

CBSE Class 12 Chemistry Question Paper 2008 with Solution PDF-Set 56/2 (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) Question nos. 1 to 8 are very short answer questions and carry 1 mark each.
- (iii) Question nos. 9 to 18 are short answer questions and carry 2 marks each.
- (iv) Question nos. 19 to 27 are also short answer questions and carry 3 marks each.
- (v) Question nos. 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 is the total number of atoms per unit cell in a face-centred cubic (fcc) structure? [1 mark]

Solution:

Concept:

- In an fcc unit cell, atoms occupy eight corners and six face centres.
- A corner atom is shared by eight cells; a face-centred atom is shared by two cells.

Step 1: Count the corner contribution The eight corner atoms each contribute only one eighth to a particular unit cell. Hence their total effective contribution is

$$8 \times \frac{1}{8} = 1.$$

Sharing must be included rather than counting each visible atom as a whole atom.

Step 2: Count the face contribution The six face-centred atoms each contribute one half, because each face is common to two adjacent cells. Their contribution is

$$6 \times \frac{1}{2} = 3.$$

There is no atom at the body centre in an fcc cell.

Step 3: Conclusion The total number of atoms per fcc unit cell is $1 + 3 = \boxed{4}$.

Quick Tip to Solve: For fcc, calculate corners plus faces: $8/8 + 6/2$; do not add a body-centred atom.

2. What is a primary cell? Give an example. [1 mark]

Solution:

Concept:

- A galvanic cell converts chemical energy into electrical energy through a spontaneous redox reaction.
- A primary cell has an essentially irreversible cell reaction and cannot be recharged for repeated use.

Step 1: Identify the defining property In a primary cell the electrode reaction proceeds during discharge, consuming the active materials. Passing current in the opposite direction does not practically regenerate the original reactants, so the cell is used until its reactants are exhausted.

Step 2: Choose a standard example The dry cell, also called the Leclanche cell, is a familiar primary cell. Its zinc container acts as the anode; the cell supplies electrical energy without being designed for repeated charging.

Step 3: Conclusion A primary cell is a non-rechargeable electrochemical cell with an essentially irreversible reaction. Example: a dry cell (Leclanche cell).

Quick Tip to Solve: Remember a dry cell for primary cells; a lead storage battery is a rechargeable secondary cell.

3. What causes Brownian movement in a colloidal solution?

[1 mark]

Solution:

Concept:

- Brownian movement is the continuous, random zigzag motion of colloidal particles.
- Molecules of the dispersion medium undergo thermal motion and collide with dispersed particles.

Step 1: Identify the moving molecules The molecules of the dispersion medium are in continuous thermal motion. They strike each colloidal particle from different directions, transferring momentum in individual collisions.

Step 2: Explain the random displacement The impacts on different sides of a colloidal particle are unequal at any instant. The resulting unbalanced force keeps changing in direction and magnitude, so the particle follows an irregular zigzag path rather than moving steadily in one direction.

Step 3: Conclusion Brownian movement is caused by unequal, incessant bombardment of colloidal particles by molecules of the dispersion medium.

Quick Tip to Solve: Name the dispersion-medium molecules as the cause; the observed zigzag movement belongs to the colloidal particles.

4. In which one of the two structures, NO_2^+ and NO_2^- , the bond angle has a higher value?

[1 mark]

Solution:

Concept:

- VSEPR theory relates molecular shape to repulsions between electron domains on the central atom.
- A multiple bond counts as one electron domain; a lone pair changes the geometry and bond angle.

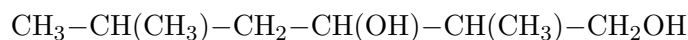
Step 1: Examine the positive ion In NO_2^+ , nitrogen has two bonding domains and no lone pair. The two domains arrange themselves opposite each other, giving a linear ion with an O–N–O angle of 180° .

Step 2: Compare the negative ion In NO_2^- , nitrogen has two bonding domains and one lone pair. The electron-domain arrangement is trigonal planar, but the molecular shape is bent. Lone-pair repulsion reduces the bond angle below 120° , so it is much smaller than the angle in the linear ion.

Step 3: Conclusion The bond angle is higher in NO_2^+ : it is 180° , whereas NO_2^- is bent.

Quick Tip to Solve: Count lone pairs on nitrogen: none in nitronium gives a linear ion; one in nitrite gives a bent ion.

5. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- Choose the longest carbon chain containing the maximum number of hydroxyl groups.
- Number the chain to give the principal hydroxyl groups the lowest set of locants before considering alkyl substituents.

Step 1: Select and number the parent chain The longest chain containing both hydroxyl groups has six carbon atoms. Numbering from the terminal CH_2OH end places the hydroxyl groups at carbon 1 and carbon 3; numbering from the other end would give 4 and 6. Thus the parent is hexane-1,3-diol.

Step 2: Locate the substituents With the chosen numbering, methyl groups are attached at carbons 2 and 5. Both identical substituents are expressed using the prefix 2,5-dimethyl. The suffix diol identifies the two hydroxyl groups as the principal functional groups.

Step 3: Conclusion The IUPAC name is 2,5-dimethylhexane-1,3-diol.

Quick Tip to Solve: Begin numbering at the terminal alcohol end: hydroxyl locants 1,3 take priority over methyl locants.

6. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- A ketone has a carbonyl group within a carbon chain; two such groups require the suffix dione.
- Choose a parent chain containing both carbonyl carbons and assign the lowest locants to the carbonyl groups.

Step 1: Identify the parent chain The structure $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CH}_3$ contains five carbon atoms in a continuous chain. Both carbonyl carbons form part of this chain, so the saturated parent hydrocarbon is pentane.

Step 2: Assign the carbonyl locants Numbering from either end places the carbonyl groups at carbons 2 and 4. The identical locants reflect the symmetry of the molecule. As there are two ketone groups, use the suffix dione with both position numbers.

Step 3: Conclusion The IUPAC name is pentane-2,4-dione.

Quick Tip to Solve: Count the carbonyl carbons in the five-carbon chain; the two ketone positions are 2 and 4.

7. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt. [1 mark]

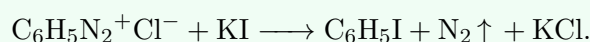
Solution:

Concept:

- Aromatic diazonium salts undergo substitution with loss of stable nitrogen gas.
- Potassium iodide supplies iodide ions that replace the diazonium group; a copper salt is unnecessary.

Step 1: Select the diazonium salt and reagent Take benzenediazonium chloride and treat it with potassium iodide. The iodide ion attacks in the substitution reaction, and the diazonium group is expelled as molecular nitrogen.

Step 2: Write the balanced reaction The reaction is



The benzene ring is retained, iodine replaces the diazonium group, and potassium chloride accounts for the remaining ions. The evolution of nitrogen gas favours the substitution.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{KI} \longrightarrow \text{C}_6\text{H}_5\text{I} + \text{N}_2\uparrow + \text{KCl}$; the organic product is iodobenzene.

Quick Tip to Solve: Use KI directly for iodination of a diazonium salt; no cuprous iodide catalyst is required.

8. Name a substance that can be used as an antiseptic as well as a disinfectant. [1 mark]

Solution:

Concept:

- Antiseptics kill or inhibit microorganisms on living tissues; disinfectants are used on inanimate surfaces.
- The suitability of some germicides depends on concentration.

Step 1: Identify a suitable substance Phenol can serve both purposes. Its germicidal action makes it useful for controlling microorganisms.

Step 2: Distinguish the concentrations A dilute, 0.2% solution of phenol acts as an antiseptic. A stronger, 1% solution acts as a disinfectant and is unsuitable for application to living tissues.

Step 3: Conclusion Phenol: 0.2% solution is an antiseptic, whereas 1% solution is a disinfectant.

Quick Tip to Solve: Remember the pair for phenol: 0.2 percent for antiseptic use and 1 percent for disinfection.

9(a). State Raoult's law for solutions of volatile liquids. Taking suitable examples explain the meaning of positive and negative deviations from Raoult's law. [2 marks]

Solution:

Concept:

- Raoult's law relates each volatile component's partial vapour pressure to its liquid-phase mole fraction.
- Unlike-molecule attractions determine the direction of deviation from ideal behaviour.

Step 1: State the law At a fixed temperature, the partial vapour pressure of each volatile component equals its mole fraction in solution multiplied by its pure-liquid vapour pressure:

$$p_A = x_A p_A^0, \quad p_B = x_B p_B^0.$$

Hence, for an ideal binary solution, $p_{\text{total}} = x_A p_A^0 + x_B p_B^0$.

Step 2: Explain positive deviation The observed vapour pressure is higher than predicted by Raoult's law. For example, ethanol and acetone show positive deviation: acetone disrupts ethanol hydrogen bonding, so the unlike-molecule attractions are weaker and molecules escape more readily.

Step 3: Explain negative deviation The observed vapour pressure is lower than predicted. Acetone and chloroform show negative deviation because hydrogen bonding between chloroform and the carbonyl oxygen of acetone produces stronger unlike-molecule attractions, reducing escape into the vapour.

Step 4: Conclusion Positive deviation means higher vapour pressure, as in ethanol–acetone; negative deviation means lower vapour pressure, as in acetone–chloroform.

Quick Tip to Solve: Compare unlike attractions with like attractions: weaker gives positive deviation; stronger gives negative deviation.

OR

9(b). Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure. [2 marks]

Solution:

Concept:

- Osmosis is the flow of solvent through a semipermeable membrane from pure solvent into a solution.
- For a dilute solution, osmotic pressure obeys $\pi V = nRT$, where T is absolute temperature.

Step 1: Define osmotic pressure Osmotic pressure, π , is the minimum excess pressure that must be applied to a solution to prevent the inward flow of solvent through a semipermeable membrane separating it from pure solvent.

Step 2: Measure the required quantities Dissolve a known mass w of the substance to prepare

Quick Tip to Solve: Use the final solution volume and kelvin temperature in $M = wRT/(\pi V)$, keeping all gas-law units consistent.

a known solution volume V . Separate this dilute solution from pure solvent by a semipermeable membrane at a known temperature T . Apply pressure to the solution until net solvent flow just stops; this pressure is π .

Step 3: Obtain the molecular mass If the molar mass is M , the solute amount is $n = w/M$. Substitution into the dilute-solution equation gives

$$\pi V = \frac{w}{M}RT, \quad M = \frac{wRT}{\pi V}.$$

Use consistent pressure and volume units with the chosen gas constant R ; the solute should not associate or dissociate in the solvent.

Step 4: Conclusion The molar mass is $M = \frac{wRT}{\pi V}$, obtained from the measured osmotic pressure of a dilute solution.

Quick Tip to Solve: Use the final solution volume and kelvin temperature in $M = wRT/(\pi V)$, keeping all gas-law units consistent.

10. The conductivity of a 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity. [2 marks]

Solution:

Concept:

- Molar conductivity is conductivity divided by molar concentration expressed per unit volume.
- With κ in S cm^{-1} and C in mol L^{-1} , $\Lambda_m = 1000\kappa/C$.

Step 1: Record the data and convert concentration The given conductivity is $\kappa = 0.0248 \text{ S cm}^{-1}$, and the concentration is $C = 0.20 \text{ mol L}^{-1}$. Since $1 \text{ L} = 1000 \text{ cm}^3$, the concentration in cubic-centimetre units is

$$c = \frac{0.20}{1000} = 2.0 \times 10^{-4} \text{ mol cm}^{-3}.$$

Step 2: Calculate the molar conductivity Using conductivity and concentration in consistent units,

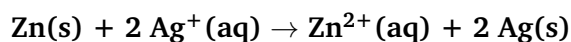
$$\Lambda_m = \frac{\kappa}{c} = \frac{0.0248}{2.0 \times 10^{-4}} = 124 \text{ S cm}^2 \text{ mol}^{-1}.$$

Equivalently, $\Lambda_m = 0.0248 \times 1000/0.20$. The centimetre powers follow from dividing cm^{-1} by cm^{-3} ; the given temperature fixes the conductivity used in this calculation.

Step 3: Conclusion The molar conductivity at 298 K is $124 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: For conductivity in S/cm and molarity in mol/L , remember the factor 1000 in the numerator.

11. Formulate the galvanic cell in which the following reaction takes place:



State:

- (i) Which one of its electrodes is negatively charged.
- (ii) The reaction taking place at each of its electrodes.
- (iii) The carriers of current within this cell.

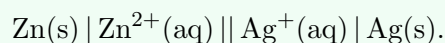
[2 marks]

Solution:

Concept:

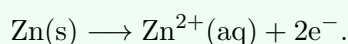
- Oxidation occurs at the anode and reduction at the cathode of a galvanic cell.
- Electrons carry current through the metallic external circuit; ions carry current through the electrolytes and salt bridge.

Step 1: Formulate the cell Zinc loses electrons while silver ions gain them. Write the oxidation half-cell on the left and the reduction half-cell on the right:

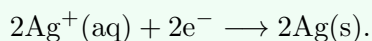


A single vertical line denotes a phase boundary and the double line denotes the salt bridge.

Step 2: Identify the negative electrode and half-reactions (i) The zinc electrode is negatively charged because it supplies electrons to the external circuit. (ii) At the zinc anode,



At the silver cathode,



Adding these gives the stated cell reaction.

Step 3: Identify the current carriers (iii) Within the cell, current is carried by ions in the electrolytes and salt bridge: cations move towards the cathode region and anions towards the anode region to maintain electrical neutrality. Electrons move from zinc to silver through the external connecting wire.

Step 4: Conclusion The cell is $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$. Zinc is the negative anode; oxidation occurs at Zn, reduction at Ag, and ions carry current within the cell.

Quick Tip to Solve: Write the metal being oxidised on the left; distinguish ionic conduction inside the cell from electron flow in its wire.

12. Define the following terms in relation to proteins:

(i) Peptide linkage

(ii) Denaturation

[2 marks]

Solution:

Concept:

- Proteins are polymers of amino acids joined by amide bonds called peptide linkages.
- A protein has a definite three-dimensional conformation, maintained by interactions such as hydrogen bonds; biological activity depends on this conformation.

Step 1: (i) Peptide linkage A peptide linkage is the amide linkage $-\text{CO} - \text{NH}-$ formed when the carboxyl group of one amino acid condenses with the amino group of another, eliminating water. Thus, the carbonyl carbon of one residue is bonded to the nitrogen of the next residue. Repetition of this condensation produces a polypeptide chain.

Step 2: (ii) Denaturation Denaturation is the loss of the native conformation and biological activity of a protein on heating or on changing conditions such as pH. The interactions maintaining its secondary and tertiary structures are disrupted, while the primary structure, that is, the amino-acid sequence joined by peptide bonds, remains intact. Coagulation of egg white on boiling is an example.

Step 3: Conclusion Peptide linkage: $-\text{CO} - \text{NH}-$ connecting amino-acid residues. Denaturation: loss of native protein structure and biological activity without cleavage of the peptide backbone.

Quick Tip to Solve: Distinguish disruption of protein folding from hydrolysis, which breaks peptide bonds.

13. List the reactions of glucose which cannot be explained by its open chain structure.

[2 marks]

Solution:

Concept:

- The open-chain formula $\text{CHO} - (\text{CHOH})_4 - \text{CH}_2\text{OH}$ contains a free aldehyde group and therefore predicts characteristic carbonyl reactions.
- An aldehyde normally gives Schiff's test, forms a bisulphite addition compound and reacts with hydroxylamine to form an oxime.

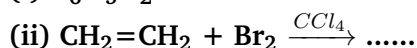
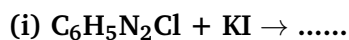
Step 1: Compare glucose with ordinary aldehydes Despite its proposed aldehyde group, glucose does not give Schiff's test and does not form an addition compound with sodium hydrogen sulphite, NaHSO_3 . These negative reactions are not accounted for by a structure containing an ordinary, freely available aldehyde group.

Step 2: Examine the pentaacetate reaction Glucose pentaacetate does not react with hydroxylamine, NH_2OH , to form an oxime. If the open-chain aldehyde structure persisted after acetylation of the five hydroxyl groups, its carbonyl group should still react. The failure indicates absence of a free aldehyde group in the pentaacetate, consistent with the cyclic structure of glucose.

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

Quick Tip to Solve: Remember that free glucose can form an oxime; the hydroxylamine failure concerns its pentaacetate.

14. Complete the following reaction equations:



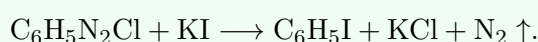
[2 marks]

Solution:

Concept:

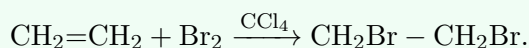
- Aryl diazonium salts react with potassium iodide to replace the diazonium group by iodine, with evolution of nitrogen gas.
- Bromine in CCl_4 adds across an alkene double bond, placing one bromine atom on each of the two carbon atoms.

Step 1: (i) Replace the diazonium group by iodine In benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, the $-\text{N}_2^+$ group is replaced by iodine from potassium iodide. Nitrogen is liberated and the remaining potassium and chloride ions form potassium chloride. The balanced equation is



The organic product is iodobenzene; a copper catalyst is not required for this iodide replacement.

Step 2: (ii) Add bromine to ethene The carbon-carbon double bond in ethene undergoes electrophilic addition of bromine. The pi bond is broken and a carbon-bromine bond forms at each carbon, giving the vicinal dibromide:



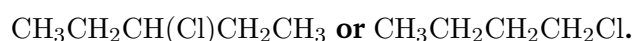
The product is 1,2-dibromoethane, and the bromine colour disappears as bromine is consumed.

Step 3: Conclusion (i) $\text{C}_6\text{H}_5\text{I} + \text{KCl} + \text{N}_2$. (ii) $\text{CH}_2\text{Br} - \text{CH}_2\text{Br}$, 1,2-dibromoethane.

Quick Tip to Solve: For bromine addition, keep both carbon atoms and attach one Br to each; do not substitute a hydrogen.

15. (i) Why is it that haloalkanes are more reactive than haloarenes towards nucleophiles?

(ii) Which one of the following reacts faster in an $\text{S}_{\text{N}}1$ reaction and why?



[2 marks]

Solution:

Concept:

- Nucleophilic substitution requires breaking the carbon-halogen bond; resonance and carbon hybridisation influence its strength.
- In an $\text{S}_{\text{N}}1$ reaction, carbocation formation is the slow step. A more stable carbocation forms more readily, increasing the reaction rate.

Step 1: (i) Compare the carbon-halogen bonds In a haloarene, a lone pair on the halogen participates in resonance with the aromatic ring. Consequently, the aryl carbon-halogen bond acquires partial double-bond character and is shorter and stronger than the corresponding bond in a haloalkane. The aryl carbon is also sp^2 -hybridised, whereas the carbon bonded to halogen in a haloalkane is

Quick Tip to Solve: For an $\text{S}_{\text{N}}1$ comparison, count alkyl groups on the carbon bearing Cl, rather than comparing total chain lengths.

sp^3 -hybridised. Cleavage of the stronger aryl bond is difficult, so haloarenes resist nucleophilic substitution under ordinary conditions.

Step 2: (ii) Compare carbocation stability The first printed compound, $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{CH}_3$ (3-chloropentane), forms a secondary carbocation on ionisation. The second, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (1-chlorobutane), would form a primary carbocation. Alkyl groups stabilise a carbocation by their electron-releasing inductive effect and hyperconjugation. The secondary carbocation is more stable, making its formation easier in the rate-determining step.

Step 3: Conclusion Haloalkanes are more reactive because their carbon-halogen bond is more readily cleaved. The first compound, 3-chloropentane, reacts faster by S_N1 because it forms a secondary carbocation.

Quick Tip to Solve: For an S_N1 comparison, count alkyl groups on the carbon bearing Cl, rather than comparing total chain lengths.

16. What are biodegradable and non-biodegradable detergents? Give one example of each class.

[2 marks]

Solution:

Concept:

- Biodegradability is the ability of microorganisms to decompose an organic substance into simpler, harmless products.
- The carbon-chain structure matters: straight hydrocarbon chains are generally more readily attacked by bacteria than highly branched chains.

Step 1: Biodegradable detergents Detergents which can be decomposed by microorganisms, such as bacteria, are called biodegradable detergents. They generally contain unbranched hydrocarbon chains, which bacterial enzymes can break down. An example is sodium n-dodecylbenzene sulphonate, a linear alkylbenzene sulphonate (LAS).

Step 2: Non-biodegradable detergents Detergents which resist decomposition by microorganisms are called non-biodegradable detergents. Highly branched hydrocarbon chains are difficult for bacterial enzymes to degrade, so these detergents persist in water and can cause foaming and pollution. An example is sodium tetrapropylbenzene sulphonate, a branched alkylbenzene sulphonate.

Step 3: Conclusion Biodegradable: sodium n-dodecylbenzene sulphonate (linear chain). Non-biodegradable: sodium tetrapropylbenzene sulphonate (branched chain).

Quick Tip to Solve: Remember linear LAS as biodegradable; associate a highly branched alkyl chain with resistance to bacterial breakdown.

17. Assign a reason for each of the following statements:

(i) Ammonia is a stronger base than phosphine.

(ii) Sulphur in vapour state exhibits a paramagnetic behaviour.

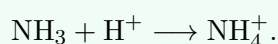
[2 marks]

Solution:

Concept:

- A Lewis base donates an electron pair. Greater availability of the central atom's lone pair favours proton acceptance.
- Paramagnetic species contain unpaired electrons and are attracted by a magnetic field.

Step 1: (i) Basicity of ammonia and phosphine Both NH_3 and PH_3 have a lone pair on the central atom. Nitrogen is smaller than phosphorus, and the lone pair in ammonia is concentrated in a smaller region and is more readily available for donation to a proton. Hence ammonia accepts H^+ more readily:



The lone pair in phosphine is less available for bond formation; therefore phosphine is a much weaker base.

Step 2: (ii) 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 in its antibonding π^* molecular orbitals. These unpaired electrons account for the attraction of sulphur vapour by a magnetic field. Thus the paramagnetism is due to molecular S_2 , rather than to the closed-shell S_8 rings of ordinary solid sulphur.

Step 3: Conclusion Ammonia is more basic because its lone pair is more available for protonation. Sulphur vapour is paramagnetic because S_2 has two unpaired electrons.

Quick Tip to Solve: For sulphur vapour, recall the diatomic species S_2 and its oxygen-like pair of unpaired electrons.

18. Draw the structures of the following molecules:

(i) SF_4

(ii) XeF_4

[2 marks]

Solution:

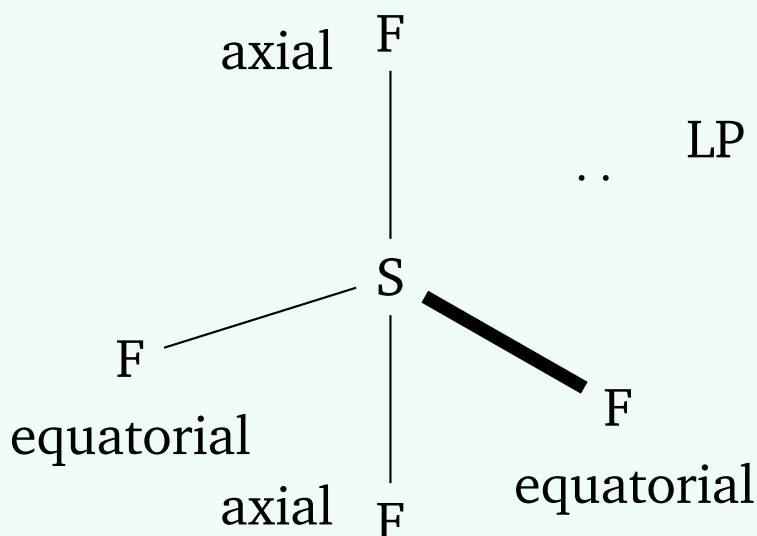
Concept:

- VSEPR theory determines molecular shape from repulsions between bonding pairs and lone pairs around the central atom.
- Lone pairs repel more strongly than bond pairs. The electron-pair geometry includes lone pairs, while molecular shape describes the positions of atoms only.

Step 1: (i) Structure of sulphur tetrafluoride Sulphur has six valence electrons. Four S–F bonds leave one lone pair on sulphur, giving five electron domains: AX_4E . Their arrangement is trigonal bipyramidal. The lone pair occupies an equatorial site because that site has fewer 90° interactions than an axial site. The four fluorine atoms therefore form a see-saw (distorted trigonal bipyramidal)

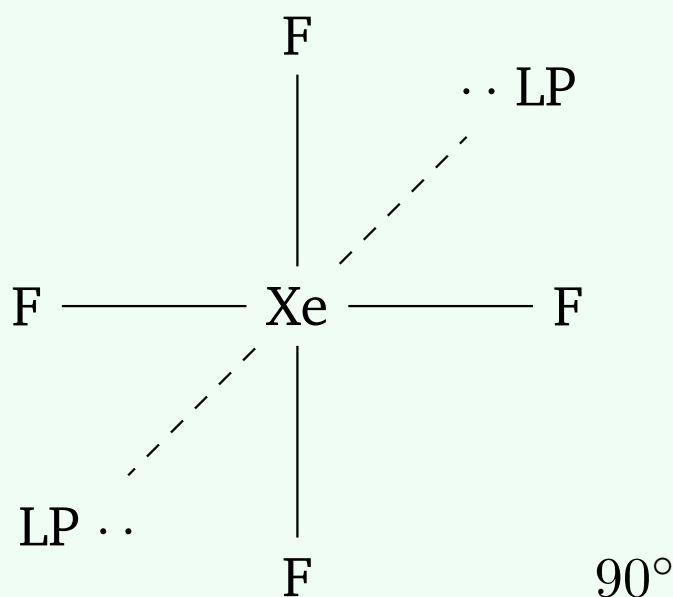
Quick Tip to Solve: Count lone pairs before naming the shape: SF_4 has five electron domains, while XeF_4 has six.

molecular structure, with two axial and two equatorial fluorine atoms.



See-saw structure of SF₄; LP denotes the equatorial lone pair.

Step 2: (ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four Xe–F bonds leave two lone pairs on xenon, giving six electron domains: AX₄E₂. Their arrangement is octahedral. The two lone pairs occupy opposite positions to minimise their mutual repulsion. The four fluorine atoms lie in a single square plane around xenon; adjacent F–Xe–F angles are 90° and opposite angles are 180°.



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

Step 3: Conclusion SF₄ is see-saw shaped with one equatorial lone pair; XeF₄ is square planar with two mutually trans lone pairs.

Quick Tip to Solve: Count lone pairs before naming the shape: SF₄ has five electron domains, while XeF₄ has six.

19. What are lyophilic and lyophobic sols? Give one example of each type. Which one of these two types of sols is easily coagulated and why? [3 marks]

Solution:

Concept:

- A sol is a colloidal dispersion of a solid in a liquid. Stability depends on the affinity between the dispersed particles and the dispersion medium.
- Solvation and electrical charge prevent particles from coming together. Coagulation is the aggregation of colloidal particles into larger particles that separate out.

Step 1: Lyophilic sols Lyophilic (solvent-loving) sols have a strong affinity between the dispersed phase and the dispersion medium. Their particles are extensively solvated; in water this is called hydration. They can generally be prepared by directly mixing the substance with a suitable solvent and are reversible. Starch sol in water is an example.

Step 2: Lyophobic sols Lyophobic (solvent-hating) sols have little affinity between the dispersed phase and the dispersion medium. Their particles are not appreciably solvated, and special methods are usually required to prepare them. They are generally irreversible. Gold sol in water is an example.

Step 3: Ease of coagulation A lyophobic sol is easily coagulated by a small amount of a suitable electrolyte. Its stability depends chiefly on the electrical charge of its particles. Oppositely charged ions neutralise this charge, reducing repulsion, so the particles aggregate. Lyophilic particles have an additional protective solvation layer, making their sols much harder to coagulate.

Step 4: Conclusion Starch sol is lyophilic, while gold sol is lyophobic. Lyophobic sols are easily coagulated because they lack substantial solvation protection and lose stability when their particle charge is neutralised.

Quick Tip to Solve: Link lyophilic stability with solvation and charge; explain lyophobic coagulation through neutralisation by counter-ions.

20. Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250 g of water will freeze.

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

[3 marks]

Solution:

Concept:

- For a dilute solution, the depression in freezing point is $\Delta T_f = iK_fm$, where m is the molality and K_f is the cryoscopic constant of the solvent.
- Glucose is a non-electrolyte and does not dissociate in water, so its van't Hoff factor is $i = 1$. Molality uses the mass of solvent in kilograms.

Step 1: Find the amount of glucose Using atomic masses $C = 12$, $H = 1$ and $O = 16$, the molar mass of glucose is

$$M(C_6H_{12}O_6) = 6(12) + 12(1) + 6(16) = 180 \text{ g mol}^{-1}.$$

Quick Tip to Solve: Divide by kilograms of water, not the total solution mass, and subtract the calculated depression from water's freezing point.

Hence the amount dissolved is $n = 54/180 = 0.300$ mol.

Step 2: Calculate the molality and depression The solvent is $250\text{ g} = 0.250\text{ kg}$ of water, so

$$m = \frac{0.300}{0.250} = 1.20\text{ mol kg}^{-1}.$$

Therefore,

$$\Delta T_f = (1)(1.86)(1.20) = 2.232\text{ K}.$$

This positive quantity is the amount by which the freezing point falls, rather than the freezing temperature itself.

Step 3: Obtain the freezing temperature Pure water freezes at 0°C . Temperature differences have the same numerical value in kelvin and degrees Celsius, so

$$T_f = 0 - 2.232 = -2.232^\circ\text{C}.$$

Equivalently, using 273.15 K for pure water, the solution freezes at 270.918 K .

Step 4: Conclusion The solution freezes at approximately -2.23°C .

Quick Tip to Solve: Divide by kilograms of water, not the total solution mass, and subtract the calculated depression from water's freezing point.

21. What is a semiconductor? Describe the two main types of semiconductors and explain mechanisms for their conduction. [3 marks]

Solution:

Concept:

- A semiconductor has electrical conductivity between that of a conductor and an insulator. Its conductivity generally increases with temperature; silicon and germanium are examples.
- Doping silicon or germanium with a small amount of a suitable impurity produces extrinsic semiconductors of two types: n-type and p-type. Charge is transported by mobile electrons and holes.

Step 1: Describe the semiconductor lattice In pure silicon or germanium, each atom forms four covalent bonds with its neighbours. At ordinary temperatures some electrons acquire enough energy to become mobile, leaving holes behind. These electron-hole pairs account for the limited conductivity of the pure, intrinsic semiconductor. Controlled doping greatly increases the number of mobile charge carriers.

Step 2: n-type semiconductor and its conduction Doping silicon or germanium with a group 15 element, such as phosphorus or arsenic, gives an n-type semiconductor. Four of the impurity atom's five valence electrons form covalent bonds with neighbouring atoms. The fifth electron is weakly bound and becomes available for conduction. Under an applied electric field these mobile electrons drift and carry current. Electrons are the majority carriers; holes are minority carriers.

Step 3: p-type semiconductor and its conduction Doping silicon or germanium with a group 13

Quick Tip to Solve: Remember group 15 supplies an extra electron for n-type; group 13 leaves an electron deficiency for p-type.

element, such as boron or aluminium, gives a p-type semiconductor. The impurity has only three valence electrons, so one of the four bonds has an electron deficiency called a hole. A neighbouring electron can fill this hole, creating a new hole at its original position. Successive electron transfers cause holes to move through the lattice under an electric field. Holes are the majority carriers; electrons are minority carriers.

Step 4: Conclusion Semiconductors have intermediate conductivity. The two main doped types are n-type, conducting mainly through electrons supplied by donor impurities, and p-type, conducting mainly through holes introduced by acceptor impurities. Both materials remain electrically neutral overall.

Quick Tip to Solve: Remember group 15 supplies an extra electron for n-type; group 13 leaves an electron deficiency for p-type.

22(a). Write chemical equations for the following processes:

(i) Chlorine reacts with a hot concentrated solution of sodium hydroxide

(ii) Orthophosphorous acid is heated

(iii) PtF_6 and xenon are mixed together

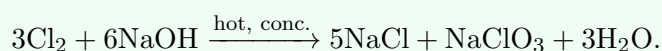
[3 marks]

Solution:

Concept:

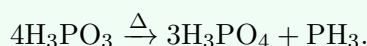
- Disproportionation is a redox process in which the same element is both oxidised and reduced; chlorine and phosphorus show this behaviour here.
- PtF_6 is a powerful oxidising agent and accepts an electron from xenon to form the salt xenon hexafluoridoplatinate.

Step 1: (i) Chlorine with hot concentrated sodium hydroxide Under the stated hot, concentrated conditions chlorine forms chloride and chlorate, rather than hypochlorite:



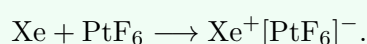
Chlorine changes from oxidation state zero to -1 in chloride and $+5$ in chlorate. Five chlorine atoms gain one electron each while one loses five, so both atoms and electrons balance.

Step 2: (ii) Heating orthophosphorous acid Orthophosphorous acid, H_3PO_3 , disproportionates on heating:



Phosphorus in oxidation state $+3$ is oxidised to $+5$ in phosphoric acid and reduced to -3 in phosphine. The equation contains four phosphorus, twelve hydrogen and twelve oxygen atoms on either side.

Step 3: (iii) Mixing xenon and platinum hexafluoride Xenon reacts with platinum hexafluoride to give xenon hexafluoridoplatinate, conventionally represented at this level as



Quick Tip to Solve: Hot concentrated alkali gives chlorate; remember the chlorine equation coefficients as 3, 6, 5, 1, 3.

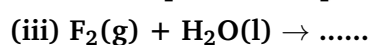
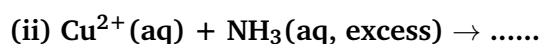
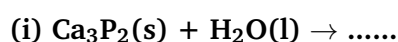
The electron-accepting action of PtF_6 enables xenon, a noble gas, to undergo oxidation and form this ionic product.

Step 4: Conclusion The products are (i) NaCl , NaClO_3 and water; (ii) H_3PO_4 and PH_3 ; and (iii) $\text{Xe}^+[\text{PtF}_6]^-$, with balanced equations given above.

Quick Tip to Solve: Hot concentrated alkali gives chlorate; remember the chlorine equation coefficients as 3, 6, 5, 1, 3.

OR

22(b). Complete the following chemical equations:



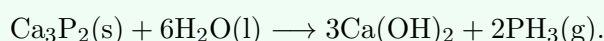
[3 marks]

Solution:

Concept:

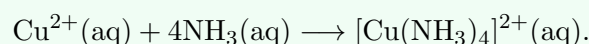
- A metal phosphide reacts with water to release phosphine, PH_3 , and form the corresponding hydroxide.
- Excess ammonia donates lone pairs to copper(II), producing a soluble deep-blue ammine complex. Fluorine oxidises water to oxygen and is itself reduced to fluoride in hydrogen fluoride.

Step 1: (i) Hydrolysis of calcium phosphide The products are calcium hydroxide and phosphine. Balance calcium and phosphorus first, then supply six water molecules:



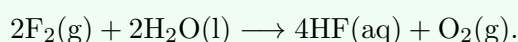
Three calcium atoms require three hydroxide formula units and two phosphorus atoms require two phosphine molecules. The twelve hydrogen atoms supplied by water appear equally in hydroxide and phosphine.

Step 2: (ii) Copper(II) with excess ammonia Excess aqueous ammonia forms the deep-blue tetraamminecopper(II) complex. The standard abbreviated complex-formation equation is



Ammonia acts as a neutral ligand, so the complex retains charge +2. In a fuller aqueous description two water ligands remain, giving $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. The excess condition means the soluble complex is the final product.

Step 3: (iii) Fluorine with water Fluorine oxidises water to oxygen and produces hydrogen fluoride:



Oxygen changes from -2 to zero, whereas fluorine changes from zero to -1 . Four fluorine atoms

Quick Tip to Solve: Read the word excess carefully: copper(II) gives the deep-blue soluble ammine complex with excess ammonia.

accept the four electrons lost by two oxygen atoms, confirming the balanced equation.

Step 4: Conclusion The completed products are (i) $3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$, (ii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with four ammonia ligands, and (iii) $4\text{HF} + \text{O}_2$ with coefficients 2 for both reactants.

Quick Tip to Solve: Read the word excess carefully: copper(II) gives the deep-blue soluble ammine complex with excess ammonia.

23. State briefly the principles which serve as basis for the following operations in metallurgy:

(i) Froth floatation process

(ii) Zone refining

(iii) Refining by liquation

[3 marks]

Solution:

Concept:

- Metallurgical separation uses a difference in a physical property of the desired material and its impurities, such as wettability, solubility or melting point.
- Froth floatation concentrates an ore; zone refining and liquation purify a metal after its extraction.

Step 1: (i) Froth floatation: difference in wettability Froth floatation is based on the preferential wetting of sulphide ore particles by oil and of gangue particles by water. Finely powdered ore is mixed with water and a suitable collector or frothing agent. Air is blown through the mixture. The oil-wetted sulphide particles attach to air bubbles and rise as froth, which is skimmed off; water-wetted gangue stays in the aqueous phase. Thus selective wetting makes the desired ore rise separately from the impurities.

Step 2: (ii) Zone refining: different solubility in melt and solid Zone refining is based on impurities being more soluble in the molten metal than in the solid metal. A narrow molten zone is produced by a movable heater in a rod of the impure metal. As the heater moves, relatively pure metal crystallises behind it, while impurities remain preferentially in the melt and travel with the molten zone. Repeated passes concentrate the impurities at one end, which is cut off. This principle gives very high purity materials such as silicon and germanium.

Step 3: (iii) Liquation: difference in melting points Liquation is based on the lower melting point of the metal compared with the associated impurities. The impure metal is heated on a sloping hearth to a temperature sufficient to melt the desired metal while the higher-melting impurities remain solid. The molten metal flows down and is collected separately, leaving the solid impurities behind. This method is suitable for low-melting metals such as tin.

Step 4: Conclusion The governing principles are (i) selective wetting by oil and water, (ii) greater impurity solubility in molten than in solid metal, and (iii) a lower melting point of the metal than of its impurities.

Quick Tip to Solve: Pair each method with one physical property: floatation with wetting, zone refining with solubility, liquation with melting point.

24. Account for the following observations:

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

(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

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

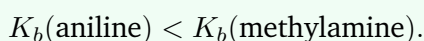
[3 marks]

Solution:

Concept:

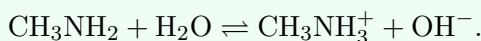
- A base accepts a proton through an available lone pair. For a base in water, $pK_b = -\log K_b$; a smaller K_b therefore means a larger pK_b .
- Resonance delocalisation decreases the availability of the nitrogen lone pair, whereas the electron-releasing inductive effect of an alkyl group increases it.
- A Lewis acid such as $AlCl_3$ accepts a lone pair from the amino group and changes the reactivity of the aromatic ring.

Step 1: (i) Compare the basic strengths In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is consequently less readily available to accept a proton. In methylamine, the lone pair remains localised on nitrogen, and the $+I$ effect of the methyl group increases electron density at nitrogen. Thus methylamine is the stronger base:

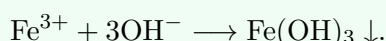


Taking negative logarithms reverses this order, explaining the higher pK_b of aniline.

Step 2: (ii) Explain the hydroxide precipitate Methylamine acts as a weak base in water and produces hydroxide ions:



Ferric chloride supplies Fe^{3+} ions, which combine with these hydroxide ions to form sparingly soluble, reddish-brown ferric hydroxide:



Removal of hydroxide ions in the precipitate allows further ionisation of methylamine.

Step 3: (iii) Explain the failure of Friedel-Crafts reaction The nitrogen lone pair of aniline coordinates strongly with the Lewis acid catalyst $AlCl_3$, forming an aniline–aluminium chloride complex. Nitrogen acquires positive character in this complex; the amino group can no longer donate its lone pair to activate the ring. Instead, the complex strongly deactivates the benzene ring towards electrophilic substitution. Therefore aniline does not undergo the usual Friedel-Crafts alkylation or acylation.

Step 4: Conclusion Aniline has the higher pK_b because its lone pair is resonance-delocalised; aqueous methylamine supplies OH^- to precipitate $Fe(OH)_3$; aniline complexes with $AlCl_3$, deactivating its ring.

Quick Tip to Solve: For amine questions, first ask whether the nitrogen lone pair is localised, resonance-delocalised, or bound to a Lewis acid.

25. Write the names and structures of the monomers of the following polymers:

(i) Buna-S

(ii) Neoprene

(iii) Nylon-6

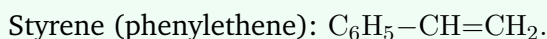
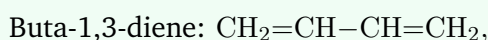
[3 marks]

Solution:

Concept:

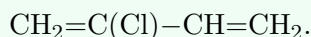
- Monomers are the small molecules whose repeated combination produces a polymer. A copolymer requires two different monomer species.
- Addition polymers of dienes retain some unsaturation. Nylon-6 is a polyamide obtained by ring opening of a cyclic amide, ϵ -caprolactam.

Step 1: (i) Identify both Buna-S monomers Buna-S is the copolymer of buta-1,3-diene and styrene. Their condensed structural formulae are



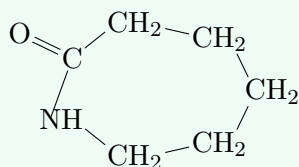
The letter S identifies the styrene component. Both monomers must be named because Buna-S is a copolymer, rather than a polymer of butadiene alone.

Step 2: (ii) Identify the neoprene monomer Neoprene is formed by polymerisation of chloroprene, whose systematic name is 2-chlorobuta-1,3-diene:



Chlorine is attached to carbon 2 of the conjugated diene chain. This substituent distinguishes chloroprene from the unsubstituted buta-1,3-diene used in Buna-S.

Step 3: (iii) Identify the nylon-6 monomer and its cyclic structure The monomer is ϵ -caprolactam, a seven-membered cyclic amide. Its structure is



Thus the carbonyl carbon is bonded directly to nitrogen as well as to the adjacent methylene group; the five methylene groups complete the ring. Ring opening gives the polyamide repeating unit $[-\text{NH}-(\text{CH}_2)_5-\text{CO}-]_n$, containing six carbon atoms per repeat unit.

Step 4: Conclusion Buna-S: buta-1,3-diene and styrene; neoprene: chloroprene; nylon-6: cyclic ϵ -caprolactam, with the structures given above.

Quick Tip to Solve: Remember Buna-S needs two monomers, neoprene needs the chlorine-substituted diene, and nylon-6 comes from a cyclic amide.

26. Name the reagents which are used in the following conversions:

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6-tribromophenol

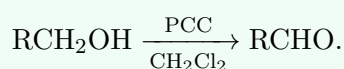
[3 marks]

Solution:

Concept:

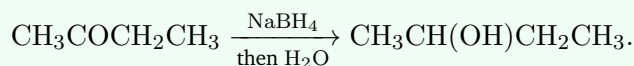
- A primary alcohol gives an aldehyde on controlled oxidation; stronger oxidation can carry the reaction further to a carboxylic acid.
- Reduction of a ketone converts its carbonyl group to a secondary alcohol without changing the carbon skeleton.
- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution to the two ortho positions and the para position.

Step 1: (i) Primary alcohol to aldehyde Use pyridinium chlorochromate (PCC), usually in anhydrous dichloromethane. This mild oxidising reagent stops the oxidation at the aldehyde stage:



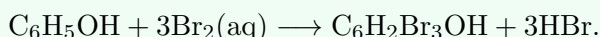
The controlled, non-aqueous conditions avoid further oxidation of the aldehyde to a carboxylic acid. Excess acidified dichromate under reflux would therefore be unsuitable when the required product is specifically an aldehyde.

Step 2: (ii) Butan-2-one to butan-2-ol Use sodium borohydride, NaBH_4 , followed by aqueous work-up. It reduces the ketone carbonyl group to the secondary alcohol:



Hydride addition to the carbonyl carbon, followed by protonation of the oxygen, gives butan-2-ol. The four-carbon skeleton and the position of the oxygen-bearing carbon are retained.

Step 3: (iii) Phenol to 2,4,6-tribromophenol Use excess bromine water, $\text{Br}_2(\text{aq})$. Phenol is sufficiently activated to undergo substitution at all three available ortho and para positions without a Lewis acid catalyst:



The product is 2,4,6-tribromophenol, obtained as a white precipitate, with decolourisation of bromine water. The aqueous reagent is important because bromination in a non-polar solvent under controlled conditions can give mainly monobrominated products.

Step 4: Conclusion The reagents are (i) PCC in anhydrous dichloromethane, (ii) NaBH_4 followed by water, and (iii) excess bromine water.

Quick Tip to Solve: Match the change first: controlled oxidation needs PCC, ketone reduction needs a hydride reagent, and triple bromination of phenol needs bromine water.

27. (a) What is a ligand? Give an example of a bidentate ligand.

(b) Explain as to how the two complexes of nickel, $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{Ni}(\text{CO})_4$, have different structures but do not differ in their magnetic behaviour. (Ni = 28) [3 marks]

Solution:

Concept:

- A ligand donates at least one lone pair of electrons to a central metal atom or ion, forming a coordinate bond.
- Hybridisation predicts geometry; the presence or absence of unpaired electrons determines magnetic behaviour.

Step 1: (a) Define ligand and identify a bidentate example A ligand is an ion or molecule that supplies an electron pair to a central metal atom or ion. A bidentate ligand has two donor atoms capable of coordinating simultaneously to the same metal centre. Ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (en), is bidentate because each nitrogen donates one lone pair.

Step 2: (b) Examine the cyanide complex In $[\text{Ni}(\text{CN})_4]^{2-}$, four cyanide ions contribute charge -4 , so nickel is in the $+2$ oxidation state. Neutral nickel is $[\text{Ar}]3d^84s^2$, whereas Ni^{2+} is $[\text{Ar}]3d^8$. The strong-field ligand CN^- causes the eight $3d$ electrons to pair in four orbitals, leaving one $3d$ orbital vacant. This orbital, one $4s$ and two $4p$ orbitals undergo dsp^2 hybridisation. Four ligand pairs occupy these hybrid orbitals, producing square-planar geometry. All metal electrons are paired.

Step 3: (b) Examine the carbonyl complex In $\text{Ni}(\text{CO})_4$, CO is neutral, so the oxidation state of nickel is zero. In the valence-bond description, the two $4s$ electrons pair into the $3d$ subshell, giving a filled $3d^{10}$ configuration. The empty $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals that accept electron pairs from CO. The complex is tetrahedral. Its filled $3d$ subshell has no unpaired electrons, just as the paired $3d^8$ arrangement of the cyanide complex has none.

Step 4: Conclusion $[\text{Ni}(\text{CN})_4]^{2-} : dsp^2$, square planar; $\text{Ni}(\text{CO})_4 : sp^3$, tetrahedral. Both are diamagnetic because both have zero unpaired electrons.

Quick Tip to Solve: First calculate nickel oxidation states: cyanide gives Ni(II), while neutral CO gives Ni(0); equal coordination numbers need not imply equal shapes.

28(a). Derive the general form of the expression for the half-life of a first order reaction.

(b) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$? [5 marks]

Solution:

Concept:

- For a first-order reaction, $-d[A]/dt = k[A]$, where $[A]$ is reactant concentration and k has units of inverse time.
- The half-life $t_{1/2}$ is the time required for the concentration to fall from $[A]_0$ to $[A]_0/2$.
- For zero-order decomposition, the reactant disappearance rate is constant; product formation rates follow the balanced stoichiometric equation.

Quick Tip to Solve: Use the disappearance rate of ammonia as k , then multiply by the stoichiometric product-to-ammonia ratios $1/2$ and $3/2$.

Step 1: (a) Integrate the first-order rate law Let the initial reactant concentration be $[A]_0$, and its concentration after time t be $[A]_t$. Separating variables and integrating between these limits gives

$$\begin{aligned}-\frac{d[A]}{[A]} &= k dt, \\ -\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} &= k \int_0^t dt, \\ \ln \frac{[A]_0}{[A]_t} &= kt.\end{aligned}$$

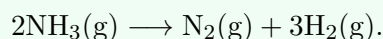
Thus the integrated first-order expression is $t = (2.303/k) \log_{10}([A]_0/[A]_t)$.

Step 2: (a) Apply the half-life condition At $t = t_{1/2}$, exactly half the original reactant remains, so $[A]_t = [A]_0/2$. Substitution gives

$$kt_{1/2} = \ln \frac{[A]_0}{[A]_0/2} = \ln 2.$$

Therefore $t_{1/2} = \ln 2/k = 0.693/k$. The initial concentration cancels; hence the half-life of a first-order reaction does not depend on its initial concentration. This result applies to each successive halving at the same temperature.

Step 3: (b) Balance ammonia decomposition and relate the rates The balanced reaction is



For the zero-order disappearance of ammonia, $-d[\text{NH}_3]/dt = k[\text{NH}_3]^0 = k$. Consequently,

$$\frac{d[\text{N}_2]}{dt} = \frac{k}{2}, \quad \frac{d[\text{H}_2]}{dt} = \frac{3k}{2}.$$

Two moles of ammonia produce one mole of nitrogen and three moles of hydrogen, so their rates must retain these ratios.

Step 4: (b) Substitute the rate constant Using the stated numerical value,

$$\begin{aligned}\frac{d[\text{N}_2]}{dt} &= \frac{2.5 \times 10^{-4}}{2} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}, \\ \frac{d[\text{H}_2]}{dt} &= \frac{3(2.5 \times 10^{-4})}{2} = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.\end{aligned}$$

The printed unit of k , $\text{mol}^{-1} \text{ L s}^{-1}$, is dimensionally inconsistent with zero order. A zero-order constant has units $\text{mol L}^{-1} \text{ s}^{-1}$; the numerical value is used with these required concentration-per-time units.

Step 5: Conclusion $t_{1/2} = 0.693/k$. The production rates are $r_{\text{N}_2} = 1.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ and $r_{\text{H}_2} = 3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.

Quick Tip to Solve: Use the disappearance rate of ammonia as k , then multiply by the stoichiometric product-to-ammonia ratios 1/2 and 3/2.

28(b). (a) List the factors on which the rate of a chemical reaction depends.

(b) The half-life for decay of radioactive ^{14}C is 5730 years. An archaeological artefact containing wood has only 80% of the ^{14}C activity as found in living trees. Calculate the age of the artefact. [5 marks]

Solution:

Concept:

- Reaction rate depends on the nature and physical state of reactants, their concentration (or gas pressure), temperature, catalyst and, for heterogeneous reactions, the exposed surface area. Light also affects photochemical reactions.
- Radioactive decay is a first-order process: $N_t = N_0 e^{-kt}$, where N_0 and N_t are the initial and remaining numbers of radioactive nuclei, k is the decay constant and t is elapsed time.
- Radioactivity $A = kN$ is proportional to the number of radioactive nuclei, so $A_t/A_0 = N_t/N_0$. For first-order decay, $k = \ln 2/t_{1/2}$.

Step 1: (a) Identify the factors controlling reaction rate The principal factors are: (i) nature of the reactants and their physical state; (ii) concentration of reactants, or partial pressures for gaseous reactants; (iii) temperature; (iv) presence of a catalyst; (v) surface area of solid reactants in heterogeneous reactions; and (vi) light intensity for photochemical reactions. Concentration and exposed area affect the frequency of effective encounters. Temperature affects both collision frequency and the fraction of molecules with sufficient activation energy. A catalyst supplies an alternative pathway with lower activation energy, while the chemical nature of the reactants influences how readily bonds can be broken and formed.

Step 2: (b) Find the radioactive decay constant The half-life is $t_{1/2} = 5730$ years. Hence

$$k = \frac{\ln 2}{5730} = 1.2097 \times 10^{-4} \text{ year}^{-1}.$$

Living wood continuously exchanges carbon with the environment. After the tree dies, replenishment ceases and its radioactive carbon decays. The activity of comparable living wood supplies the initial reference activity A_0 .

Step 3: Use the remaining activity to calculate elapsed time The artefact retains 80% of its original activity, so $A_t/A_0 = 0.80$. The fraction decayed is 0.20, but the first-order law requires the fraction remaining. Thus

$$\begin{aligned} t &= \frac{1}{k} \ln \frac{A_0}{A_t} \\ &= \frac{5730}{\ln 2} \ln \frac{1}{0.80} \\ &= \frac{5730(0.22314)}{0.69315} \\ &\approx 1845 \text{ years.} \end{aligned}$$

Since more than half of the activity remains, the calculated age should be less than one half-life; this provides a consistency check on the result.

Step 4: Conclusion (a) Rate depends on reactant nature and physical state, concentration or gas

Quick Tip to Solve: In radiocarbon dating, use the remaining activity directly: $t = t_{1/2} \ln(1/f) / \ln 2$, with $f = 0.80$, rather than the fraction lost.

pressure, temperature, catalyst, exposed solid surface area and light for photochemical reactions. (b) The age of the artefact is approximately 1.845×10^3 years.

Quick Tip to Solve: In radiocarbon dating, use the remaining activity directly: $t = t_{1/2} \ln(1/f) / \ln 2$, with $f = 0.80$, rather than the fraction lost.

29(a). How will you bring about the following conversions?

(i) Ethanol to acetone

(ii) Benzene to acetophenone

(iii) Benzoic acid to benzaldehyde

(b) Describe the following giving a suitable example in each case:

(i) Decarboxylation

(ii) Cannizzaro's reaction

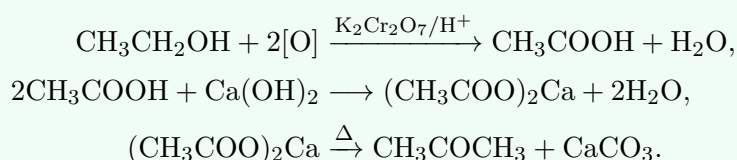
[5 marks]

Solution:

Concept:

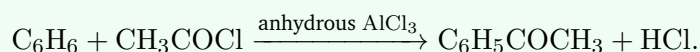
- Alcohols can be oxidised to carboxylic acids. Dry distillation of the calcium salt of a carboxylic acid gives a ketone.
- Friedel–Crafts acylation introduces an acyl group into benzene using an acyl chloride and anhydrous aluminium chloride.
- Rosenmund reduction converts an acid chloride into an aldehyde. Soda-lime decarboxylation removes a carboxyl carbon, whereas the Cannizzaro reaction disproportionates aldehydes having no α hydrogen.

Step 1: (a)(i) Convert ethanol into acetone First oxidise ethanol to ethanoic acid with acidified potassium dichromate on heating. Neutralise the acid with calcium hydroxide to obtain calcium acetate, then dry-distil the calcium salt:



Dry distillation of calcium acetate joins the two methyl-containing fragments through a carbonyl group, producing acetone.

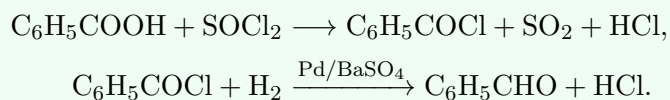
Step 2: (a)(ii) Convert benzene into acetophenone Treat benzene with acetyl chloride in the presence of anhydrous aluminium chloride. This Friedel–Crafts acylation substitutes an acetyl group for one hydrogen atom of benzene:



The aluminium chloride promotes formation of the electrophile from acetyl chloride; aqueous work-up releases the ketone from its catalytic complex.

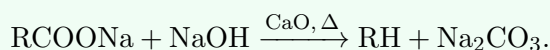
Quick Tip to Solve: Use an acid chloride for both aromatic conversions: acetyl chloride adds the acetyl group to benzene, while benzoyl chloride undergoes selective Rosenmund reduction.

Step 3: (a)(iii) Convert benzoic acid into benzaldehyde First prepare benzoyl chloride using thionyl chloride. Then carry out Rosenmund reduction using hydrogen and palladium supported on barium sulphate:

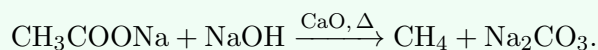


The deactivated catalyst limits reduction to the aldehyde stage, preventing further reduction to benzyl alcohol.

Step 4: (b)(i) Describe decarboxylation Decarboxylation is removal of the carboxyl group as carbon dioxide. In the standard soda-lime reaction, a sodium carboxylate is heated with soda lime, a mixture of sodium hydroxide and calcium oxide. It gives an alkane with one fewer carbon atom than the parent acid:

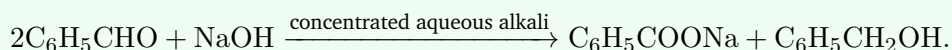


For example, sodium acetate gives methane:



Here the removed carboxyl carbon is retained in sodium carbonate under the alkaline reaction conditions.

Step 5: (b)(ii) Describe Cannizzaro's reaction An aldehyde containing no α hydrogen undergoes disproportionation with concentrated aqueous alkali: one molecule is oxidised to a carboxylate salt and another is reduced to a primary alcohol. Benzaldehyde is a suitable example because it has no α hydrogen:



Thus sodium benzoate and benzyl alcohol are formed together. The carboxylic acid itself is obtained only after acidification of the carboxylate salt.

Step 6: Conclusion Ethanol gives acetone through ethanoic acid and calcium acetate; benzene gives acetophenone by Friedel–Crafts acylation; benzoic acid gives benzaldehyde through benzoyl chloride and Rosenmund reduction. Sodium acetate giving methane illustrates decarboxylation, and benzaldehyde giving sodium benzoate plus benzyl alcohol illustrates Cannizzaro's reaction.

Quick Tip to Solve: Use an acid chloride for both aromatic conversions: acetyl chloride adds the acetyl group to benzene, while benzoyl chloride undergoes selective Rosenmund reduction.

29(b). (a) An organic compound contains 69.77% carbon, 11.63% hydrogen and the rest is oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogen sulphite and gives a positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Deduce the possible structure of the organic compound.

(b) State reasons for the following:

(i) Monochloroethanoic acid has a higher pK_a value than dichloroethanoic acid.

(ii) Ethanoic acid is a weaker acid than benzoic acid.

[5 marks]

Solution:

Concept:

- Elemental percentages give the empirical formula; comparison of empirical formula mass with molecular mass gives the molecular formula.
- Ketones form carbonyl addition products but generally do not reduce Tollens' reagent. A methyl ketone, CH_3COR , gives the iodoform test.
- Electron-withdrawing groups stabilise a carboxylate conjugate base and increase acid strength; electron-releasing groups have the opposite effect. Since $pK_a = -\log K_a$, a stronger acid has a smaller pK_a .

Step 1: (a) Obtain the molecular formula In 100 g of compound, the oxygen content is

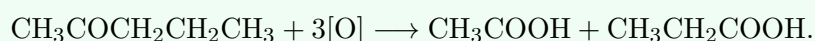
$$100 - 69.77 - 11.63 = 18.60 \text{ g.}$$

The relative numbers of atoms are

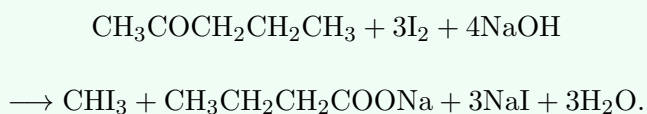
$$\text{C} : \text{H} : \text{O} = \frac{69.77}{12} : \frac{11.63}{1} : \frac{18.60}{16} = 5.814 : 11.630 : 1.1625 \approx 5 : 10 : 1.$$

Thus the empirical formula is $\text{C}_5\text{H}_{10}\text{O}$, with empirical formula mass $5(12) + 10(1) + 16 = 86$. This equals the given molecular mass, so the molecular formula is also $\text{C}_5\text{H}_{10}\text{O}$.

Step 2: (a) Identify the carbonyl compound Formation of an addition compound with sodium hydrogen sulphite indicates a reactive carbonyl group. Failure to reduce Tollens' reagent identifies the compound as a ketone rather than an ordinary aldehyde. The positive iodoform test requires the methyl ketone group $\text{CH}_3\text{CO}-$. The straight-chain candidate is therefore $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. The other methyl ketone with this molecular formula, $\text{CH}_3\text{COCH}(\text{CH}_3)_2$, has a branched skeleton and does not account for the stated ethanoic acid and straight-chain propanoic acid oxidation products. Vigorous oxidative cleavage of pentan-2-one accounts for the specified acids:



Its iodoform reaction provides an additional check:



Quick Tip to Solve: Combine the negative Tollens' test with the positive iodoform test to identify a methyl ketone, then use the oxidation fragments to select its carbon skeleton.

The yellow precipitate is iodoform, CHI_3 .

Step 3: (b)(i) Compare the chloroethanoic acids Chlorine withdraws electron density through its negative inductive effect. Two chlorine atoms in dichloroethanoic acid exert a stronger electron-withdrawing effect than the single chlorine atom in monochloroethanoic acid. Consequently, $\text{CHCl}_2\text{COO}^-$ is better stabilised than $\text{CH}_2\text{ClCOO}^-$, so dichloroethanoic acid loses a proton more readily. Hence

$$K_a(\text{CHCl}_2\text{COOH}) > K_a(\text{CH}_2\text{ClCOOH}),$$

and monochloroethanoic acid has the higher $\text{p}K_a$.

Step 4: (b)(ii) Compare ethanoic acid and benzoic acid In ethanoic acid, the methyl group has a positive inductive effect. It pushes electron density towards the carboxylate group and tends to destabilise the negative charge in the ethanoate ion. In benzoic acid, the phenyl group has an electron-withdrawing inductive effect, which favours stabilisation of the benzoate ion relative to ethanoate. Proton loss is therefore more favourable for benzoic acid, making ethanoic acid the weaker acid. Both conjugate bases have resonance within the carboxylate group; the difference in their substituent effects explains their relative acidity.

Step 5: Conclusion (a) The compound is pentan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. (b)(i) The stronger negative inductive effect of two chlorine atoms makes dichloroethanoic acid stronger and lowers its $\text{p}K_a$. (ii) The methyl group's electron-releasing effect makes ethanoic acid weaker than benzoic acid.

Quick Tip to Solve: Combine the negative Tollens' test with the positive iodoform test to identify a methyl ketone, then use the oxidation fragments to select its carbon skeleton.

30(a). Assign reasons for the following:

- (i) The enthalpies of atomisation of transition elements are high.
- (ii) The transition metals and many of their compounds act as good catalyst.
- (iii) From element to element the actinoid contraction is greater than the lanthanoid contraction.
- (iv) The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.
- (v) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element.

[5 marks]

Solution:

Concept:

- Metallic bonding in transition metals involves the outer ns and $(n-1)d$ electrons; stronger bonding requires more energy for atomisation.
- Electronic configurations govern oxidation-state stability. Half-filled d^5 and, in suitable environments, d^3 configurations have enhanced stability.
- Poor shielding by f electrons increases effective nuclear charge across an inner-transition series and causes contraction.

Step 1: (i) High enthalpies of atomisation Transition metals have several valence electrons, including unpaired d electrons, available for participation in metallic bonding. The resulting interatomic

Quick Tip to Solve: For each reduction potential, write the d configurations on both sides before comparing which reduction produces the more stable ion.

attraction is strong. Therefore, appreciable energy is needed to separate the solid metal into individual gaseous atoms, giving high enthalpies of atomisation.

Step 2: (ii) Catalytic activity Transition metals can use their available d orbitals to adsorb reactant molecules on their surfaces, bringing reactants together and weakening bonds. Many transition-metal ions also change oxidation state readily and form intermediate compounds with reactants. These processes supply an alternative reaction pathway with lower activation energy; the catalyst is regenerated during the reaction.

Step 3: (iii) Greater actinoid contraction Across the actinoid series, the added $5f$ electrons shield the increasing nuclear charge less effectively than $4f$ electrons do in the lanthanoid series. Consequently, the effective nuclear attraction increases more strongly from one actinoid to the next, producing a greater decrease in size.

Step 4: (iv) Compare the reduction couples The reductions are $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$ and $\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$. Manganese changes from $3d^4$ to the especially stable half-filled $3d^5$ configuration, so reduction of Mn^{3+} is favoured. Chromium changes from stable $3d^3$ to $3d^4$; this reduction is less favourable. Thus the manganese couple has a much more positive standard reduction potential.

Step 5: (v) Classification of scandium The ground-state configuration of scandium is $[\text{Ar}] 3d^1 4s^2$. Its atom therefore has an incompletely filled d subshell, satisfying the definition of a transition element. Loss of its three outer electrons gives the stable $[\text{Ar}]$ configuration of Sc^{3+} , explaining why +3 is its characteristic oxidation state and variable oxidation states are not normally observed.

Step 6: Conclusion Strong metallic bonding, accessible reaction intermediates, poor $5f$ shielding and electronic-configuration stability explain (i)–(iv). Scandium qualifies through the partially filled $3d$ subshell of its neutral atom.

Quick Tip to Solve: For each reduction potential, write the d configurations on both sides before comparing which reduction produces the more stable ion.

OR

30(a). What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms:

$3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

[3 marks]

Solution:

Concept:

- The $4s$ electrons are removed before the $3d$ electrons when first-row transition-metal atoms form cations.
- Similar energies of $3d$ and $4s$ electrons allow variable oxidation states. A half-filled d^5 subshell favours stability; actual relative stability also depends on the medium and ligands.

Step 1: Configuration $3d^3 4s^2$: vanadium Vanadium can show +2, +3, +4 and +5 oxidation states, corresponding formally to d^3 , d^2 , d^1 and d^0 , respectively. Its highest oxidation state, +5, uses all five valence electrons and is particularly stable in oxides and oxoanions. The lower states also exist, but

Quick Tip to Solve: Remove the two $4s$ electrons first, then count d electrons: Mn(II) and Fe(III) both acquire the stable half-filled d^5 configuration.

+2 and +3 are reducing and readily oxidised under suitable conditions; +4 is also common, as in vanadyl species. Thus +5 is the characteristic stable high oxidation state, rather than all four states being equally stable.

Step 2: Configuration $3d^5 4s^2$: manganese The commonly encountered oxidation states are +2, +3, +4, +5, +6 and +7. Removal of the two 4s electrons produces Mn^{2+} , with the particularly stable half-filled $3d^5$ configuration. Hence +2 is especially stable, while Mn^{3+} , which is d^4 , tends to gain an electron to form Mn^{2+} . The high states are stabilised by oxygen, for example +4 in MnO_2 , +6 in manganate and +7 in permanganate; permanganate is strongly oxidising, especially in acid.

Step 3: Configuration $3d^6 4s^2$: iron The principal oxidation states are +2 and +3. Their configurations are $Fe^{2+} : 3d^6$ and $Fe^{3+} : 3d^5$. The half-filled d^5 arrangement favours +3, so Fe^{2+} is readily oxidised to Fe^{3+} in the presence of suitable oxidants. Both states are common and their relative stability depends on conditions. Iron can also attain +6 in ferrate, stabilised by oxygen, but this is an uncommon, strongly oxidising state.

Step 4: Conclusion Vanadium: +2, +3, +4, +5, with +5 a stable high state. Manganese: commonly +2 to +7, with +2 especially stable. Iron: mainly +2, +3, with the half-filled configuration favouring +3; +6 occurs in ferrate.

Quick Tip to Solve: Remove the two 4s electrons first, then count d electrons: Mn(II) and Fe(III) both acquire the stable half-filled d5 configuration.

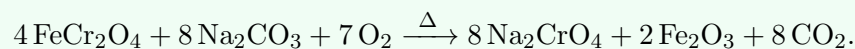
30(b). Write steps involved in the preparation of (i) Na_2CrO_4 from chromite ore and (ii) K_2MnO_4 from pyrolusite ore. [2 marks]

Solution:

Concept:

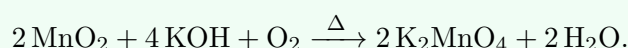
- Oxidative roasting or fusion in an alkaline medium converts the chromium and manganese present in their ores into soluble chromate and manganate salts.
- Chromite is $FeCr_2O_4$, containing chromium in the +3 state; pyrolusite is MnO_2 , containing manganese in the +4 state. Oxidation produces chromium(VI) and manganese(VI), respectively.

Step 1: Prepare sodium chromate from chromite Finely powdered chromite ore is roasted with sodium carbonate in excess air. Oxygen oxidises chromium(III) to chromium(VI), forming sodium chromate:



Extract the roasted mass with water. Sodium chromate dissolves, while insoluble ferric oxide and gangue are removed by filtration. The filtrate contains Na_2CrO_4 .

Step 2: Prepare potassium manganate from pyrolusite Fuse powdered pyrolusite with potassium hydroxide in the presence of air or oxygen. Manganese(IV) is oxidised to manganese(VI):



The green fused product is potassium manganate. Extract it with water while maintaining alkaline

Quick Tip to Solve: Remember the alkali pair: chromite uses sodium carbonate; pyrolusite uses potassium hydroxide. Both preparations require an oxidising atmosphere.

conditions, and separate insoluble impurities by filtration.

Step 3: Conclusion Roast chromite with Na_2CO_3 in air to obtain Na_2CrO_4 ; fuse pyrolusite with KOH in air to obtain green K_2MnO_4 .

Quick Tip to Solve: Remember the alkali pair: chromite uses sodium carbonate; pyrolusite uses potassium hydroxide. Both preparations require an oxidising atmosphere.