 - \text{C}_5$, so the carbonyl carbon receives locant 2.

Step 2: Add the methyl substituent Attach CH_3 to carbon 4. Carbon 3 retains one hydrogen, while carbon 4 has none because it forms a double bond and two single bonds. The labelled structural formula is shown below.



Structure of 4-methylpent-3-en-2-one

Step 3: Conclusion The required structure is $\text{CH}_3 - \text{C}(=\text{O}) - \text{CH} = \text{C}(\text{CH}_3) - \text{CH}_3$.

Quick Tip to Solve: Place the ketone first, then the double bond; finally attach the methyl group at carbon 4.

6. Compare the relative stability of the following species and indicate their magnetic (diamagnetic or paramagnetic) properties:

C_2^{2-} and O_2^-

[2 marks]

Solution:

Concept:

- Bond order is $\text{BO} = \frac{1}{2}(N_b - N_a)$, where N_b and N_a are the numbers of electrons in bonding and antibonding molecular orbitals. Higher bond order indicates greater bond stability.
- A species with all electrons paired is diamagnetic; a species containing an unpaired electron is paramagnetic. Filled core orbitals cancel in the bond-order calculation.

Step 1: Examine the carbide dianion C_2^{2-} has 14 electrons. Its valence configuration is

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2.$$

Thus $N_b = 8$, $N_a = 2$ and $\text{BO} = (8 - 2)/2 = 3$. Every occupied orbital contains paired electrons, so this species is diamagnetic.

Step 2: Examine the superoxide ion O_2^- has 17 electrons. Its valence configuration is

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_x}^*)^2(\pi_{2p_y}^*)^1.$$

The equivalent antibonding π^* orbitals contain three electrons in total. Thus $N_b = 8$, $N_a = 5$ and $\text{BO} = (8 - 5)/2 = 1.5$. One electron remains unpaired, giving paramagnetism.

Step 3: Conclusion On the bond-order criterion, $\text{C}_2^{2-} > \text{O}_2^-$ in relative bond stability. C_2^{2-} is diamagnetic, whereas O_2^- is paramagnetic.

Quick Tip to Solve: Count total electrons first: the 14-electron species has paired electrons; superoxide has one unpaired electron.

7. How does molar conductivity vary with concentration for (i) weak electrolyte and for (ii) strong electrolyte? Give reasons for these variations. [2 marks]

Solution:

Concept:

- Molar conductivity Λ_m measures the conductance associated with one mole of electrolyte. If c is in mol L^{-1} and conductivity κ is in S cm^{-1} , then $\Lambda_m = 1000\kappa/c$.
- Dilution reduces interionic interactions. For a weak electrolyte, dilution also increases the fraction of solute present as ions.

Step 1: Weak electrolyte As concentration decreases, molar conductivity increases sharply, especially near infinite dilution. A weak electrolyte is only partially ionised; dilution shifts its dissociation equilibrium towards ions and greatly increases the number of charge carriers per mole. Reduced interionic interactions also improve ionic mobility. Conversely, increasing concentration reduces ionisation and lowers Λ_m .

Step 2: Strong electrolyte A strong electrolyte is already almost completely dissociated. Its molar conductivity rises gradually on dilution mainly because interionic attractions decrease and the ions move more freely. At low concentrations the dependence is

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{c},$$

where Λ_m° is the limiting molar conductivity and A is a positive constant for the electrolyte, solvent and temperature. Thus increasing concentration lowers Λ_m .

Step 3: Conclusion On dilution, molar conductivity increases sharply for a weak electrolyte and gradually for a strong electrolyte. The main causes are increased ionisation for the former and increased ionic mobility for the latter.

Quick Tip to Solve: Distinguish conductivity from molar conductivity: dilution can lower conductivity while raising molar conductivity.

8. Give the chemical reactions as an evidence for each of the following observations:

(i) Tin (II) is a reducing agent whereas Pb (II) is not.

(ii) +1 gallium undergoes disproportionation reaction. [2 marks]

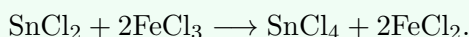
Solution:

Concept:

- A reducing agent loses electrons and is itself oxidised. The inert-pair effect stabilises the lower oxidation state increasingly down Group 14.
- Disproportionation simultaneously oxidises and reduces atoms of the same element initially in one oxidation state.

Step 1: (i) Compare tin(II) and lead(II) Tin(II) readily loses two electrons to become tin(IV), so it

reduces iron(III) to iron(II):



Here tin changes from +2 to +4, while iron changes from +3 to +2. Lead(II) is much more stable because of the stronger inert-pair effect, so PbCl_2 does not show the corresponding reducing reaction with FeCl_3 . Thus the same oxidation to the tetravalent state is not favoured for lead(II).

Step 2: (ii) Disproportionation of gallium(I) The reaction is



One gallium(I) ion loses two electrons to form gallium(III); two other gallium(I) ions each gain one electron to form gallium metal. Both the number of gallium atoms and the net charge (+3) balance.

Step 3: Conclusion SnCl_2 reduces FeCl_3 , whereas PbCl_2 does not; $3\text{Ga}^+ \rightarrow \text{Ga}^{3+} + 2\text{Ga}$ demonstrates gallium(I) disproportionation.

Quick Tip to Solve: For disproportionation, balance the electrons lost and gained before writing the overall equation.

9. Identify and indicate the presence of centre of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centre?

(i) 1,2-dichloropropane

(ii) 3-bromo-pent-1-ene

[2 marks]

Solution:

Concept:

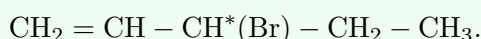
- A tetrahedral carbon bonded to four different groups is a centre of chirality; mark it with an asterisk.
- One independent chiral centre gives two enantiomers, the *R* and *S* forms, provided no other stereogenic element is present.

Step 1: (i) 1,2-Dichloropropane The structure is



Carbon 2 is bonded to four distinct groups: H, Cl, CH_3 and CH_2Cl . It is therefore the sole centre of chirality. Carbon 1 has two identical hydrogen atoms and cannot be chiral; carbon 3 has three identical hydrogen atoms. Hence this molecule has $2^1 = 2$ stereoisomers, an enantiomeric pair.

Step 2: (ii) 3-Bromopent-1-ene Its structure is



Carbon 3 has four different substituents: H, Br, vinyl ($\text{CH} = \text{CH}_2$) and ethyl (CH_2CH_3). Thus carbon 3 is chiral, giving two enantiomers. The terminal double bond introduces no *E/Z* isomerism because

its terminal carbon bears two identical hydrogen atoms.

Step 3: Conclusion 1,2-Dichloropropane: chiral centre at C-2, two stereoisomers. 3-Bromopent-1-ene: chiral centre at C-3, two stereoisomers.

Quick Tip to Solve: Compare entire substituent groups, not just their first atoms: vinyl and ethyl are different groups.

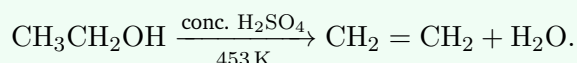
10. What happens when ethanol is heated with concentrated sulphuric acid at 453 K? Explain the mechanism of this reaction. [2 marks]

Solution:

Concept:

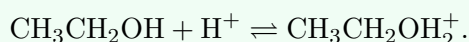
- Concentrated sulphuric acid catalyses dehydration of ethanol at 453 K, removing water to form ethene.
- Protonation converts the poor leaving group -OH into water; loss of water and elimination of a proton regenerate the acid catalyst.

Step 1: Write the overall reaction On heating, ethanol forms ethene:

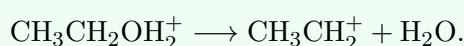


This is an elimination reaction: the alcohol loses the elements of water from adjacent carbon atoms.

Step 2: Explain the acid-catalysed mechanism First the oxygen lone pair accepts a proton, giving protonated ethanol:



In the usual board-level representation, water then leaves to give the ethyl carbocation:



Finally removal of a proton from the adjacent carbon gives the double bond:



The carbon-hydrogen bond electrons form the carbon-carbon pi bond. The regenerated proton shows that sulphuric acid acts as a catalyst in this mechanism.

Step 3: Conclusion Ethanol undergoes acid-catalysed dehydration at 453 K, yielding ethene and water.

Quick Tip to Solve: Remember the temperature: at 453 K, elimination from ethanol produces ethene.

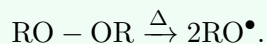
11. Write the mode of free radical addition polymerization of an alkene. Clearly indicate the role of an initiator in it. [2 marks]

Solution:

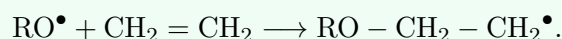
Concept:

- In free-radical addition polymerisation, an alkene double bond opens and many monomers join without elimination of a small molecule.
- An initiator such as an organic peroxide supplies radicals by homolytic bond cleavage; the growing chain carries an unpaired electron.

Step 1: Initiation and the initiator Using ethene as the alkene, an organic peroxide first splits on heating:



The oxygen-oxygen bond breaks homolytically, each oxygen retaining one bonding electron. An initiator radical attacks the ethene double bond:



Thus the initiator creates the first reactive chain radical; it starts the chain and its fragment becomes a chain end.

Step 2: Propagation The chain radical adds further ethene molecules repeatedly:



Each addition consumes a double bond and leaves a radical at the new chain end. Repetition produces a long chain with repeating unit $-\text{CH}_2 - \text{CH}_2-$.

Step 3: Termination Chain growth stops when two chain radicals combine:



where $\text{P}^\bullet$ denotes a growing polymer chain. Pairing the radical electrons forms a covalent bond, leaving no active radical at that junction.

Step 4: Conclusion Free-radical addition polymerisation proceeds by initiation, propagation and termination. Peroxide initiates ethene polymerisation by supplying radicals, producing polyethene, $[-\text{CH}_2 - \text{CH}_2-]_n$.

Quick Tip to Solve: Place a radical dot at the growing chain end after every propagation step; remove it on combination.

12(a). Write the major classes in which the carbohydrates are divided depending upon whether these undergo hydrolysis, and if so, on the number of products formed. [2 marks]

Solution:

Concept:

- Carbohydrates are classified by whether hydrolysis breaks their glycosidic bonds and by the number of monosaccharide units released.
- A monosaccharide is the simplest carbohydrate unit; hydrolysis cannot split it into simpler carbohydrates.

Step 1: Identify carbohydrates that cannot be hydrolysed Monosaccharides do not undergo hydrolysis to yield simpler carbohydrates. Examples are glucose, fructose and ribose. Their classification therefore depends on the absence of smaller carbohydrate units, rather than merely on whether they taste sweet or dissolve in water.

Step 2: Classify carbohydrates that yield a limited number of units Oligosaccharides give two to ten monosaccharide units per molecule on complete hydrolysis. They include disaccharides such as sucrose and maltose, which yield two units, and trisaccharides such as raffinose, which yields three. The units formed may be identical or different; the classification counts the total number of units released.

Step 3: Identify carbohydrates that yield many units Polysaccharides give a large number of monosaccharide units on complete hydrolysis. Starch, cellulose and glycogen are examples; their hydrolysis ultimately yields many glucose molecules. Thus they contain long chains of monosaccharide residues linked by glycosidic bonds.

Step 4: Conclusion The three major classes are monosaccharides (no further hydrolysis), oligosaccharides (two to ten monosaccharide units) and polysaccharides (a large number of units).

Quick Tip to Solve: Classify by the number of monosaccharide units released per molecule, not the number of different sugars produced.

OR

12(b). Explain mutarotation taking D-glucose as an example. [2 marks]

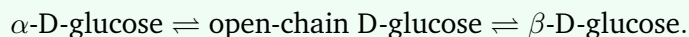
Solution:

Concept:

- Mutarotation is the change in specific optical rotation of a freshly prepared sugar solution with time until an equilibrium value is reached.
- Anomers differ in configuration at the anomeric carbon; in D-glucose this is carbon C-1.

Step 1: Compare the two anomers of D-glucose Crystalline α -D-glucose and β -D-glucose have specific rotations of approximately $+112^\circ$ and $+19^\circ$, respectively. When either form is dissolved separately in water, its initial specific rotation does not remain constant: the rotation of the alpha form decreases, whereas that of the beta form increases.

Step 2: Explain the molecular interconversion In aqueous solution, the cyclic hemiacetal ring opens reversibly to a small amount of open-chain aldehyde. Ring closure can then produce either configuration at C-1. Consequently, the two anomers interconvert through the open-chain form:



This changes the relative amounts of the anomers and therefore the observed optical rotation.

Step 3: State the equilibrium observation Both freshly prepared solutions eventually attain the same specific rotation, approximately $+52.5^\circ$, at ordinary temperature. At this point the composition is an equilibrium mixture, predominantly the beta anomer, and the optical rotation remains constant although molecular interconversion continues.

Step 4: Conclusion The gradual change of the specific rotation of either D-glucose anomer to the common equilibrium value of about $+52.5^\circ$ is called mutarotation.

Quick Tip to Solve: Always connect the change in rotation to reversible ring opening and reclosure at the anomeric carbon.

13. What do you understand by (i) Radial probability density, R^2 and (ii) Radial probability function, $4\pi r^2 R^2$? Draw the curves which show their variation with r for $2s$ orbital of hydrogen atom. [3 marks]

Solution:

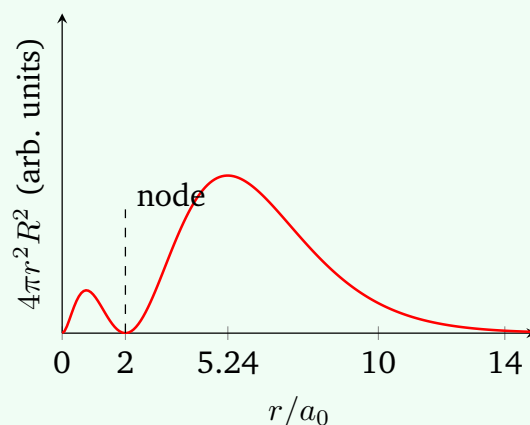
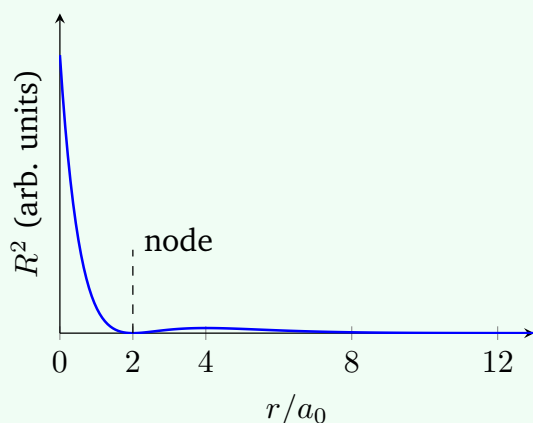
Concept:

- For an s orbital the wavefunction is spherically symmetric. In the convention used in the question, $R^2(r)$ denotes the probability density at a point a distance r from the nucleus.
- A spherical shell of radius r and thickness dr has volume $4\pi r^2 dr$; its probability is $4\pi r^2 R^2 dr$.
- For hydrogen $2s$, the radial dependence is $R^2 = C(2 - r/a_0)^2 e^{-r/a_0}$, where $C > 0$ is a normalization constant and a_0 is the Bohr radius.

Step 1: Define radial probability density The quantity $R^2(r)$ gives probability per unit volume at a point at radial distance r . For the $2s$ orbital it is finite and greatest at the nucleus. It decreases to zero at the radial node $r = 2a_0$, rises to a smaller secondary maximum at $r = 4a_0$, then tends to zero as $r \rightarrow \infty$. The zero at the node separates the inner and outer radial regions.

Step 2: Define the radial probability function The radial probability function $P(r) = 4\pi r^2 R^2(r)$ gives probability per unit radial distance. Thus $P(r)dr$ is the probability of finding the electron anywhere in the thin spherical shell from r to $r + dr$. Its value at the nucleus is zero because of the r^2 factor, even though the local density there is finite. It is also zero at the radial node and approaches zero at large distance.

Step 3: Draw and compare the two curves The curves below use separate arbitrary vertical scales and the horizontal coordinate $x = r/a_0$. The radial probability function has two maxima, at $x = 3 - \sqrt{5} \approx 0.764$ and $x = 3 + \sqrt{5} \approx 5.236$, with the outer maximum higher. These follow by differentiating $x^2(2 - x)^2 e^{-x}$. The shared node at $x = 2$ is the single radial node of the $2s$ orbital. The shell-volume factor explains why a maximum in local density need not be a maximum in radial probability.



Radial density and radial probability for hydrogen 2s; vertical scales are independent.

Step 4: Conclusion R^2 is the local probability density; $4\pi r^2 R^2$ accounts for the volume of a spherical shell. For hydrogen 2s, both curves have one radial node at $r = 2a_0$, but only the shell probability function vanishes at the nucleus.

Quick Tip to Solve: At the nucleus, distinguish finite local density from zero shell probability: the shell volume contains a factor of radius squared.

14. Calculate the value of Avogadro constant from the following data:

Density of NaCl = 2.165 g cm^{-3}

Distance between Na^+ and Cl^- in NaCl = 281 pm

(Molar mass of NaCl = 58.5 g mol^{-1})

[3 marks]

Solution:

Concept:

- Rock-salt NaCl has four formula units per cubic unit cell: $Z = 4$. The nearest sodium and chloride ions are separated by half the edge length, so $d = a/2$.
- The density relation is $\rho = ZM/(N_A a^3)$, where M is molar mass, a is cell edge and N_A is the Avogadro constant.

Step 1: Find the edge of the unit cell The given distance is the nearest unlike-ion separation, not the entire cell edge. Along an edge of the rock-salt unit cell, a chloride ion at a corner and a sodium ion at the edge centre are separated by $a/2$. Hence

$$a = 2d = 2(281) = 562 \text{ pm} = 5.62 \times 10^{-8} \text{ cm}.$$

Here $1 \text{ pm} = 10^{-10} \text{ cm}$; centimetres are used because the density is in g cm^{-3} .

Step 2: Relate unit-cell mass and volume The face-centred arrangement contributes $8(1/8) + 6(1/2) = 4$ chloride ions, with four sodium ions in the octahedral sites. Thus one unit cell contains four NaCl

formula units and has mass $4M/N_A$. Its volume is

$$a^3 = (5.62 \times 10^{-8})^3 = 1.7750488 \times 10^{-22} \text{ cm}^3.$$

Therefore

$$N_A = \frac{4M}{\rho a^3} = \frac{4(58.5)}{2.165(1.7750488 \times 10^{-22})} = 6.089 \times 10^{23} \text{ mol}^{-1}.$$

The numerical estimate follows from the rounded crystal data supplied in the question.

Step 3: Conclusion The Avogadro constant calculated from the given data is $N_A \approx 6.09 \times 10^{23} \text{ mol}^{-1}$.

Quick Tip to Solve: For rock-salt NaCl, double the nearest unlike-ion distance before cubing it in the density formula.

15. The elements A and B form purely covalent compounds having molecular formulae AB_2 and AB_4 . When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate the atomic mass of A and atomic mass of B. [3 marks]

Solution:

Concept:

- For a dilute solution, $\Delta T_f = iK_f m$. Purely covalent solutes are taken to remain as molecules, so $i = 1$.
- If w grams of solute of molar mass M dissolve in W grams of solvent, $\Delta T_f = K_f(1000w)/(MW)$.

Step 1: Calculate both molecular molar masses Each solution contains $W = 20 \text{ g} = 0.020 \text{ kg}$ of benzene and $w = 1 \text{ g}$ of solute. Molality counts moles of solute per kilogram of solvent, so the solvent mass, rather than total solution mass, is used. Rearranging the freezing-point expression gives

$$M = \frac{K_f 1000w}{\Delta T_f W}.$$

For the two compounds,

$$M(\text{AB}_2) = \frac{5.1(1000)(1)}{2.3(20)} = 110.8696 \text{ g mol}^{-1},$$

$$M(\text{AB}_4) = \frac{5.1(1000)(1)}{1.3(20)} = 196.1538 \text{ g mol}^{-1}.$$

The smaller depression for the second compound indicates fewer dissolved molecules and therefore a larger molar mass.

Step 2: Solve for the atomic masses Let the numerical atomic masses of A and B be x and y . The molecular formulae then give

$$x + 2y = 110.8696,$$

$$x + 4y = 196.1538.$$

Subtracting eliminates A:

$$2y = 85.2842, \quad y = 42.6421.$$

Substitution into the first equation yields

$$x = 110.8696 - 2(42.6421) = 25.5854.$$

Retaining extra digits during the calculation avoids early rounding of the difference of molecular masses.

Step 3: Conclusion The atomic masses are $A \approx 25.6 \text{ u}$, $B \approx 42.6 \text{ u}$ (relative atomic masses approximately 25.6 and 42.6).

Quick Tip to Solve: Subtract the two molecular-mass equations first: the difference equals twice the atomic mass of B.

16. Write the Nernst equation and calculate the e.m.f. of the following cell at 298 K:



Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ and $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$.

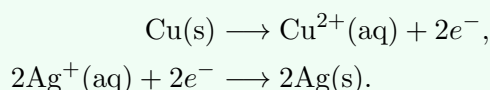
[3 marks]

Solution:

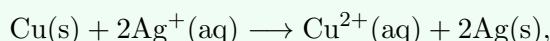
Concept:

- The Nernst equation is $E = E^\circ - (RT/nF) \ln Q$, where Q is the reaction quotient and n is the number of transferred electrons.
- At 298 K, $E = E^\circ - (0.0591/n) \log_{10} Q$. Pure solids have unit activity and are omitted from Q .

Step 1: Write the cell reaction and standard potential For the cell as written, copper is oxidised at the left electrode and silver ions are reduced at the right electrode:



Thus



with $n = 2$. Using the given reduction potentials,

$$E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.80 - 0.34 = 0.46 \text{ V}.$$

Electrode potentials are not multiplied by the stoichiometric coefficients.

Step 2: Evaluate the reaction quotient and apply Nernst equation Approximating ionic activities by concentrations relative to the standard concentration,

$$Q = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.130}{(1.00 \times 10^{-4})^2} = 1.30 \times 10^7.$$

The silver-ion concentration is squared because two silver ions occur in the balanced reaction. Hence

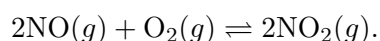
$$\begin{aligned}E_{\text{cell}} &= 0.46 - \frac{0.0591}{2} \log_{10}(1.30 \times 10^7) \\&= 0.46 - 0.02955(7.11394) \\&= 0.2498 \text{ V}.\end{aligned}$$

The large reaction quotient lowers the emf from its standard value, as expected for a very small silver-ion concentration.

Step 3: Conclusion The cell emf at 298 K is $E_{\text{cell}} \approx +0.250 \text{ V}$.

Quick Tip to Solve: Balance the cell reaction first: it fixes both the two-electron divisor and the square on silver-ion concentration.

17. Following reaction takes place in one step,



How will the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Will there be any change in the order of the reaction with the reduced volume? [3 marks]

Solution:

Concept:

- For a one-step elementary reaction, the reactant coefficients give the powers of their concentrations in the forward rate law.
- Concentration is amount divided by volume: $c = n/V$. Compression increases concentration without changing the rate-law exponents.

Step 1: Write the rate law The forward reaction consumes two molecules of nitric oxide with one molecule of oxygen in the elementary step. Its rate law is therefore

$$r = k[\text{NO}]^2[\text{O}_2].$$

Here k is the rate constant at the specified temperature. Adding the concentration exponents gives the overall order: $2 + 1 = 3$. The one-step condition is essential: stoichiometric coefficients do not generally give the rate law for a multistep reaction.

Step 2: Apply the volume change Immediately after the volume changes from V to $V/3$, each gas has the same amount as before compression. Thus

$$[\text{NO}]' = 3[\text{NO}], \quad [\text{O}_2]' = 3[\text{O}_2].$$

At unchanged temperature,

$$\frac{r'}{r} = \frac{k(3[\text{NO}])^2(3[\text{O}_2])}{k[\text{NO}]^2[\text{O}_2]} = 3^2 \times 3 = 27.$$

The concentration powers remain unchanged, so the reaction is still third order. For the reversible equation printed, this calculation refers to the immediate forward rate; a net rate would also require the reverse rate and product concentration.

Step 3: Conclusion The forward rate increases to 27 times its initial value. The order remains 3.

Quick Tip to Solve: Raise the compression factor to the total order: here the rate multiplier is 3^3 .

18(a). Explain what is observed when

(i) an electrolyte is added to ferric hydroxide sol.

(ii) an emulsion is subjected to centrifugation.

(iii) direct current is passed through a colloidal sol.

[3 marks]

Solution:

Concept:

- Colloidal particles carry like charges and repel one another; removing that charge allows coagulation.
- An emulsion contains droplets of one liquid dispersed in another. Charged sol particles migrate in an electric field by electrophoresis.

Step 1: (i) Add an electrolyte to ferric hydroxide sol Ferric hydroxide sol is positively charged. Anions from the electrolyte are attracted to its particles and neutralise their charge. When sufficient electrolyte is added to reach the coagulation concentration, repulsion between particles is lost; particles aggregate and settle as a precipitate. Thus coagulation or flocculation of the sol is observed. The anion is the effective coagulating ion for this positively charged sol.

Step 2: (ii) Centrifuge an emulsion Centrifugation accelerates the separation of the dispersed droplets from the dispersion medium because the two liquids have different densities. Droplets collect together and the emulsion separates into its constituent liquid layers. This breaking of an emulsion is called demulsification; the denser liquid collects farther from the axis of rotation.

Step 3: (iii) Pass direct current through a sol The colloidal particles move towards the electrode with charge opposite to their own. Positively charged particles move towards the cathode, while negatively charged particles move towards the anode. This directed migration, visible as movement of the colloidal boundary, is called electrophoresis. At the electrode the particles may lose charge and coagulate. Their direction of motion therefore reveals the sign of their charge.

Step 4: Conclusion (i) Coagulation of ferric hydroxide sol; (ii) separation of the emulsion into liquid layers; (iii) electrophoretic migration of colloidal particles towards the oppositely charged electrode.

Quick Tip to Solve: Identify the dispersed particle charge first: its counter-ion coagulates it and the oppositely charged electrode attracts it.

18(b). Define adsorption and write two important differences between physical adsorption and chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon: the adsorbed substance is the adsorbate and the surface providing material is the adsorbent.
- Physical adsorption involves weak intermolecular forces; chemisorption involves formation of chemical bonds at the surface.

Step 1: Define adsorption Adsorption is the accumulation of molecules, atoms or ions of a substance at the surface of another substance, giving a higher concentration at the surface than in the bulk. The substance accumulated is called the adsorbate, and the material on whose surface it accumulates is the adsorbent. For example, gases can accumulate on the large accessible surface of activated charcoal. This definition distinguishes surface accumulation from absorption, in which a substance enters the bulk of another material.

Step 2: First difference: nature of attraction In physical adsorption, also called physisorption, adsorbate particles are held by weak van der Waals forces. No new chemical bonds are formed between the adsorbate and adsorbent. In chemisorption, strong chemical bonds form between surface sites and the adsorbate. Consequently, the enthalpy of adsorption is generally much lower in magnitude for physisorption than for chemisorption, consistent with the different strengths of the interactions involved.

Step 3: Second difference: specificity Physical adsorption is comparatively non-specific: many gases can be adsorbed on a given suitable surface through intermolecular attraction. Chemisorption is highly specific, because chemical bonds form only when the adsorbate and the surface are chemically compatible. Thus the identity and chemical nature of both the adsorbate and adsorbent are crucial for chemisorption.

Step 4: Conclusion Adsorption is accumulation at a surface. The two differences are weak van der Waals forces versus chemical bonding, and comparatively non-specific versus highly specific adsorption.

Quick Tip to Solve: For two clear differences, compare the binding force first and chemical specificity second.

19. Draw a figure to show splitting of degenerate d orbitals in an octahedral field. How is the magnitude of Δ_o affected by (i) nature of ligand and (ii) oxidation state of metal ion? [3 marks]

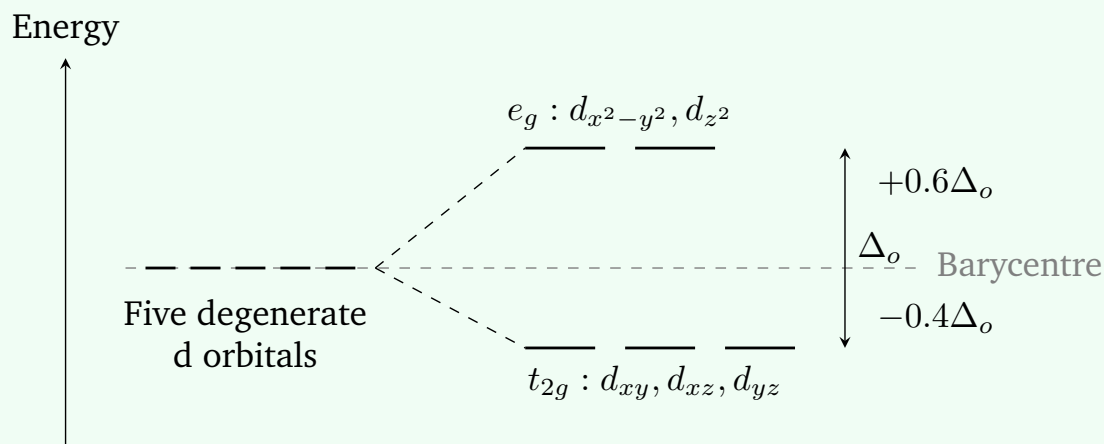
Solution:

Concept:

- In an octahedral complex, six ligands approach the metal along the coordinate axes. Their electron pairs repel the metal d electrons and remove the degeneracy of the five d orbitals.

- The octahedral splitting energy is $\Delta_o = E(e_g) - E(t_{2g})$. Relative to the barycentre, each t_{2g} orbital has energy $-0.4\Delta_o$, while each e_g orbital has energy $+0.6\Delta_o$.

Step 1: Split the five degenerate d orbitals The $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the incoming ligands, experience greater repulsion, and form the higher-energy e_g pair. The d_{xy} , d_{xz} and d_{yz} orbitals point between the ligand directions and form the lower-energy t_{2g} triplet. The weighted average remains unchanged: $2(0.6\Delta_o) + 3(-0.4\Delta_o) = 0$. The diagram shows orbital energies, without specifying an electron configuration.



Splitting of d orbitals in an octahedral ligand field

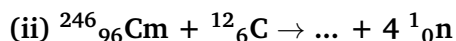
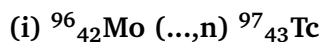
Step 2: Effect of the nature of the ligand For the same metal ion and oxidation state, strong-field ligands cause a larger Δ_o than weak-field ligands. For example, the increasing splitting order includes $I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < CN^- < CO$. Thus a cyanide complex generally has greater octahedral splitting than a corresponding water complex.

Step 3: Effect of the oxidation state For the same metal and the same ligands in comparable octahedral complexes, increasing the oxidation state increases Δ_o . The more highly charged metal ion attracts ligand electron density more strongly and generally has shorter metal-ligand distances, increasing the interaction and the splitting. Thus the corresponding metal(III) complex generally has greater splitting than metal(II).

Step 4: Conclusion Octahedral splitting gives a lower t_{2g} triplet and an upper e_g doublet separated by Δ_o . Stronger-field ligands and a higher metal oxidation state increase Δ_o .

Quick Tip to Solve: Place the two axis-directed orbitals above the barycentre and the three between-axis orbitals below it; their weighted shifts must add to zero.

20. Complete the following nuclear reactions:



(Note: Use symbol 'X' where element is not known)

[3 marks]

Solution:

Concept:

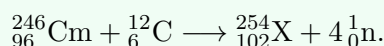
- In a nuclear reaction, the sum of mass numbers A and the sum of atomic numbers Z are each conserved. Write nuclei as ${}^A_Z\text{X}$.
- A neutron is ${}^1_0\text{n}$, an alpha particle is ${}^4_2\text{He}$, and a beta-minus particle is ${}^0_{-1}\text{e}$. In $T(a, b)P$, a is incident on target T , b is emitted, and P is the product.

Step 1: (i) Identify the incident particle Let the incident particle have mass number a and atomic number z . Conservation gives $96 + a = 97 + 1$ and $42 + z = 43 + 0$, hence $a = 2$, $z = 1$. The missing particle is a deuteron, ${}^2_1\text{H}$, so



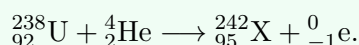
Both sides have total mass number 98 and total atomic number 43.

Step 2: (ii) Find the product nucleus The initial totals are $A = 246 + 12 = 258$ and $Z = 96 + 6 = 102$. Four emitted neutrons remove four mass units and no charge. The residual nucleus therefore has $A = 254$ and $Z = 102$:



The symbol X follows the question instruction; element 102 is nobelium, No. The totals on the right are $254 + 4 = 258$ and $102 + 0 = 102$.

Step 3: (iii) Balance alpha capture and beta emission In the printed (α, β) notation an alpha particle is absorbed and a beta-minus particle is emitted. Thus $238 + 4 = A + 0$ and $92 + 2 = Z - 1$, giving $A = 242$ and $Z = 95$. Therefore



Element 95 is americium, Am. The charge check is $94 = 95 - 1$; beta-minus emission increases the residual atomic number by one and leaves its mass number unchanged.

Step 4: Conclusion The missing entries are (i) ${}^2_1\text{H}$ (deuteron), (ii) ${}^{254}_{102}\text{X}$ (nobelium), and (iii) ${}^{242}_{95}\text{X}$ (americium).

Quick Tip to Solve: For a reaction written as (a, b) , add the incoming particle first, then subtract the emitted particle separately in the mass and charge balances.

21. Describe simple chemical tests to distinguish between the following pairs of compounds:

(i) Propanal and Propanone

(ii) Phenol and Benzoic acid

(iii) Diethyl ether and Propanol

[3 marks]

Solution:

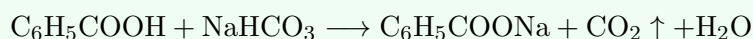
Concept:

- A distinguishing test gives a visible positive result for one member of a pair and a negative result for the other under the same conditions.
- Aldehydes reduce Tollens' reagent; carboxylic acids liberate carbon dioxide from bicarbonate; alcohols liberate hydrogen with sodium metal.

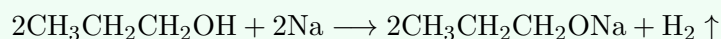
Step 1: (i) Propanal and propanone Warm separate samples with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the inner wall of the test tube because its aldehyde group is oxidised to propanoate while silver(I) is reduced. Propanone gives no silver mirror under these conditions.



Step 2: (ii) Phenol and benzoic acid Add aqueous sodium hydrogen carbonate to each sample. Benzoic acid produces brisk effervescence of carbon dioxide, whereas phenol does not. The gas turns limewater milky. Benzoic acid is sufficiently acidic to displace carbonic acid from its salt; phenol is weaker than carbonic acid.



Step 3: (iii) Diethyl ether and propanol Add a small piece of sodium metal to separate dry samples. Propanol evolves bubbles of hydrogen gas, whereas diethyl ether gives no such reaction. The alcohol contains an O-H hydrogen that sodium can replace; the ether has no O-H bond.



Step 4: Conclusion Propanal gives Tollens' silver mirror; benzoic acid effervesces with NaHCO_3 ; propanol evolves H_2 with sodium. The other compound in each respective pair gives a negative test.

Quick Tip to Solve: Use separate portions for each reagent; the sodium test needs dry samples because water also releases hydrogen with sodium.

22. Give appropriate reasons for each of the following observations:

(i) The aromatic amines are weaker bases than aliphatic amines.

(ii) Even under mild conditions aniline on bromination gives 2,4,6-tribromoaniline instantaneously.

(iii) The diazonium ion acts as an electrophile.

[3 marks]

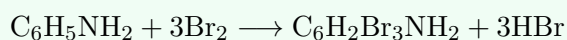
Solution:

Concept:

- An amine acts as a base by donating the nitrogen lone pair to a proton. Greater availability of this pair generally increases basicity.
- Resonance donation by $-\text{NH}_2$ increases electron density at the ortho and para positions of an aromatic ring. An electrophile accepts an electron pair.

Step 1: (i) Aromatic versus aliphatic amines In an aromatic amine such as aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less readily available for attachment to a proton. Protonation removes that lone pair from conjugation, so the resonance stabilisation of the free amine also opposes protonation. In aliphatic amines the lone pair is localised on nitrogen, and the electron-releasing inductive effect of alkyl groups increases electron density on nitrogen. Consequently, aromatic amines are weaker bases than comparable aliphatic amines.

Step 2: (ii) Instantaneous tribromination of aniline The amino group strongly activates the benzene ring through its resonance electron-donating effect. This increases electron density particularly at both ortho positions and the para position, making electrophilic substitution very fast. Hence bromine water reacts even under mild conditions, without a Lewis-acid catalyst, to substitute all three activated positions and form a white precipitate of 2,4,6-tribromoaniline.



Step 3: (iii) Electrophilic nature of the diazonium ion The arenediazonium ion, $\text{Ar}-\text{N} \equiv \text{N}^+$, carries a positive charge and is electron deficient. Its terminal nitrogen can accept an electron pair from an electron-rich aromatic ring, such as that of phenol or aniline, in an azo-coupling reaction. It therefore acts as the electrophile, and the new carbon–nitrogen bond gives the azo linkage $\text{Ar}-\text{N} = \text{N}-\text{Ar}'$.

Step 4: Conclusion The observations follow respectively from reduced availability of the aromatic amine lone pair, strong ortho/para activation by $-\text{NH}_2$, and electron-pair acceptance by the positively charged diazonium group.

Quick Tip to Solve: Distinguish the two effects of the amino lone pair: donation into the ring lowers basicity at nitrogen but increases ring reactivity.

23. Enumerate the structural differences between DNA and RNA. Write down the structure of sugar present in DNA. [3 marks]

Solution:

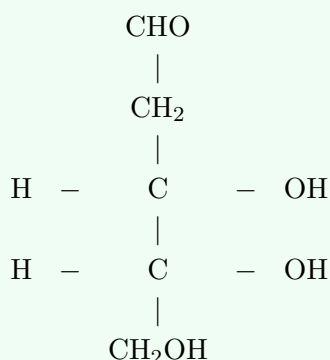
Concept:

- DNA and RNA are polynucleotides. Each nucleotide contains a pentose sugar, a phosphate group and a nitrogenous base.
- The sugar carbons are numbered with primes to distinguish them from the atoms of the bases. The decisive sugar difference is at carbon 2'.

Step 1: Compare the sugars and bases DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. DNA therefore has H at the 2' position where RNA has an OH group. Both contain the purine bases adenine (A) and guanine (G), and the pyrimidine cytosine (C). The other pyrimidine is thymine (T) in DNA and uracil (U) in RNA. Thus the base sets are A, G, C, T for DNA and A, G, C, U for RNA.

Step 2: Compare the chain arrangement DNA is generally composed of two antiparallel polynucleotide strands coiled into a double helix. The strands are joined by complementary base pairing: A pairs with T and G with C through hydrogen bonds. RNA is generally a single polynucleotide strand, although it can fold back on itself to produce locally paired regions; where pairing occurs, A pairs with U. Both polymers have a sugar-phosphate backbone with 3'-5' phosphodiester linkages, so the backbone linkage itself is a similarity.

Step 3: Write the structure of the DNA sugar The sugar is 2-deoxy-D-ribose, $C_5H_{10}O_4$. Its open-chain Fischer structure is shown below; horizontal bonds project towards the observer.



The second carbon is CH_2 , confirming the absence of the hydroxyl group present at that carbon in ribose. In DNA the sugar occurs in the cyclic 2-deoxyribofuranose form.

Step 4: Conclusion DNA differs from RNA in its deoxyribose sugar, thymine instead of uracil, and generally double-stranded helical structure. The DNA sugar is 2-deoxy-D-ribose.

Quick Tip to Solve: Remember the name literally: 2-deoxy means the OH at carbon 2 of ribose is replaced by H; retain the OH groups at carbons 3 and 4 in its Fischer structure.

24. Describe the following with example in each case:

(i) Antioxidants

(ii) Biodegradable detergents

(iii) Hybrid propellants

[3 marks]

Solution:

Concept:

- Antioxidants inhibit oxidation, particularly oxidation of fats and oils that causes rancidity.
- Microorganisms can break biodegradable detergents down into simpler products; a straight hydrocarbon chain favours this process.
- A hybrid rocket propellant has fuel and oxidiser in different physical states.

Step 1: (i) Antioxidants Antioxidants are substances added in small quantities to retard oxidation of an oxidisable material. In food containing fats or oils, they delay rancidity and help preserve flavour and quality by interrupting oxidation reactions. An example is butylated hydroxyanisole (BHA), used as a food antioxidant; butylated hydroxytoluene (BHT) is another example.

Step 2: (ii) Biodegradable detergents These are detergents that bacteria and other microorganisms can decompose after use. Detergents with straight, unbranched alkyl chains are readily attacked by microorganisms, so they do not persist as strongly as highly branched detergents. An example is sodium n-dodecylbenzenesulphonate, a linear alkylbenzene sulphonate detergent.

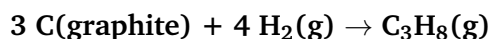
Step 3: (iii) Hybrid propellants Hybrid propellants are rocket propellant systems in which the fuel and oxidiser are present in different physical states. The components react in the combustion chamber to produce hot gases, whose rapid expulsion provides thrust. A typical example is solid polybutadiene fuel used with liquid oxygen as the oxidiser; the fuel is solid while oxygen is supplied as a liquid.

Step 4: Conclusion Examples are BHA for antioxidants, sodium n-dodecylbenzenesulphonate for biodegradable detergents, and solid polybutadiene with liquid oxygen for a hybrid propellant.

Quick Tip to Solve: For each term, state its defining function or physical feature before naming a specific example.

25. (a) What is meant by an entropy driven reaction? How can a reaction with positive enthalpy and entropy changes be made entropy driven?

(b) Calculate the standard Gibbs energy change for the formation of propane, $\text{C}_3\text{H}_8(\text{g})$ at 298 K.



Given: $\Delta_f H^\circ$ for propane is $-103.85 \text{ kJ mol}^{-1}$.

$S^\circ_{\text{m}} \text{C}_3\text{H}_8(\text{g}) = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ_{\text{m}} \text{H}_2(\text{g}) = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ_{\text{m}} \text{C}(\text{graphite}) = 5.74 \text{ J K}^{-1} \text{ mol}^{-1}$. [5 marks]

Solution:

Concept:

- At constant temperature and pressure, a reaction is spontaneous when its Gibbs energy change is negative: $\Delta G = \Delta H - T\Delta S < 0$.
- The reaction entropy is the sum of stoichiometric molar entropies of products minus that of reactants. Unlike standard formation enthalpies, standard molar entropies of elements are not zero.
- Enthalpy and entropy must use consistent energy units when evaluating ΔG ; $1 \text{ kJ} = 1000 \text{ J}$.

Step 1: (a) Meaning of an entropy driven reaction An entropy driven reaction is one whose spontaneity is brought about by the favourable entropy contribution, $-T\Delta S$, to its Gibbs energy change. In particular, an endothermic reaction can proceed spontaneously even though its enthalpy change opposes the process, if the increase in entropy is sufficiently large at the specified temperature. Here T is the absolute temperature in kelvin.

Step 2: (a) Temperature condition when both changes are positive If $\Delta H > 0$ and $\Delta S > 0$, increasing temperature increases the magnitude of the negative term $-T\Delta S$. For spontaneity,

$$\Delta H - T\Delta S < 0 \implies T\Delta S > \Delta H \implies T > \frac{\Delta H}{\Delta S}.$$

Thus heat the system above this threshold, assuming the signs and values of the changes remain applicable over the temperature interval. At equality the reaction has $\Delta G = 0$, rather than a spontaneous forward driving force.

Step 3: (b) Standard entropy change of formation For $3\text{C}(\text{graphite}) + 4\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$, apply the stoichiometric coefficients:

$$\begin{aligned}\Delta_f S^\circ &= 270.2 - [3(5.74) + 4(130.68)] \\ &= 270.2 - (17.22 + 522.72) \\ &= -269.74 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -0.26974 \text{ kJ K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

The negative value is consistent with consuming four moles of gaseous hydrogen to form one mole of gaseous propane, with carbon also consumed as a solid.

Step 4: (b) Substitute into the Gibbs energy relation Using $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$ and $T = 298 \text{ K}$,

$$\begin{aligned}\Delta_f G^\circ &= \Delta_f H^\circ - T\Delta_f S^\circ \\ &= -103.85 - 298(-0.26974) \\ &= -103.85 + 80.38252 \\ &= -23.46748 \text{ kJ mol}^{-1}.\end{aligned}$$

In this formation reaction the negative entropy change opposes spontaneity; the favourable enthalpy change is large enough to give a negative standard Gibbs energy at 298 K.

Step 5: Conclusion (a) An entropy driven reaction is made spontaneous by its favourable entropy term; for $\Delta H > 0$ and $\Delta S > 0$, it requires $T > \Delta H/\Delta S$. (b) $\Delta_f G^\circ(298 \text{ K}) = -23.47 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Multiply each molar entropy by its reaction coefficient and convert the resulting entropy to kJ before combining it with enthalpy.

26(a). Give reasons for the following observations:

- (i) The tendency for catenation decreases down the group in Group 14.
- (ii) The decreasing stability of +3 oxidation state with increasing atomic number in Group 13.
- (iii) SF_6 is not easily hydrolysed though thermodynamically it should be.

(b) Draw the structures of the following species:

- (i) $(\text{Si}_2\text{O}_7)^{6-}$
- (ii) ClO_4^-

[5 marks]

Solution:

Concept:

- Catenation is the formation of chains through element-element covalent bonds; its extent depends chiefly on the strength of these bonds.
- The inert-pair effect is the increasing reluctance of the outer ns^2 electron pair to participate in bonding down a group.
- Thermodynamic feasibility does not determine reaction speed: a large activation barrier can make a favourable reaction very slow.
- A silicate tetrahedron has four oxygen atoms around silicon. Four bonding regions around the central chlorine in ClO_4^- also give a tetrahedral arrangement.

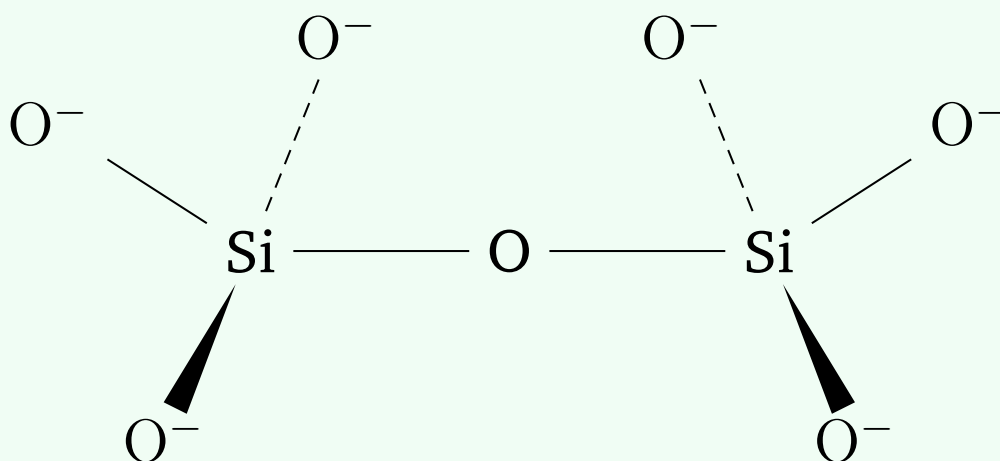
Step 1: (a)(i) Relate catenation to bond strength Down Group 14, atomic size increases. The larger valence orbitals overlap less effectively when neighbouring atoms form an element-element bond. Consequently, these bonds become weaker and long chains become less stable. Carbon, with its small size and strong C–C bonds, therefore shows the greatest catenation. The general tendency decreases down the group as the ability to maintain strong links between identical atoms decreases.

Step 2: (a)(ii) Apply the inert-pair effect Group 13 elements have outer electronic configuration ns^2np^1 . The +3 state involves all three outer electrons, whereas the +1 state involves mainly the np

electron, leaving the ns^2 pair uninvolved. Down the group, intervening d and f electrons shield the nuclear charge poorly, and the s pair is held more firmly. Thus the inert-pair effect increases: the +1 state becomes more stable relative to +3, so the stability of the +3 oxidation state decreases with increasing atomic number.

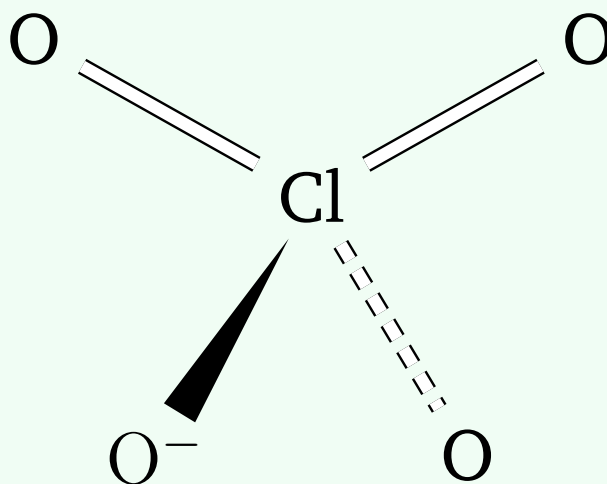
Step 3: (a)(iii) Distinguish kinetic inertness from feasibility In SF_6 , six fluorine atoms closely surround the sulphur atom in an octahedral arrangement and shield it from attack by water. The strong S–F bonds and the difficulty of reaching sulphur give hydrolysis a large activation barrier. Thus, although hydrolysis may be thermodynamically favourable, its rate is extremely small under ordinary conditions. SF_6 is therefore kinetically inert towards hydrolysis.

Step 4: (b)(i) Join two silicate tetrahedra through one oxygen The $\text{Si}_2\text{O}_7^{6-}$ ion consists of two SiO_4 tetrahedra sharing one corner oxygen. Each silicon remains bonded to four oxygen atoms: one bridging oxygen and three terminal oxygens. The total number of distinct oxygens is $4 + 4 - 1 = 7$. In the single-bond Lewis representation, the six terminal oxygen atoms each carry charge -1, while the bridging oxygen has two bonds and is neutral. The total ionic charge is therefore -6. Solid wedges point towards the observer; dashed bonds point away.



Two corner-sharing tetrahedra in $\text{Si}_2\text{O}_7^{6-}$

Step 5: (b)(ii) Arrange the perchlorate oxygens tetrahedrally In ClO_4^- , the central chlorine has four bonding regions and no lone pair. The oxygen atoms occupy the corners of a tetrahedron, with O–Cl–O angles approximately 109.5° . The drawing shows one conventional resonance contributor with three double bonds and one single bond to O^- . Four equivalent contributors place the singly bonded oxygen at each possible position, so the actual ion has four equivalent chlorine-oxygen bonds and a delocalised negative charge.



Tetrahedral perchlorate ion: one resonance contributor

Step 6: Conclusion Catenation decreases because element-element bonds weaken; the +3 state of Group 13 becomes less stable because the inert-pair effect increases; and SF_6 resists hydrolysis because of its high kinetic barrier. $\text{Si}_2\text{O}_7^{6-}$ contains two corner-sharing tetrahedra, while ClO_4^- is tetrahedral.

Quick Tip to Solve: Count shared oxygens only once: two tetrahedra sharing one corner give seven oxygens. For perchlorate, count four bonding directions around chlorine, regardless of resonance bond orders.

OR

26(b). (a) Assign reasons for the following observations:

- (i) PbO_2 is a stronger oxidising agent than SnO_2 .
- (ii) The bond energy of F_2 is less than that of Cl_2 .
- (iii) Sulphur in vapour state exhibits paramagnetism.

(b) Draw the structures of the following species:

- (i) $(\text{SiO}_3^{2-})_n$
- (ii) BrO_4^-

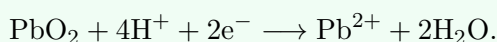
[5 marks]

Solution:

Concept:

- The inert-pair effect stabilises the lower oxidation state of heavier p-block elements: the outer ns^2 pair participates less readily in bonding.
- Bond strength depends on both bonding overlap and repulsion between nonbonding electron pairs. Unpaired electrons cause paramagnetism.
- Silicates contain tetrahedral SiO_4 units. The number of shared oxygen vertices determines their composition; perbromate has four bonding directions around bromine.

Step 1: (a)(i) Compare the stability of oxidation states The inert-pair effect is stronger in lead than in tin. Hence the +2 oxidation state of lead is more stable relative to its +4 state, whereas the +4 state of tin is comparatively more stable. Lead(IV) in PbO_2 therefore accepts electrons and is reduced to lead(II) more readily than tin(IV) in SnO_2 is reduced to tin(II). For example, its reduction in acid is

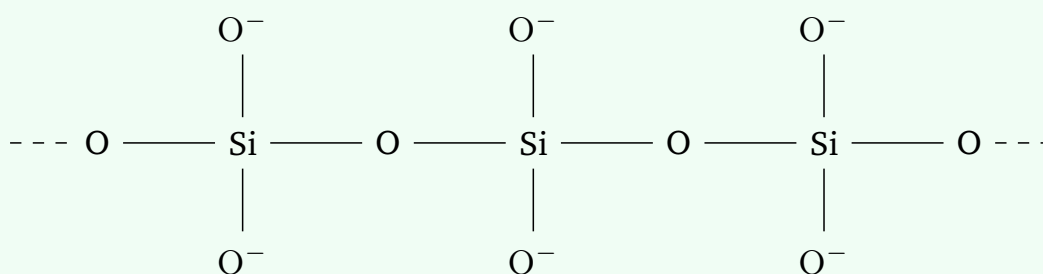


Greater readiness to undergo reduction makes PbO_2 the stronger oxidising agent.

Step 2: (a)(ii) Account for the weak fluorine bond Each halogen atom in X_2 carries three lone pairs. Fluorine atoms are very small, so the nonbonding electron pairs on the two atoms are crowded into a small region and repel one another strongly. This unusually strong lone-pair repulsion weakens the F–F bond. Chlorine's larger size reduces this repulsion, so the Cl–Cl bond has a greater bond dissociation energy despite its greater length.

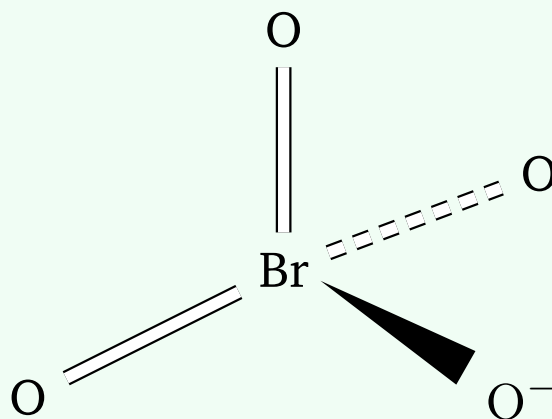
Step 3: (a)(iii) Explain sulphur vapour paramagnetism At high temperature sulphur vapour contains diatomic S_2 molecules. Like O_2 , S_2 has two unpaired electrons in its two degenerate antibonding π^* molecular orbitals. These unpaired electrons produce a magnetic moment, causing attraction towards a magnetic field. Thus sulphur vapour exhibits paramagnetism; this explanation concerns the diatomic species present in hot vapour.

Step 4: (b)(i) Draw the chain silicate Each SiO_4 tetrahedron shares two oxygen vertices with neighbouring tetrahedra, producing an infinite single chain. Each silicon therefore has two terminal oxygen atoms and two bridging oxygen atoms. Counting half of each bridging oxygen gives $2 + 2/2 = 3$ oxygens per silicon, so the repeat composition is SiO_3^{2-} . The drawing shows connectivity of three tetrahedra; bonds above and below the chain represent the terminal oxygen vertices, and the chain continues at both ends.



Connectivity of the single-chain silicate; each silicon has tetrahedral coordination.

Step 5: (b)(ii) Draw the perbromate ion In BrO_4^- , bromine is surrounded by four oxygen atoms in a tetrahedral arrangement, with O–Br–O angles approximately 109.5° . A conventional Lewis contributor has three Br=O bonds and one Br–O[−] bond. The negative charge is delocalised over the oxygen atoms through equivalent resonance contributors, so all four Br–O positions are equivalent in the ion. The wedge and dashed bond indicate bonds directed towards and away from the observer.



Tetrahedral perbromate: one Lewis resonance contributor.

Step 6: Conclusion (a) The stronger inert-pair effect in Pb favours reduction to Pb(II); strong lone-pair repulsion weakens F-F; and hot sulphur vapour contains S_2 with two unpaired electrons. (b) $(SiO_3^{2-})_n$ is an infinite single-chain silicate, and BrO_4^- is tetrahedral, as drawn.

Quick Tip to Solve: For a single-chain silicate, count two terminal oxygens plus half of each of two shared oxygens per silicon.

27. (a) Describe the variability of oxidation states in the first row of the transition elements (Sc – Cu) and indicate the general trend.

(b) Write chemical reactions involved in the following:

(i) When matte is charged into silica lined converter in the metallurgy of copper.

(ii) When a solution of chromate is acidified.

(iii) A developed photographic film is subjected to fixing.

[5 marks]

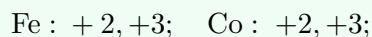
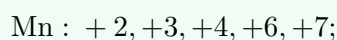
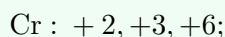
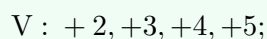
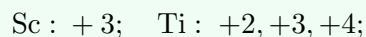
Solution:

Concept:

- Transition elements show variable oxidation states because their $3d$ and $4s$ orbitals have comparable energies, so different numbers of these electrons can participate in bonding.
- In a copper converter, iron sulphide is oxidised and removed as silicate slag; copper sulphide undergoes partial oxidation followed by self-reduction.
- Acidification shifts the chromate–dichromate equilibrium towards dichromate. Fixing removes undecomposed silver bromide through formation of a soluble thiosulphate complex.

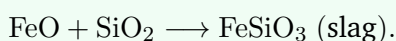
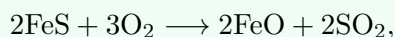
Step 1: (a) Explain variable oxidation states and their trend The outer configurations of these elements involve $3d$ and $4s$ electrons. The small energy difference between these subshells allows both sets of electrons to take part in bond formation, giving several oxidation states. The $4s$ electrons are generally lost first; participation of different numbers of $3d$ electrons gives the higher states.

Commonly encountered oxidation states illustrate the variation:

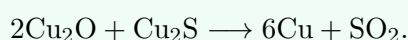
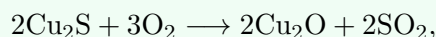


The maximum oxidation state and the range of accessible states generally increase from Sc to Mn, where the maximum is +7, and decrease towards Cu. Higher states are usually stabilised by oxygen or fluorine. The +2 state is common for most members after Sc; the list gives common states rather than every possible state. The stability of particular electronic configurations also matters: for example, Mn^{2+} has a half-filled $3d^5$ subshell.

Step 2: (b)(i) Reactions in the silica-lined copper converter Matte contains chiefly Cu_2S and FeS . Air blown through the hot matte oxidises iron sulphide; silica combines with the resulting iron(II) oxide to produce slag:

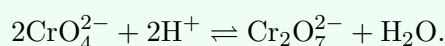


Some copper(I) sulphide is oxidised to copper(I) oxide, which reacts with the remaining sulphide to give copper:



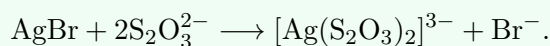
The last reaction is self-reduction and produces blister copper.

Step 3: (b)(ii) Acidify the chromate solution Yellow chromate ions combine in acidic medium to form orange dichromate ions:



Both sides have total charge -2 ; chromium remains in oxidation state $+6$. This is an acid–base equilibrium, not a redox reaction.

Step 4: (b)(iii) Fix the developed photographic film The developed image contains metallic silver, while unexposed silver bromide remains in the film. Sodium thiosulphate (hypo) dissolves this residual silver bromide as a soluble complex:



Equivalently,



Washing removes the soluble salts, leaving the metallic silver image and preventing further darkening on exposure to light.

Step 5: Conclusion Oxidation-state variability generally rises from Sc to Mn and then falls towards

Cu. In the converter, FeS is removed as FeSiO_3 slag and Cu_2S yields copper by self-reduction; acidified chromate gives orange dichromate; fixing removes residual AgBr as soluble $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.

Quick Tip to Solve: Remember the converter sequence: oxidise FeS, slag FeO with silica, partially oxidise Cu_2S , then self-reduce; keep two thiosulphate ions per silver ion in fixing.