CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-2-1

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) Section A : Questions number **1 to 5** are very short answer questions and carry **1 mark** each.

(iii) Section B : Questions number **6 to 12** are short answer questions and carry **2 marks** each.

(iv) Section C : Questions number **13 to 24** are also short answer questions and carry **3 marks** each.

(v) Section D : Questions number **25 to 27** are long answer questions and carry **5 marks** each.

(vi) There is no overall choice. However, an internal choice has been provided in two questions of one mark, two questions of two marks, four questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.

(vii) Use of log tables, if necessary. Use of calculators is not allowed.

Section A (5 marks)

1(a). Out of KCl and AgCl, which one shows Schottky defect and why? [1 mark]

Solution:

Concept:

- A Schottky defect consists of equal numbers of cation and anion vacancies, preserving electrical neutrality.
- This defect is favoured in ionic crystals with cations and anions of comparable size and high coordination number.

Step 1: Identify the suitable ionic solid In KCl, the sizes of K^+ and Cl^- are sufficiently comparable for paired vacancies to occur in its highly coordinated ionic lattice.

Step 2: Explain the comparison Equal numbers of potassium and chloride ions can be absent from their normal lattice positions. The crystal remains electrically neutral, but its density decreases. In AgCl, the relatively small silver ion can occupy interstitial positions, so it characteristically exhibits a Frenkel defect.

Step 3: Conclusion $\boxed{KCl}$ shows Schottky defect because its cation and anion have comparable sizes.

Quick Tip to Solve: For a Schottky defect, look for comparable ion sizes and paired vacancies.

OR

1(b). Why does ZnO appear yellow on heating? [1 mark]

Solution:

Concept:

- Metal-excess defects can arise when oxygen is lost from a metal oxide.
- Electrons retained in the crystal maintain charge balance and may impart colour.

Step 1: Describe the change on heating On heating, ZnO loses a small amount of oxygen and becomes non-stoichiometric, with an excess of zinc relative to oxygen. This is a metal-excess defect.

Step 2: Explain the colour The excess zinc ions occupy interstitial sites and electrons occupy neighbouring interstitial sites to maintain electrical neutrality. These trapped electrons give heated ZnO its yellow colour; on cooling in air, oxygen is taken up and the white colour returns.

Step 3: Conclusion ZnO appears yellow on heating because oxygen loss produces a metal-excess defect with trapped electrons.

Quick Tip to Solve: Link the yellow colour to oxygen loss and trapped electrons, not to a new bulk compound.

2. Arrange the following in decreasing order of basic character:

$C_6H_5NH_2$, $(CH_3)_3N$, $C_2H_5NH_2$ [1 mark]

Solution:

Concept:

- Basic strength depends on how readily the nitrogen lone pair accepts a proton.
- In aqueous solution, electron donation and hydration of the conjugate acid both influence basicity.

Step 1: Compare the aliphatic amines In aqueous solution, ethylamine is more basic than trimethylamine. Although three methyl groups donate electron density, the bulky trimethylammonium ion is less effectively hydrated than the ethylammonium ion. The hydration advantage makes ethylamine the stronger base in this comparison.

Step 2: Place aniline in the order In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available for protonation than in either aliphatic amine. Consequently, aniline is the weakest of the three bases.

Step 3: Conclusion

$$\boxed{C_2H_5NH_2 > (CH_3)_3N > C_6H_5NH_2}$$

Quick Tip to Solve: For aqueous basicity, include hydration; do not rank amines by alkyl-group count alone.

3. What type of colloid is formed when a solid is dispersed in a liquid? Give an example. [1 mark]

Solution:

Concept:

- A colloid is classified using the physical states of its dispersed phase and dispersion medium.
- A sol contains solid particles dispersed in a liquid medium.

Step 1: Identify the two phases The solid is the dispersed phase because it is present as finely divided colloidal particles. The liquid is the dispersion medium because it forms the continuous phase surrounding those particles.

Step 2: Classify and give an example This combination is called a sol. For example, a gold sol contains colloidal solid gold particles dispersed in water. It is not a gel: in a gel the relevant classification is liquid dispersed in a solid medium. The order of the two phases must therefore be kept clear.

Step 3: Conclusion The colloid is a $\boxed{\text{sol}}$; an example is gold sol (solid gold dispersed in water).

Quick Tip to Solve: Write the dispersed phase first: solid in liquid means sol.

4. Out of Chlorobenzene and Cyclohexyl chloride, which one is more reactive towards nucleophilic substitution reaction and why? [1 mark]

Solution:

Concept:

- Nucleophilic substitution requires displacement of the halide from the carbon bonded to it.
- Resonance in an aryl halide gives its carbon-halogen bond partial double-bond character.

Step 1: Examine chlorobenzene In chlorobenzene, a chlorine lone pair overlaps with the benzene ring. Resonance gives the $\mathrm{C-Cl}$ bond partial double-bond character, making it shorter and stronger. The chlorine is attached to an sp^2-hybridised carbon, which further strengthens the bond.

Step 2: Compare cyclohexyl chloride In cyclohexyl chloride, chlorine is bonded to an sp^3-hybridised saturated carbon by an ordinary single bond. This bond has no resonance-induced double-bond character and can be cleaved more readily during nucleophilic substitution.

Step 3: Conclusion $\boxed{\text{Cyclohexyl chloride}}$ is more reactive because chlorobenzene has a stronger, resonance-stabilised $\mathrm{C-Cl}$ bond.

Quick Tip to Solve: Check whether chlorine is bonded directly to an aromatic ring before comparing substitution.

5(a). What is the basic structural difference between starch and cellulose? [1 mark]

Solution:

Concept:

- Starch and cellulose are both polysaccharides built from glucose units.
- The configuration of the glucose units and their glycosidic linkages determines the polymer structure.

Step 1: Describe starch Starch is a polymer of α-D-glucose. Its amylose component has $\alpha(1 \rightarrow 4)$ glycosidic linkages, while amylopectin also contains $\alpha(1 \rightarrow 6)$ linkages at branch points.

Step 2: Describe cellulose Cellulose is a linear polymer of β-D-glucose joined by $\beta(1 \rightarrow 4)$ glycosidic linkages. Thus the basic distinction is the alpha configuration in starch and beta configuration in cellulose, rather than a difference in the identity of the monosaccharide.

Step 3: Conclusion Starch consists of α-D-glucose units, whereas cellulose consists of β-D-glucose units.

Quick Tip to Solve: Remember the key distinction as alpha-glucose for starch and beta-glucose for cellulose.

OR

5(b). Write the products obtained after hydrolysis of DNA. [1 mark]

Solution:

Concept:

- DNA is a polymer of nucleotides, each containing a sugar, phosphate and nitrogenous base.
- Complete hydrolysis breaks DNA into its constituent sugar, phosphoric acid and bases.

Step 1: Identify sugar and phosphate products The sugar component of DNA is 2-deoxy-D-ribose, not ribose. Hydrolysis also releases phosphoric acid from the phosphate groups that form the backbone between successive sugar units.

Step 2: Identify the nitrogenous bases The four nitrogenous bases present in DNA are adenine, guanine, cytosine and thymine. Adenine and guanine are purine bases, while cytosine and thymine are pyrimidine bases. Uracil is associated with RNA and is not a normal hydrolysis product of DNA.

Step 3: Conclusion Complete hydrolysis of DNA yields phosphoric acid, 2-deoxy-D-ribose, adenine, guanine, cytosine and thymine.

Quick Tip to Solve: List all three component types, and remember DNA contains thymine and deoxyribose.

Section B (14 marks)

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

(a) Cl_2 is passed through slaked lime.

(b) SO_2 gas is passed through an aqueous solution of Fe(III) salt. [2 marks]

Solution:

Concept:

- Chlorine reacts with dry slaked lime to form bleaching powder, conventionally represented by $CaOCl_2$.
- Sulphur dioxide is a reducing agent: sulphur changes from oxidation state $+4$ to $+6$, while iron changes from $+3$ to $+2$.

Step 1: (a) Reaction with slaked lime Slaked lime is calcium hydroxide. Passing chlorine over it produces bleaching powder and water:

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O.$$

The conventional formula of bleaching powder is calcium oxychloride. The equation has one calcium atom, two chlorine atoms, two oxygen atoms and two hydrogen atoms on each side.

Step 2: (b) Reduction of an Fe(III) salt In aqueous solution, sulphur dioxide is oxidised to sulphate and reduces ferric ions to ferrous ions. The balanced ionic equation is

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+.$$

Quick Tip to Solve: For the ferric-ion equation, balance the two-electron oxidation of sulphur with two ferric ions.

Two ferric ions accept the two electrons released by one sulphur atom. Both atoms and total charge are balanced: the charge is $+6$ on each side.

Step 3: Conclusion (a) $Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$.
(b) $2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$.

Quick Tip to Solve: For the ferric-ion equation, balance the two-electron oxidation of sulphur with two ferric ions.

OR

6(b). (a) Write two poisonous gases prepared from chlorine gas.
(b) Why does Cu^{2+} solution give blue colour on reaction with ammonia? [2 marks]

Solution:

Concept:

- Chlorine is used in preparing the highly poisonous compounds phosgene and mustard gas.
- Ammonia acts as a ligand, donating its lone pair to Cu^{2+} and forming a characteristic deep-blue coordination complex.

Step 1: (a) Name the poisonous gases Two poisonous gases prepared using chlorine are phosgene, $COCl_2$, and mustard gas, $(ClCH_2CH_2)_2S$. Their common names identify the requested compounds; the formulae distinguish phosgene from other carbon chlorides and mustard gas from simple sulphur chlorides.

Step 2: (b) Explain the blue colour When sufficient ammonia is added to an aqueous copper(II) solution, ammonia molecules coordinate to the copper ion. The pale-blue aqua complex is converted into the deep-blue tetraammine complex:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O.$$

This is commonly written as $[Cu(NH_3)_4]^{2+}$. The changed ligand environment changes the splitting of the copper d orbitals and hence its visible-light absorption, giving the characteristic deep-blue colour.

Step 3: Conclusion (a) Phosgene and mustard gas. (b) The blue colour is due to formation of the deep-blue $[Cu(NH_3)_4]^{2+}$ complex.

Quick Tip to Solve: Remember that excess ammonia produces the deep-blue soluble copper ammine complex.

7. Give reasons:

(a) Cooking is faster in pressure cooker than in cooking pan.

(b) Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water. [2 marks]

Solution:

Concept:

- A liquid boils when its vapour pressure equals the pressure above it. Increasing external pressure therefore raises its boiling point.
- Osmosis is the flow of solvent through a semipermeable membrane towards the solution of higher solute concentration.

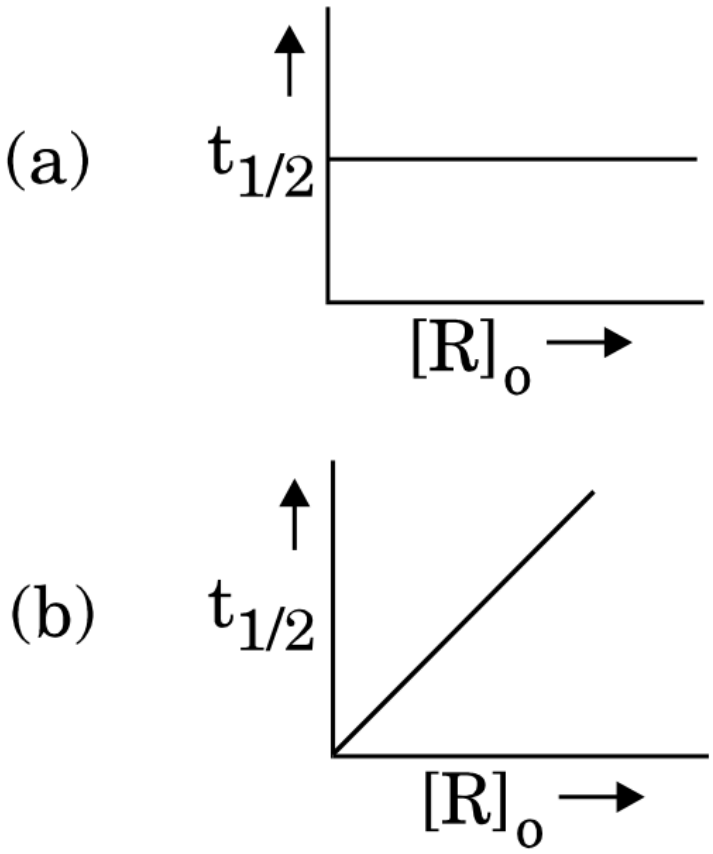
Step 1: (a) Cooking in a pressure cooker A pressure cooker traps steam, so the pressure inside it rises above atmospheric pressure. Water must then reach a higher temperature before its vapour pressure equals this increased pressure. Its boiling point becomes higher than $100\,^{\circ}\mathrm{C}$, whereas an open pan boils near $100\,^{\circ}\mathrm{C}$ at atmospheric pressure. Food therefore cooks at a higher temperature and the cooking reactions proceed faster.

Step 2: (b) Change in the size of RBCs The RBC membrane is semipermeable. The saline water in the question is hypertonic relative to the cell fluid: its solute concentration is higher. Water moves out of the RBC by osmosis, so the cell shrinks. Distilled water is hypotonic relative to the cell fluid. Water enters the RBC by osmosis, increasing its volume and causing swelling; excessive entry can rupture the cell. Isotonic saline would leave the cell size essentially unchanged.

Step 3: Conclusion (a) Increased pressure raises the boiling point of water and the cooking temperature. (b) RBCs lose water in hypertonic saline and gain water in distilled water by osmosis.

Quick Tip to Solve: Track the movement of water, not salt: water moves towards the more concentrated solution.

8. Define order of reaction. Predict the order of reaction in the given graphs: where $[R]_0$ is the initial concentration of reactant and $t_{1/2}$ is half-life. [2 marks]



Solution:

Concept:

- For a rate law $r = k[A]^m[B]^n$, the overall order is $m + n$, the sum of the powers of concentration in the experimentally determined rate equation.
- Half-life $t_{1/2}$ is the time for the reactant concentration to decrease from $[R]_0$ to $[R]_0/2$.

Step 1: (a) Horizontal half-life graph The horizontal line shows that $t_{1/2}$ is independent of the initial reactant concentration $[R]_0$. For a first-order reaction, the integrated rate law gives

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

There is no $[R]_0$ in this expression, so changing the starting concentration does not change the half-life. Thus graph (a) represents a first-order reaction.

Step 2: (b) Half-life proportional to initial concentration The straight line through the origin shows $t_{1/2} \propto [R]_0$. For a zero-order reaction, $[R] = [R]_0 - kt$. At half-life, substitute $[R] = [R]_0/2$:

$$\frac{[R]_0}{2} = [R]_0 - kt_{1/2} \quad \Rightarrow \quad t_{1/2} = \frac{[R]_0}{2k}.$$

This has exactly the linear dependence shown, so graph (b) represents a zero-order reaction.

Quick Tip to Solve: Compare the half-life formula with the graph: constant means first order; proportional to initial concentration means zero order.

Step 3: Conclusion Order is the sum of the powers of reactant concentrations in the rate law. Graph (a): first order; graph (b): zero order.

Quick Tip to Solve: Compare the half-life formula with the graph: constant means first order; proportional to initial concentration means zero order.

9. When $FeCr_2O_4$ is fused with Na_2CO_3 in the presence of air it gives a yellow solution of compound (A). Compound (A) on acidification gives compound (B). Compound (B) on reaction with KCl forms an orange coloured compound (C). An acidified solution of compound (C) oxidises Na_2SO_3 to (D). Identify (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Oxidative fusion of chromite converts chromium(III) to yellow chromate, containing chromium(VI).
- Acidification converts yellow chromate into orange dichromate. Acidified dichromate oxidises sulphite to sulphate while chromium(VI) is reduced to chromium(III).

Step 1: Identify the chromate and dichromates The yellow compound (A) is sodium chromate, Na_2CrO_4. Fusion with sodium carbonate in air gives

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow \quad 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

On acidification, chromate ions form dichromate ions:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O.$$

Thus (B) is sodium dichromate, $Na_2Cr_2O_7$. Addition of potassium chloride forms the less soluble orange potassium dichromate (C):

$$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl.$$

Step 2: Identify the oxidation product Acidified potassium dichromate oxidises sulphite, containing sulphur in the $+4$ state, to sulphate, containing sulphur in the $+6$ state:

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O.$$

Hence sodium sulphite becomes sodium sulphate, so compound (D) is Na_2SO_4.

Step 3: Conclusion (A) Na_2CrO_4; (B) $Na_2Cr_2O_7$; (C) $K_2Cr_2O_7$; (D) Na_2SO_4.

Quick Tip to Solve: Follow the colours and ions: yellow chromate becomes orange dichromate; sulphite gains oxygen to form sulphate.

10(a). Write IUPAC name of the complex $[Co(en)_2(NO_2)Cl]^+$. What type of structural isomerism is shown by this complex? [2 marks]

Solution:

Concept:

- Ligand names precede the metal name and its oxidation state; alphabetise ligands without counting multiplicative prefixes.
- Ethane-1,2-diamine (en) is neutral, while chlorido and nitrito each have charge -1. An ambidentate ligand can bind through two alternative donor atoms.

Step 1: Find the oxidation state Let cobalt have oxidation state x. The two en ligands are neutral. Since NO_2^- and Cl^- each contribute -1, the charge equation is $x - 1 - 1 = +1$. Thus cobalt is in the $+3$ oxidation state. The complex is a cation, so the metal is named cobalt(III).

Step 2: Name the complex and identify the isomerism Alphabetical ligand order is chlorido, ethane-1,2-diamine, then nitrito. Use bis for the two en ligands. The written NO_2 ligand is N-bound, giving chloridobis(ethane-1,2-diamine)nitrito-N-cobalt(III) ion. Nitrite is ambidentate: it can alternatively bind through oxygen, represented by ONO. Replacing the N-bound nitrite with O-bound nitrite changes the donor atom but not the composition; this is linkage isomerism.

Step 3: Conclusion The name is chloridobis(ethane-1,2-diamine)nitrito-N-cobalt(III) ion; it exhibits linkage isomerism through N-bound NO_2^- and O-bound ONO^-.

Quick Tip to Solve: First establish cobalt as +3; the NO2/ONO change of donor atom then identifies linkage isomerism.

OR

10(b). Using IUPAC norms, write the formulae for the following complexes:

(a) Hexaaquachromium(III) chloride

(b) Sodium trioxalatoferrate(III) [2 marks]

Solution:

Concept:

- Write the metal and all coordinated ligands inside square brackets; place counter-ions outside the brackets.
- Aqua is neutral and oxalato, $C_2O_4^{2-}$, has charge -2. The total charge of a salt must be zero.

Step 1: Write hexaaquachromium(III) chloride Hexaaqua specifies six water ligands surrounding chromium. Chromium(III) has oxidation state $+3$, and all six water molecules are neutral, so the coordination cation is $[Cr(H_2O)_6]^{3+}$. Three chloride ions, each of charge -1, are needed outside the coordination sphere to neutralise its charge. Hence the formula is $[Cr(H_2O)_6]Cl_3$.

Step 2: Write sodium trioxalatoferrate(III) Trioxalato specifies three oxalate ligands coordinated to iron. Ferrate denotes an anionic iron complex, and (III) specifies iron in oxidation state $+3$. Its charge is $+3 + 3(-2) = -3$, so the coordination anion is $[Fe(C_2O_4)_3]^{3-}$. Three sodium ions balance

Quick Tip to Solve: Count ligand charges before adding counter-ions: aqua contributes zero, while each oxalato contributes -2.

this negative charge. Thus the salt formula is $Na_3[Fe(C_2O_4)_3]$.

Step 3: Conclusion (a) $[Cr(H_2O)_6]Cl_3$; (b) $Na_3[Fe(C_2O_4)_3]$.

Quick Tip to Solve: Count ligand charges before adding counter-ions: aqua contributes zero, while each oxalato contributes -2.

11. (a) Although both $[NiCl_4]^{2-}$ and $[Ni(CO)_4]$ have sp^3 hybridisation yet $[NiCl_4]^{2-}$ is paramagnetic and $[Ni(CO)_4]$ is diamagnetic. Give reason. (Atomic no. of Ni = 28)

(b) Write the electronic configuration of d^5 on the basis of crystal field theory when

(i) $\Delta_o < P$ and

(ii) $\Delta_o > P$ [2 marks]

Solution:

Concept:

- Magnetism depends on unpaired electrons, rather than hybridisation alone. Nickel has atomic number 28; Ni^{2+} is $3d^8$, while zero-valent nickel in its carbonyl has a paired $3d^{10}$ configuration.
- In an octahedral field, t_{2g} orbitals lie below e_g. Compare the splitting energy Δ_o with pairing energy P to decide whether electrons pair.

Step 1: Explain the different magnetic behaviours In $[NiCl_4]^{2-}$, the charge equation $x + 4(-1) = -2$ gives $x = +2$, hence a $3d^8$ metal ion. Chloride is a weak-field ligand, and the tetrahedral complex retains two unpaired electrons; it is paramagnetic. In $[Ni(CO)_4]$, neutral CO makes nickel zero-valent. The strong-field CO ligands favour a completely paired $3d^{10}$ arrangement. There are no unpaired electrons, so this complex is diamagnetic. Both employ four sp^3 hybrid orbitals, but their metal d-electron occupations differ.

Step 2: Distribute the five d electrons in the octahedral field For the printed d^5 configuration, when $\Delta_o < P$, promotion to e_g costs less energy than pairing. Each of the five d orbitals is singly occupied, giving high-spin $t_{2g}^3 e_g^2$, with five unpaired electrons. When $\Delta_o > P$, pairing in the lower t_{2g} orbitals is preferred to occupying e_g. The configuration is low-spin $t_{2g}^5 e_g^0$, with one unpaired electron.

Step 3: Conclusion (a) $[NiCl_4]^{2-}$ has two unpaired electrons, whereas $[Ni(CO)_4]$ has none. (b) $\Delta_o < P : t_{2g}^3 e_g^2$; $\Delta_o > P : t_{2g}^5 e_g^0$.

Quick Tip to Solve: Determine nickel oxidation states separately, and use the printed d5 count before comparing splitting with pairing energy.

12. Write structures of main compounds A and B in each of the following reactions:

(a) $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{H_2/Pd\text{-}BaSO_4} B$

(b) $CH_3CN \xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr} A \xrightarrow{Zn(Hg)/conc.\ HCl} B$ [2 marks]

Solution:

Concept:

- PCl_5 converts a carboxylic acid into its acyl chloride; Rosenmund reduction with $H_2/Pd - BaSO_4$ converts an acyl chloride into an aldehyde.
- A nitrile reacts with a Grignard reagent to form an intermediate which gives a ketone on acidic hydrolysis. Clemmensen reduction converts the carbonyl group into a methylene group.

Step 1: Identify the benzene-series products Benzoic acid loses its carboxyl OH in favour of chlorine upon treatment with PCl_5, giving benzoyl chloride: $A = C_6H_5 - C(=O) - Cl$. The subsequent poisoned-palladium hydrogenation is Rosenmund reduction, which stops at the aldehyde. Therefore $B = C_6H_5 - C(=O) - H$, benzaldehyde. The benzene ring and the carbonyl carbon are retained in both transformations.

Step 2: Identify the nitrile-series products The methyl group from CH_3MgBr adds to the nitrile carbon of CH_3CN. Acidic hydrolysis of the resulting imine magnesium salt produces $A = CH_3 - C(=O) - CH_3$, propanone (acetone). With $Zn(Hg)$ and concentrated HCl, its carbonyl group is reduced to CH_2, without changing the three-carbon skeleton. Hence $B = CH_3 - CH_2 - CH_3$, propane.

Step 3: Conclusion (a) A: $C_6H_5 - C(=O) - Cl$; B: $C_6H_5 - C(=O) - H$. (b) A: $CH_3 - C(=O) - CH_3$; B: $CH_3 - CH_2 - CH_3$.

Quick Tip to Solve: For nitrile plus Grignard, retain the nitrile carbon and add the reagent alkyl group; hydrolysis gives the ketone.

Section C (36 marks)

13. The following data were obtained for the reaction:

A + 2B $\longrightarrow$ C

Experiment	[A]/M	[B]/M	Initial rate of formation of C /M min^{-1}
1	0.2	0.3	4.2×10^{-2}
2	0.1	0.1	6.0×10^{-3}
3	0.4	0.3	1.68×10^{-1}
4	0.1	0.4	2.40×10^{-2}

(a) Find the order of reaction with respect to A and B.

(b) Write the rate law and overall order of reaction.

(c) Calculate the rate constant (k). [3 marks]

Solution:

Concept:

- Initial-rate law: $r = k[A]^m[B]^n$, where r is the formation rate of C, k is the rate constant and m, n are partial orders.
- Compare experiments with one concentration unchanged. Overall order is $m + n$; stoichiometric coefficients need not equal the orders.

Step 1: (a) Find the partial orders Experiments 1 and 3 keep $[B] = 0.3\,\text{M}$ constant:

$$\frac{1.68 \times 10^{-1}}{4.2 \times 10^{-2}} = \left(\frac{0.4}{0.2}\right)^m, \qquad 4 = 2^m, \qquad m = 2.$$

Experiments 2 and 4 keep $[A] = 0.1\,\text{M}$ constant:

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \left(\frac{0.4}{0.1}\right)^n, \qquad 4 = 4^n, \qquad n = 1.$$

Thus these comparisons give second order in A and first order in B.

Step 2: (b) Write the rate law and overall order The inferred rate law is $r = k[A]^2[B]$. Its overall order is $2 + 1 = 3$. Orders are determined experimentally, not from reaction coefficients.

Step 3: (c) Calculate and verify the rate constant From experiment 2,

$$k = \frac{6.0 \times 10^{-3}}{(0.1)^2(0.1)} = 6.0\,\text{M}^{-2}\,\text{min}^{-1}.$$

Experiment 4 gives the same value. But experiment 1 gives

$$k = \frac{4.2 \times 10^{-2}}{(0.2)^2(0.3)} = 3.5\,\text{M}^{-2}\,\text{min}^{-1},$$

and experiment 3 also gives 3.5. The printed data are internally inconsistent: the pairs infer the above orders, but a single k does not fit all four experiments. Units follow from $(\text{M}\,\text{min}^{-1})/\text{M}^3$.

Quick Tip to Solve: Compare rows 1 and 3 for A and rows 2 and 4 for B, then check the value of k against every row.

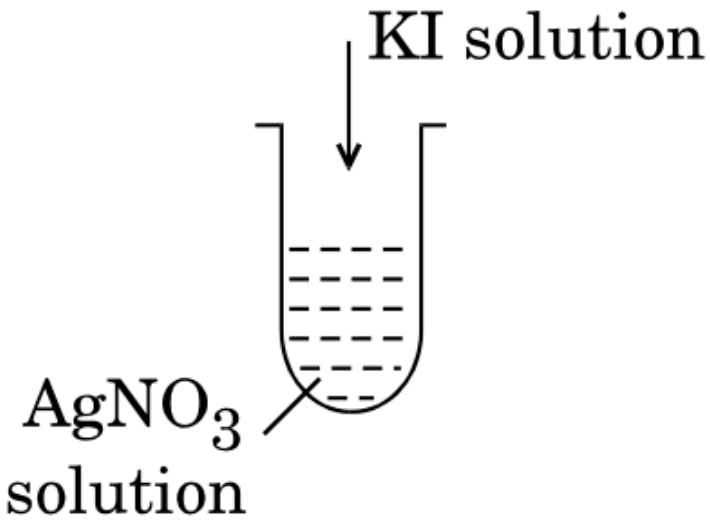
Step 4: Conclusion $m = 2$, $n = 1$, $r = k[A]^2[B]$; overall order 3. The inconsistent printed data give $k = 6.0$ or $3.5\,\text{M}^{-2}\,\text{min}^{-1}$, as shown above.

Quick Tip to Solve: Compare rows 1 and 3 for A and rows 2 and 4 for B, then check the value of k against every row.

14. (a) Write the dispersed phase and dispersion medium of dust.

(b) Why is physisorption reversible whereas chemisorption is irreversible?

(c) A colloidal sol is prepared by the method given in the figure. What is the charge on AgI colloidal particles formed in the test tube? How is this sol represented? [3 marks]



Solution:

Concept:

- Dust is a solid aerosol: solid particles (dispersed phase) in air (dispersion medium).
- Physisorption uses weak van der Waals forces; chemisorption forms strong chemical bonds.
- Preferential adsorption of a constituent ion in excess determines a sol particle's charge.

Step 1: (a) Identify the two phases of dust The fine solid dust particles constitute the dispersed phase. Air, a gaseous mixture, is the dispersion medium. Thus dust in air is a solid aerosol.

Step 2: (b) Explain the reversibility of adsorption In physisorption, the adsorbate is held to the surface by weak van der Waals forces. These attractions can be overcome readily, for example by increasing temperature or lowering gas pressure, so the adsorbate can leave the surface and adsorption is reversible. In chemisorption, strong chemical bonds are formed between the adsorbate and the surface. These bonds do not readily break on reversing conditions, making chemisorption generally irreversible.

Step 3: (c) Determine the AgI sol charge from the figure The figure shows KI solution being added to $AgNO_3$ solution already in the test tube. AgI forms by

$$AgNO_3 + KI \longrightarrow AgI + KNO_3.$$

Quick Tip to Solve: Read the receiving solution in the test tube: excess AgNO3 supplies adsorbed Ag+ and gives a positive AgI sol.

The receiving solution provides excess Ag^+ ions. The AgI particles preferentially adsorb these constituent ions and therefore acquire positive charge. The sol is represented as AgI/Ag^+.

Step 4: Conclusion (a) Solid dust in gaseous air. (b) Weak physical forces allow reversibility; chemical bonds resist it. (c) Positive AgI sol: AgI/Ag^+.

Quick Tip to Solve: Read the receiving solution in the test tube: excess AgNO3 supplies adsorbed Ag+ and gives a positive AgI sol.

15. An element X with an atomic mass of 81 u has density 10.2 g cm^{-3}. If the volume of unit cell is 2.7 $\times$ 10^{-23} cm^3, identify the type of cubic unit cell. (Given: N_A = 6.022 $\times$ 10^{23} mol^{-1}) [3 marks]

Solution:

Concept:

- Unit-cell density is $\rho = ZM/(N_A V)$, where Z is the number of atoms per cell, M is molar mass, N_A is Avogadro's constant and V is cell volume.
- Cubic cells contain $Z = 1$ for simple cubic, $Z = 2$ for body-centred cubic and $Z = 4$ for face-centred cubic.

Step 1: Express the mass of one unit cell An atomic mass of $81\,\text{u}$ corresponds to a molar mass of $81\,\text{g mol}^{-1}$. From the given density and volume, the unit-cell mass is

$$m_{\text{cell}} = \rho V = (10.2\,\text{g cm}^{-3})(2.7 \times 10^{-23}\,\text{cm}^3) = 2.754 \times 10^{-22}\,\text{g}.$$

Since each atom has mass M/N_A, a cell containing Z atoms has mass ZM/N_A. This connects the measured cell mass to its atomic occupancy.

Step 2: Calculate the number of atoms per cell Rearranging the density relation gives

$$\begin{aligned} Z &= \frac{\rho V N_A}{M} \\ &= \frac{(10.2)(2.7 \times 10^{-23})(6.022 \times 10^{23})}{81} \\ &= \frac{165.84588}{81} = 2.04748 \approx 2. \end{aligned}$$

The powers of ten cancel. The units also cancel because $(\text{g cm}^{-3})(\text{cm}^3)(\text{mol}^{-1})/(\text{g mol}^{-1})$ is dimensionless. The calculated occupancy is close to the integer 2; the given physical data have limited precision.

Step 3: Identify the cubic arrangement A body-centred cubic cell has eight corner atoms, each contributing one-eighth to the cell, and one atom entirely at the body centre. Its effective occupancy is

$$Z = 8\left(\frac{1}{8}\right) + 1 = 2.$$

This matches the inferred occupancy, while simple cubic and face-centred cubic would require 1 and 4 atoms per cell respectively.

Quick Tip to Solve: When cell volume is already given, use Z = density times volume times Avogadro constant divided by molar mass.

Step 4: Conclusion $Z \approx 2$, so element X has a body-centred cubic (bcc) unit cell.

Quick Tip to Solve: When cell volume is already given, use Z = density times volume times Avogadro constant divided by molar mass.

16. A solution containing 1.9 g per 100 mL of KCl (M = 74.5 g mol^{-1}) is isotonic with a solution containing 3 g per 100 mL of urea (M = 60 g mol^{-1}). Calculate the degree of dissociation of KCl solution. Assume that both the solutions have same temperature. [3 marks]

Solution:

Concept:

- Isotonic solutions have equal osmotic pressures. For a dilute solution, $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature.
- Urea is a non-electrolyte, so its van't Hoff factor is 1. KCl dissociates as $\mathrm{KCl} \rightarrow \mathrm{K^+} + \mathrm{Cl^-}$; if its degree of dissociation is α, then $i = 1 + \alpha$.

Step 1: Calculate the concentrations Both masses refer to $100\,\mathrm{mL} = 0.100\,\mathrm{L}$ of solution. Hence

$$C_{\mathrm{KCl}} = \frac{1.9/74.5}{0.100} = 0.2550\,\mathrm{mol\ L^{-1}}, \qquad C_{\mathrm{urea}} = \frac{3/60}{0.100} = 0.500\,\mathrm{mol\ L^{-1}}.$$

Molarity counts formula units before dissociation; additional ions are accounted for by the factor i.

Step 2: Use the isotonic condition Equal temperatures and osmotic pressures allow RT to cancel:

$$i_{\mathrm{KCl}} C_{\mathrm{KCl}} = C_{\mathrm{urea}}, \qquad i_{\mathrm{KCl}} = \frac{3/60}{1.9/74.5} = \frac{223.5}{114} = 1.9605.$$

The common solution volume also cancels, so the ratio may be calculated directly from the two mole amounts.

Step 3: Obtain the degree of dissociation From one mole of KCl, $(1 - \alpha)$ mole remains undissociated and α mole each of potassium and chloride ions forms. Total particles therefore amount to $1 - \alpha + \alpha + \alpha = 1 + \alpha$ mole. Thus

$$\alpha = i - 1 = 1.9605 - 1 = 0.9605.$$

This lies between zero and one, as required for a degree of dissociation.

Step 4: Conclusion The degree of dissociation is $\boxed{\alpha \approx 0.961}$, or approximately $\boxed{96.1\%}$.

Quick Tip to Solve: For equal-volume isotonic solutions, divide the mole amounts to find i; for KCl, subtract 1 to find the degree of dissociation.

17. Write the name and principle of the method used for refining of (a) Zinc, (b) Germanium, (c) Titanium. [3 marks]

Solution:

Concept:

- A refining method separates a metal from its impurities by exploiting differences in volatility, solubility or the ability to form a volatile compound.
- The refining method must suit the metal and the purity required. Zinc is volatile, germanium requires very high purity, and titanium can be transported as a volatile iodide.

Step 1: (a) Zinc: distillation Zinc is refined by distillation. The principle is the difference in volatility between zinc and its less volatile impurities. Impure zinc is heated so that zinc vaporises, while the non-volatile impurities remain behind. The zinc vapour is then cooled and condensed to obtain purified zinc. The process therefore separates the metal itself by vaporisation and condensation.

Step 2: (b) Germanium: zone refining Germanium is refined by zone refining. Its principle is that impurities are more soluble in the molten metal than in the solid metal. A moving heater produces a narrow molten zone in a germanium rod. As the heater advances, pure germanium crystallises behind it, while impurities remain preferentially in the melt and travel with the molten zone. Repeated passes concentrate the impurities at one end of the rod, which is then cut off. This produces the high-purity germanium needed for semiconductor applications.

Step 3: (c) Titanium: van Arkel method Titanium is refined by the van Arkel or iodide process. The principle is conversion of titanium into a volatile compound followed by its decomposition to deposit pure metal. On heating impure titanium with iodine, volatile titanium tetraiodide forms; the impurities remain behind. The vapour passes over a hot tungsten filament, where it decomposes:

$$\mathrm{Ti} + 2\mathrm{I}_2 \longrightarrow \mathrm{TiI}_4, \qquad \mathrm{TiI}_4 \longrightarrow \mathrm{Ti} + 2\mathrm{I}_2.$$

Pure titanium is deposited on the filament, while iodine is liberated.

Step 4: Conclusion Zinc: distillation (volatility); germanium: zone refining (greater impurity solubility in the melt); titanium: van Arkel process (volatile iodide formation and decomposition).

Quick Tip to Solve: Associate Zn with vaporisation, Ge with a travelling molten zone, and Ti with volatile TiI4 and a hot filament.

18. Give reasons for the following:

(a) Transition metals form complex compounds.

(b) E° values for (Zn^{2+}/Zn) and (Mn^{2+}/Mn) are more negative than expected.

(c) Actinoids show wide range of oxidation states. [3 marks]

Solution:

Concept:

- Complex formation depends on a metal ion accepting electron pairs from ligands to form coordinate bonds; high charge density strengthens this interaction.

Quick Tip to Solve: For the potential anomaly, first write Zn2+ as d10 and Mn2+ as d5, then link ion stability to a lower tendency for reduction.

- The standard reduction potential E° for $M^{2+} + 2e^- \rightarrow M$ reflects the relative stability of the metal and its aqueous ion.
- Oxidation states depend on which valence electrons can participate in bonding. Closely spaced orbital energies allow more combinations of electrons to be used.

Step 1: (a) Formation of complexes Transition-metal ions generally have small ionic sizes and relatively high ionic charges, giving them high charge densities. They attract ligands strongly. They also have suitable vacant orbitals available to accept lone pairs of electrons donated by ligands. Formation of these coordinate bonds leads to complex compounds, for example $[Cu(NH_3)_4]^{2+}$. Thus both the strong metal-ion attraction for donor ligands and the ability to accept their electron pairs favour complex formation.

Step 2: (b) More negative reduction potentials Zn^{2+} has the completely filled $3d^{10}$ configuration, whereas Mn^{2+} has the half-filled $3d^5$ configuration. These electronic configurations give the divalent ions extra stability. Consequently, conversion of these stable aqueous ions into the metals by reduction is less favourable than the general trend suggests. Their standard reduction potentials $E^\circ(Zn^{2+}/Zn)$ and $E^\circ(Mn^{2+}/Mn)$ are therefore more negative than expected. A more negative reduction potential indicates a smaller tendency of the ion to undergo reduction under standard conditions.

Step 3: (c) Range of actinoid oxidation states In actinoids, the energies of the $5f$, $6d$ and $7s$ orbitals are close to one another. Electrons from these orbitals can therefore participate in bonding, and different numbers of electrons may be involved in different compounds. This gives actinoids a wide range of oxidation states. For example, uranium commonly exhibits $+3$, $+4$, $+5$ and $+6$ states. The small energy separation, rather than participation of only the outermost electrons, is the key reason for this variability.

Step 4: Conclusion Transition metals form complexes through high charge density and electron-pair acceptance; stable $3d^{10}$ and $3d^5$ ions explain the unusually negative potentials; similar $5f$, $6d$ and $7s$ energies explain actinoid oxidation-state variability.

Quick Tip to Solve: For the potential anomaly, first write Zn2+ as d10 and Mn2+ as d5, then link ion stability to a lower tendency for reduction.

19(a). Write the structures of monomers used for getting the following polymers:

(a) Nylon-6

(b) Terylene

(c) Buna-N [3 marks]

Solution:

Concept:

- Monomers are small molecules whose functional groups or double bonds react to produce a polymer chain. Identifying a polymer therefore requires identifying the complete starting molecules.
- Nylon-6 is a polyamide formed by ring-opening polymerisation of caprolactam. Terylene is a condensation polyester, whereas Buna-N is an addition copolymer.

Quick Tip to Solve: Remember that nylon-6 uses one cyclic monomer, terylene uses a diol plus a para-diacid, and the N in Buna-N points to the nitrile-containing monomer.

Step 1: Identify the monomer of nylon-6 (a) The monomer is caprolactam, a cyclic amide. Its condensed ring structure is

$$\text{cyclic } [-\mathrm{NH}-(\mathrm{CH_2})_5-\mathrm{C}(=\mathrm{O})-].$$

The terminal bonds in this representation are joined to form a seven-membered ring: five methylene carbons, a carbonyl carbon and a nitrogen. Ring opening produces the nylon-6 repeat unit $[-\mathrm{NH}-(\mathrm{CH_2})_5-\mathrm{CO}-]_n$. Thus nylon-6 uses one cyclic monomer, rather than the two monomers used for nylon-6,6.

Step 2: Write both monomers of terylene (b) Terylene is made from ethylene glycol (ethane-1,2-diol) and terephthalic acid (benzene-1,4-dicarboxylic acid):

$$\mathrm{HO}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{OH}, \qquad \mathrm{HOOC}-\mathrm{C_6H_4}-\mathrm{COOH}\ (\text{para}).$$

The two carboxyl groups occupy positions 1 and 4 on the benzene ring. The hydroxyl groups of the diol react with the carboxyl groups of the diacid to form ester links, with elimination of water.

Step 3: Write both monomers of Buna-N (c) Buna-N is made by copolymerisation of buta-1,3-diene and acrylonitrile (prop-2-enenitrile):

$$\mathrm{CH_2}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH_2}, \qquad \mathrm{CH_2}=\mathrm{CH}-\mathrm{CN}.$$

Both monomers contain carbon-carbon double bonds that participate in addition polymerisation. The nitrile group belongs to acrylonitrile and distinguishes Buna-N from Buna-S, whose second monomer is styrene.

Step 4: Conclusion (a) Nylon-6: caprolactam, cyclic $[-\mathrm{NH}-(\mathrm{CH_2})_5-\mathrm{C}(=\mathrm{O})-]$. (b) Terylene: $\mathrm{HO}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{OH}$ and para-$\mathrm{HOOC}-\mathrm{C_6H_4}-\mathrm{COOH}$. (c) Buna-N: $\mathrm{CH_2}=\mathrm{CH}-\mathrm{CH}=\mathrm{CH_2}$ and $\mathrm{CH_2}=\mathrm{CH}-\mathrm{CN}$.

Quick Tip to Solve: Remember that nylon-6 uses one cyclic monomer, terylene uses a diol plus a para-diacid, and the N in Buna-N points to the nitrile-containing monomer.

OR

19(b). (a) Is —[CH_2—$CH(C_6H_5)$]—$_n$ a homopolymer or copolymer? Give reason.

(b) Write the monomers of the following polymer:

—[O—$CH(CH_3)$—CH_2—C(=O)—O—$CH(C_2H_5)$—CH_2—C(=O)]—$_n$

(c) Write the role of benzoyl peroxide in polymerisation of ethene. [3 marks]

$$\left\{ O - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle O}{\underset{\|}{C}} - O - \underset{\displaystyle C_2H_5}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle O}{\underset{\|}{C}} \right\}_n$$

Solution:

Concept:

- A homopolymer is formed from one monomer species; a copolymer is formed from two or more distinct monomer species.
- Polyester monomers can be found by reversing the ester linkage: restore a hydroxyl group at the alcohol end and a carboxyl group at the carbonyl end.
- Organic peroxides contain a weak oxygen-oxygen bond. Its homolytic cleavage generates radicals that initiate addition polymerisation.

Step 1: Classify the given addition polymer (a) The repeat unit $[-CH_2-CH(C_6H_5)-]_n$ is that of polystyrene. Its single monomer is styrene, $CH_2{=}CH{-}C_6H_5$. Opening the double bond of this one monomer gives the entire repeat unit. Therefore it is a homopolymer; the phenyl substituent does not represent a separate monomer.

Step 2: Recover the two hydroxy-acid monomers (b) The polyester shown is PHBV. Restoring the hydroxyl and carboxyl groups on either side of the ester bonds gives:

$$\begin{aligned} \text{3-Hydroxybutanoic acid:} &\quad CH_3{-}CH(OH){-}CH_2{-}COOH, \\ \text{3-Hydroxypentanoic acid:} &\quad CH_3{-}CH_2{-}CH(OH){-}CH_2{-}COOH. \end{aligned}$$

The first monomer has a methyl substituent at the hydroxyl-bearing carbon; the second has an ethyl substituent. These match the two side groups in the printed polymer. Their condensation forms ester links with loss of water.

Step 3: Explain initiation by benzoyl peroxide (c) Benzoyl peroxide acts as a free-radical initiator. On heating, its oxygen-oxygen bond cleaves homolytically:

$$(C_6H_5COO)_2 \xrightarrow{\text{heat}} 2\,C_6H_5COO^{\bullet}.$$

The radicals, or phenyl radicals formed after loss of CO_2, attack an ethene double bond, producing a new carbon-centred radical. That radical adds further ethene molecules and starts chain growth.

Step 4: Conclusion (a) Polystyrene is a homopolymer of styrene. (b) The monomers are $CH_3{-}CH(OH){-}CH_2{-}COOH$ and $CH_3{-}CH_2{-}CH(OH){-}CH_2{-}COOH$. (c) Benzoyl peroxide initiates free-radical polymerisation of ethene.

Quick Tip to Solve: To identify PHBV monomers, replace each ester connection by the original OH and COOH groups while keeping the methyl and ethyl side groups unchanged.

20(a). Pick out the odd one from the following on the basis of their medicinal properties:
Equanil, Seconal, Bithional, Luminal
(b) What type of detergents are used in dishwashing liquids?
(c) Why is the use of aspartame limited to cold foods? [3 marks]

Solution:

Concept:

- Drugs are classified according to their medicinal action. Tranquillisers act on the nervous system, whereas antiseptics inhibit microorganisms on living tissues.
- Detergents are classified by the charge on their hydrophilic part. Non-ionic detergents have an uncharged hydrophilic group.
- An artificial sweetener used during heating must remain chemically stable at cooking temperatures; thermal decomposition restricts its use.

Step 1: Identify the medicinal odd one out (a) Bithional is the odd one out: its medicinal action is antiseptic. It is used for antimicrobial action, including in soaps. Equanil, Seconal and Luminal belong to the tranquilliser class in this classification and act on the central nervous system. Thus Bithional differs in medicinal action, rather than merely in its name or chemical structure.

Step 2: Classify dishwashing detergents (b) Non-ionic detergents are used in dishwashing liquids. Their water-attracting portion has polar groups but carries no ionic charge, while the hydrocarbon portion associates with oily dirt. This combination enables the detergent to disperse grease in water so that it can be rinsed away. The required classification is non-ionic; anionic and cationic refer to detergents whose hydrophilic portions carry negative and positive charges respectively.

Step 3: Explain the temperature restriction on aspartame (c) Aspartame is an artificial sweetener that is unstable at cooking temperatures. Heating causes its decomposition, so it cannot reliably retain its sweetening action during cooking. Consequently, its use is limited to cold foods and soft drinks where high-temperature treatment is not required. The limitation concerns thermal stability, rather than an inability to dissolve in food.

Step 4: Conclusion (a) Bithional is the odd one out: it is an antiseptic, whereas the others are tranquillisers. (b) Dishwashing liquids use non-ionic detergents. (c) Aspartame decomposes at cooking temperatures and is therefore used in cold foods.

Quick Tip to Solve: Classify the drugs by their action, identify the detergent by the charge of its hydrophilic group, and link the cold-food restriction directly to thermal decomposition.

OR

20(b). Define the following terms with a suitable example of each:

(a) Antibiotics

(b) Antiseptics

(c) Anionic detergents [3 marks]

Solution:

Concept:

- Antibiotics act against microorganisms inside the body, whereas antiseptics prevent microbial growth on living tissue.
- A detergent has a long hydrophobic hydrocarbon chain and a hydrophilic head; an anionic detergent has a negatively charged active head.

Step 1: (a) Antibiotics Antibiotics are chemical substances originally produced by microorganisms which, in low concentrations, kill other microorganisms or inhibit their growth. The term also includes suitable synthetic or semisynthetic counterparts. They are used to treat susceptible microbial infections. Penicillin is a suitable example: it inhibits bacterial cell-wall synthesis. An antibiotic is selected for its action against a microorganism and is not a general surface-cleaning agent.

Step 2: (b) Antiseptics Antiseptics are chemicals that kill microorganisms or prevent their growth and can be applied to living tissues, such as skin, wounds and cuts, at suitable concentrations. Dettol is an example; its active antiseptic constituents include chloroxylenol. Their safe use on living tissue distinguishes antiseptics from disinfectants used on non-living objects. Concentration matters: a chemical suitable as an antiseptic in dilute form may damage tissue in concentrated form.

Step 3: (c) Anionic detergents Anionic detergents are detergents in which the anionic part of the molecule is responsible for cleansing. They are commonly sodium salts of long-chain alkyl hydrogen sulphates or alkylbenzene sulphonic acids. Sodium lauryl sulphate, $CH_3(CH_2)_{11}OSO_3^-Na^+$, is an example. Its long hydrocarbon tail associates with grease, while its negatively charged sulphate head interacts with water, enabling greasy dirt to be carried away.

Step 4: Conclusion Suitable examples are penicillin for antibiotics, Dettol for antiseptics, and sodium lauryl sulphate for anionic detergents.

Quick Tip to Solve: Identify the site of use for medicinal agents and the charge on the cleansing head for detergents.

21. Among all the isomers of molecular formula C_4H_9Br, identify

(a) the one isomer which is optically active.

(b) the one isomer which is highly reactive towards S_N2.

(c) the two isomers which give same product on dehydrohalogenation with alcoholic KOH. [3 marks]

Solution:

Concept:

- Optical activity requires a chiral centre: a tetrahedral carbon attached to four different groups.
- An S_N2 reaction involves backside attack; less steric hindrance increases its rate.
- Alcoholic KOH causes elimination of HBr from adjacent carbon atoms to form an alkene.

Step 1: List the four constitutional isomers The isomers of C_4H_9Br are 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. Their condensed structures are respectively $CH_3CH_2CH_2CH_2Br$, $CH_3CH(Br)CH_2CH_3$, $(CH_3)_2CHCH_2Br$ and $(CH_3)_3CBr$. Checking this complete list prevents confusion between straight-chain and branched isomers.

Step 2: (a) Identify the optically active isomer In 2-bromobutane, carbon 2 is bonded to H, Br, CH_3 and C_2H_5, four different groups. It is therefore chiral, and an individual enantiomer is optically active. The other three constitutional isomers have no such carbon. A racemic mixture of the two enantiomers is optically inactive because their rotations cancel.

Step 3: (b) Compare substitution reactivity 1-Bromobutane is most reactive towards S_N2. Its bromine-bearing carbon is primary and the unbranched chain presents the least hindrance to backside attack. Although 1-bromo-2-methylpropane is also primary, branching at the adjacent carbon slows the attack. The secondary isomer is more hindered, and the tertiary isomer strongly resists this mechanism.

Step 4: (c) Find the common elimination product The required pair is 1-bromo-2-methylpropane and 2-bromo-2-methylpropane. Each forms 2-methylpropene on eliminating HBr:

$$(CH_3)_2CHCH_2Br \xrightarrow{\text{alc. KOH}} CH_2 = C(CH_3)_2,$$

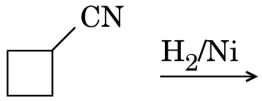
$$(CH_3)_3CBr \xrightarrow{\text{alc. KOH}} CH_2 = C(CH_3)_2.$$

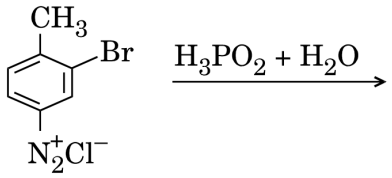
In the first reactant only the adjacent methine carbon supplies the beta hydrogen; in the second, all three methyl groups are equivalent, so eliminating from any of them gives the same alkene.

Step 5: Conclusion (a) 2-Bromobutane; (b) 1-bromobutane; (c) 1-bromo-2-methylpropane and 2-bromo-2-methylpropane, both giving 2-methylpropene.

Quick Tip to Solve: For elimination, preserve the carbon skeleton and inspect the beta carbons before comparing alkene products.

22(a). Complete the following reactions: [3 marks]

(a) 

(b) 

(c) 

Solution:

Concept:

- Catalytic hydrogenation reduces a nitrile group $-C \equiv N$ to $-CH_2NH_2$; the nitrile carbon remains in the product.
- Hypophosphorous acid replaces an aromatic diazonium group by hydrogen, with liberation of nitrogen.
- Primary amines react with chloroform and alcoholic KOH to form isocyanides in the carbylamine reaction.

Step 1: (a) Reduce the nitrile group The printed ring is cyclobutane and its substituent is $-CN$. Hydrogen in the presence of nickel converts this group to $-CH_2NH_2$, leaving the four-membered carbon ring unchanged. Let $c-C_4H_7$ denote the cyclobutyl group. The balanced reaction is

$$c-C_4H_7CN + 2H_2 \xrightarrow{Ni} c-C_4H_7CH_2NH_2.$$

The product is cyclobutylmethanamine, also called cyclobutylmethylamine. The carbon of the nitrile becomes the methylene carbon; the product is therefore not cyclobutylamine.

Step 2: (b) Replace the diazonium group by hydrogen In the printed aromatic structure, methyl is para and bromine is meta to the diazonium group. Treatment with H_3PO_2 and water replaces only $-N_2^+$ by H:

$$ArN_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl.$$

Here the original methyl and bromine substituents are retained. They occupy adjacent positions, so the product is 2-bromotoluene (1-bromo-2-methylbenzene). Naming the product afresh avoids retaining the diazonium compound's obsolete numbering.

Step 3: (c) Apply the carbylamine reaction The printed reactant is benzylamine, $C_6H_5CH_2NH_2$, a primary amine. With chloroform and ethanolic KOH it gives benzyl isocyanide:

$$C_6H_5CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5CH_2NC + 3KCl + 3H_2O.$$

Quick Tip to Solve: Track the group attached to nitrogen: nitrile reduction retains its carbon, while carbylamine formation gives RNC.

The benzyl group remains attached to nitrogen, giving the linkage $-N \equiv C$. This is an isocyanide, not a nitrile with a $-C \equiv N$ linkage; the distinction is essential when completing this reaction.

Step 4: Conclusion The products are (a) cyclobutylmethanamine, (b) 2-bromotoluene, and (c) benzyl isocyanide, $C_6H_5CH_2NC$.

Quick Tip to Solve: Track the group attached to nitrogen: nitrile reduction retains its carbon, while carbylamine formation gives RNC.

OR

22(b). How do you convert the following:

(a) N-phenylethanamide to p-bromoaniline

(b) Benzene diazonium chloride to nitrobenzene

(c) Benzoic acid to aniline [3 marks]

Solution:

Concept:

- Protection of the amino group as an acetamide controls bromination; the group $-NHCOCH_3$ directs electrophilic substitution mainly to the para position.
- The diazonium chloride is converted to diazonium fluoroborate with HBF_4; heating this salt with aqueous sodium nitrite and copper replaces the diazonium group by $-NO_2$.
- Hofmann bromamide degradation converts $RCONH_2$ into RNH_2, with loss of the carbonyl carbon.

Step 1: (a) Brominate the protected amine, then hydrolyse N-Phenylethanamide is acetanilide, $C_6H_5NHCOCH_3$. Treat it with bromine in glacial acetic acid to obtain mainly p-bromoacetanilide. Hydrolyse the amide with aqueous acid on heating, then make alkaline to liberate p-bromoaniline. The acetyl group protects the amino group against uncontrolled bromination.

$$C_6H_5NHCOCH_3 \xrightarrow{Br_2/CH_3COOH} p-BrC_6H_4NHCOCH_3$$
$$\xrightarrow[\text{then base}]{H_3O^+,\ \text{heat}} p-BrC_6H_4NH_2.$$

Step 2: (b) Replace the diazonium group by a nitro group Add fluoroboric acid, HBF_4, to benzene diazonium chloride to obtain benzene diazonium fluoroborate. Heat this salt with aqueous sodium nitrite in the presence of copper to obtain nitrobenzene, with evolution of nitrogen gas.

$$C_6H_5N_2^+Cl^- \xrightarrow{HBF_4} C_6H_5N_2^+BF_4^-$$
$$\xrightarrow{NaNO_2(aq),\ Cu,\ \text{heat}} C_6H_5NO_2.$$

Step 3: (c) Form benzamide and carry out Hofmann degradation First treat benzoic acid with ammonia and heat the resulting ammonium benzoate to obtain benzamide. Treat benzamide with

Quick Tip to Solve: For benzoic acid to aniline, form the amide first: Hofmann degradation removes exactly the carbonyl carbon.

bromine and aqueous sodium hydroxide to obtain aniline.

$$C_6H_5COOH \xrightarrow{NH_3} C_6H_5COO^-NH_4^+ \xrightarrow{heat} C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} C_6H_5NH_2.$$

Hofmann degradation removes the carbonyl carbon.

Step 4: Conclusion The required sequences are: (a) bromination followed by acidic hydrolysis and basification; (b) HBF_4, then aqueous $NaNO_2/Cu$ on heating; (c) benzamide formation followed by $Br_2/NaOH$.

Quick Tip to Solve: For benzoic acid to aniline, form the amide first: Hofmann degradation removes exactly the carbonyl carbon.

23. (a) Give reasons:

(i) Benzoic acid is a stronger acid than acetic acid.

(ii) Methanal is more reactive towards nucleophilic addition reaction than ethanal.

(b) Give a simple chemical test to distinguish between propanal and propanone. [3 marks]

Solution:

Concept:

- Acid strength depends on the stability of the conjugate carboxylate ion: electron withdrawal favours dissociation, whereas electron donation opposes it.
- Nucleophilic addition is favoured by a more electrophilic carbonyl carbon and less steric obstruction.
- Tollens' reagent oxidises aldehydes to carboxylate ions and is reduced to metallic silver; ordinary ketones do not give this test.

Step 1: (a)(i) Compare the inductive effects In benzoic acid, the phenyl group exerts an electron-withdrawing inductive effect and stabilises the benzoate ion. In acetic acid, the methyl group has an electron-releasing $+I$ effect, increasing electron density on the carboxylate group and destabilising the acetate ion relative to benzoate. Consequently, loss of H^+ is easier from benzoic acid, which is therefore the stronger acid. Both conjugate bases have resonance within their carboxylate groups; the difference is explained by the substituent effect.

Step 2: (a)(ii) Compare electrophilicity and steric hindrance Methanal, $HCHO$, has two hydrogen atoms attached to its carbonyl carbon, whereas ethanal, CH_3CHO, has one methyl group. The methyl group donates electron density through its $+I$ effect and reduces the partial positive charge on the carbonyl carbon of ethanal. It also obstructs the approach of a nucleophile more than hydrogen does. Methanal therefore undergoes nucleophilic addition more readily because of both electronic and steric factors.

Step 3: (b) Perform Tollens' test Warm each sample gently with freshly prepared Tollens' reagent (ammoniacal silver nitrate). Propanal produces a silver mirror on the test-tube wall, whereas

Quick Tip to Solve: Use Tollens' reagent for this aldehyde-ketone pair: a silver mirror identifies propanal immediately.

propanone gives no silver mirror. The balanced ionic reaction for propanal is

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Propanal is oxidised to propanoate while silver(I) is reduced to silver metal.

Step 4: Conclusion Benzoic acid is stronger because of the electron-withdrawing phenyl group; methanal is more reactive because it lacks an electron-donating and bulky methyl group. Tollens' reagent gives a silver mirror with propanal only.

Quick Tip to Solve: Use Tollens' reagent for this aldehyde-ketone pair: a silver mirror identifies propanal immediately.

24(a). What are the products of hydrolysis of maltose?

(b) What type of bonding provides stability to α-helix structure of protein?

(c) Name the vitamin whose deficiency causes pernicious anaemia. [3 marks]

Solution:

Concept:

- A disaccharide undergoes hydrolysis when water cleaves its glycosidic bond, regenerating its constituent monosaccharides.
- The α-helix is a secondary structure stabilised by hydrogen bonds between peptide backbone groups.
- Vitamin B_{12}, also called cobalamin, is associated with normal red blood cell formation.

Step 1: (a) Identify the monosaccharides in maltose Maltose consists of two D-glucose units joined by an $\alpha(1 \to 4)$ glycosidic linkage. On hydrolysis with dilute acid or the enzyme maltase, this linkage is cleaved and two molecules of D-glucose are formed.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{hydrolysis}} 2C_6H_{12}O_6.$$

Thus both constituent sugar units are glucose; fructose is not a product of maltose hydrolysis.

Step 2: (b) State the bonding that stabilises the helix The α-helix is stabilised by intramolecular hydrogen bonds between the carbonyl oxygen, $C = O$, of one peptide bond and the hydrogen of a backbone $N - H$ group four residues ahead in the same polypeptide chain. The repeated hydrogen-bond arrangement holds the chain in its helical shape. Peptide covalent bonds connect amino acids along the chain, but hydrogen bonds provide the characteristic stability of this secondary structure.

Step 3: (c) Identify the deficient vitamin The vitamin is B_{12} (cobalamin). Its deficiency causes pernicious anaemia in the standard vitamin-deficiency classification. This identifies the specific B-group vitamin, rather than naming the entire vitamin B complex.

Step 4: Conclusion (a) Two molecules of D-glucose. (b) Intramolecular hydrogen bonding between peptide $C = O$ and $N - H$ groups. (c) Vitamin B_{12} (cobalamin).

Quick Tip to Solve: Remember maltose as glucose plus glucose, the alpha-helix as backbone hydrogen bonds, and pernicious anaemia as vitamin B12 deficiency.

OR

24(b). Define the following terms:

(a) Invert sugar

(b) Native protein

(c) Nucleotide [3 marks]

Solution:

Concept:

- Hydrolysis breaks a glycosidic linkage by addition of water. Sucrose hydrolysis produces sugars whose net optical rotation differs from that of sucrose.
- Protein function depends on its naturally folded three-dimensional structure. A nucleotide, the building unit of a nucleic acid, contains a base, sugar and phosphate.

Step 1: (a) Define invert sugar Invert sugar is the equimolar mixture of D-glucose and D-fructose obtained by hydrolysis of sucrose, using dilute acid or the enzyme invertase:

$$\text{Sucrose} + H_2O \longrightarrow \text{D-glucose} + \text{D-fructose}.$$

Sucrose is dextrorotatory, whereas the product mixture is laevorotatory because the magnitude of the negative rotation of fructose exceeds the positive rotation of glucose. This reversal of the direction of optical rotation gives the mixture its name.

Step 2: (b) Define native protein A native protein is a protein in its natural, biologically active form, with its characteristic three-dimensional conformation intact. Its secondary and tertiary structure, and quaternary structure where present, allow it to carry out its normal biological function. Denaturation disrupts this natural conformation and generally destroys biological activity without breaking the primary peptide-chain sequence.

Step 3: (c) Define nucleotide A nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group. The pentose is ribose in RNA or 2-deoxyribose in DNA. The base and sugar together constitute a nucleoside; attachment of phosphate to the sugar gives a nucleotide. Nucleotides join through phosphodiester linkages to form nucleic acids.

Step 4: Conclusion (a) Invert sugar: the equimolar glucose-fructose mixture formed by sucrose hydrolysis. (b) Native protein: the naturally folded, biologically active protein. (c) Nucleotide: a nitrogenous base linked to a pentose sugar bearing a phosphate group.

Quick Tip to Solve: Remember nucleotide as nucleoside plus phosphate; invert sugar refers to sucrose hydrolysis, not maltose hydrolysis.

Section D (15 marks)

25(a). The conductivity of 0.001 mol L^{-1} acetic acid is 4.95 $\times$ 10^{-5} S cm^{-1}. Calculate the dissociation constant if Λ_m° for acetic acid is 390.5 S cm^2 mol^{-1}.

(b) Write Nernst equation for the reaction at 25°C:

2 Al(s) + 3 Cu^{2+}(aq) $\longrightarrow$ 2 Al^{3+}(aq) + 3 Cu(s)

(c) What are secondary batteries? Give an example. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$, when conductivity κ is in $\mathrm{S\,cm^{-1}}$ and concentration c is in $\mathrm{mol\,L^{-1}}$. For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- For a monoprotic weak acid, $K_a = c\alpha^2/(1-\alpha)$. At 25°C, the Nernst equation is $E = E^\circ - (0.0591/n)\log_{10} Q$, with n the electrons transferred and Q the reaction quotient.
- Secondary batteries have reversible electrode reactions and can be recharged by an external source of electrical energy.

Step 1: (a) Calculate molar conductivity and dissociation The given acid concentration is $c = 0.001\,\mathrm{mol\,L^{-1}}$ and its conductivity is $\kappa = 4.95 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$. Hence,

$$\Lambda_m = \frac{1000(4.95 \times 10^{-5})}{0.001} = 49.5\,\mathrm{S\,cm^2\,mol^{-1}},$$
$$\alpha = \frac{49.5}{390.5} = 0.12676.$$

Thus about 12.68% of the acetic acid is dissociated. The limiting molar conductivity corresponds to complete dissociation, so comparison with it gives the fraction ionised at this concentration.

Step 2: (a) Apply the weak-acid equilibrium expression For $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, the equilibrium concentrations are $c(1-\alpha)$ for the undissociated acid and $c\alpha$ for each ion. Therefore,

$$K_a = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{0.001(0.12676)^2}{1-0.12676} = 1.84 \times 10^{-5}.$$

Keeping the factor $1-\alpha$ is appropriate here, since the dissociated fraction is appreciable; replacing it by unity would give a less accurate result. This is the conventional concentration-based value used for this calculation.

Step 3: (b) Determine electron transfer and write Nernst equation The oxidation and reduction half-reactions are

$$2\mathrm{Al(s)} \longrightarrow 2\mathrm{Al^{3+}(aq)} + 6e^-,$$
$$3\mathrm{Cu^{2+}(aq)} + 6e^- \longrightarrow 3\mathrm{Cu(s)}.$$

Thus $n = 6$. Pure solid aluminium and copper have unit activity, so they are omitted from Q. Using the usual concentration form for aqueous ions,

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0591}{6}\log_{10}\frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}.$$

Quick Tip to Solve: In Nernst equations, balance the electron transfer first: here six electrons, not two or three, determine the denominator.

The powers two and three come from the stoichiometric coefficients in the balanced reaction. Strictly, each concentration represents its ratio to the standard concentration, so the logarithm's argument is dimensionless.

Step 4: (c) Explain secondary batteries with an example Secondary batteries are rechargeable batteries whose cell reactions can be reversed by passing current from an external electrical source in the opposite direction to the discharge process. Charging regenerates the active electrode materials, allowing repeated use. A lead storage battery, used in automobiles, is an example: its lead and lead dioxide electrodes are regenerated from lead sulphate during charging.

Step 5: Conclusion (a) $K_a = 1.84 \times 10^{-5}$. (b) $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{6} \log_{10}\left([\text{Al}^{3+}]^2/[\text{Cu}^{2+}]^3\right)$ at 25°C. (c) Secondary batteries are rechargeable cells with reversible reactions; a lead storage battery is an example.

Quick Tip to Solve: In Nernst equations, balance the electron transfer first: here six electrons, not two or three, determine the denominator.

OR

25(b). (a) Represent the cell in which the following reaction takes place:

$2\,\text{Al(s)} + 3\,\text{Ni}^{2+}(0.1\text{ M}) \longrightarrow 2\,\text{Al}^{3+}(0.01\text{ M}) + 3\,\text{Ni(s)}$

Calculate its emf if $E^\circ_{\text{cell}} = 1.41$ V.

(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ°_m) for weak electrolyte? [5 marks]

Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction at the cathode. Cell notation places the anode on the left and the cathode on the right; a double vertical line represents the salt bridge.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- Molar conductivity Λ_m is the conductance associated with one mole of electrolyte. Kohlrausch's law states that at infinite dilution each ion contributes independently to Λ°_m.

Step 1: (a) Identify the electrodes and represent the cell Aluminium loses electrons, whereas nickel ions gain electrons:

$$2\text{Al(s)} \longrightarrow 2\text{Al}^{3+}(\text{aq}) + 6e^-$$
$$3\text{Ni}^{2+}(\text{aq}) + 6e^- \longrightarrow 3\text{Ni(s)}.$$

Hence aluminium is the anode and nickel is the cathode. The cell is

$$\text{Al(s)} \mid \text{Al}^{3+}(\text{aq},\ 0.01\,\text{M}) \parallel \text{Ni}^{2+}(\text{aq},\ 0.1\,\text{M}) \mid \text{Ni(s)}.$$

The balanced overall reaction transfers $n = 6$ electrons, not two or three.

Step 2: (a) Substitute into the Nernst equation Taking the aqueous concentrations relative to the

Quick Tip to Solve: Balance the half-reactions first to obtain six electrons, and omit solid Al and Ni from the reaction quotient.

standard concentration and omitting the solids,

$$Q = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Ni}^{2+}]^3} = \frac{(0.01)^2}{(0.1)^3} = 0.1.$$

Using the standard 25°C form of the equation,

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}\log(0.1) \\ &= 1.41 + 0.00985 = 1.41985\,\text{V}. \end{aligned}$$

Since $Q < 1$, the concentration correction increases the emf above its standard value.

Step 3: (b) Explain the effect of increasing concentration For both strong and weak electrolytes, molar conductivity decreases as concentration increases. A strong electrolyte is already almost completely dissociated; increasing concentration strengthens interionic interactions and reduces ionic mobility. At low concentrations its behaviour is expressed by $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$, where A is a positive constant for the electrolyte and solvent at the given temperature. For a weak electrolyte, increasing concentration also reduces its degree of ionisation. Thus its molar conductivity decreases much more sharply. Conversely, dilution greatly increases the number of ions per mole of a weak electrolyte. This statement concerns molar conductivity; it must not be confused with conductivity per unit volume.

Step 4: (b) Obtain the limiting value for a weak electrolyte The strongly curved concentration dependence of a weak electrolyte prevents reliable direct extrapolation to zero concentration. Instead, apply Kohlrausch's law using limiting molar conductivities of suitable strong electrolytes. For example,

$$\begin{aligned} \Lambda_m^\circ(\mathrm{CH_3COOH}) = {} & \Lambda_m^\circ(\mathrm{HCl}) \\ & + \Lambda_m^\circ(\mathrm{CH_3COONa}) \\ & - \Lambda_m^\circ(\mathrm{NaCl}). \end{aligned}$$

On writing each term as the sum of its ionic contributions, the sodium and chloride contributions cancel, leaving $\lambda^\circ(\mathrm{H}^+) + \lambda^\circ(\mathrm{CH_3COO}^-)$. The limiting values of the strong electrolytes can be found by extrapolating their dilute-solution plots against $\sqrt{c}$ to zero concentration.

Step 5: Conclusion The cell is $\mathrm{Al} \mid \mathrm{Al}^{3+}(0.01\,M) \parallel \mathrm{Ni}^{2+}(0.1\,M) \mid \mathrm{Ni}$, and its emf is approximately $1.42\,\text{V}$ at $298\,\text{K}$. Molar conductivity decreases on increasing concentration for both electrolyte types, more sharply for a weak electrolyte. Its limiting value is obtained using Kohlrausch's law of independent ionic migration.

Quick Tip to Solve: Balance the half-reactions first to obtain six electrons, and omit solid Al and Ni from the reaction quotient.

26(a). Give equations of the following reactions:

(i) Phenol is treated with conc. HNO_3.

(ii) Propene is treated with B_2H_6 followed by H_2O_2/OH^-.

(iii) Sodium t-butoxide is treated with CH_3Cl.

(b) How will you distinguish between butan-1-ol and butan-2-ol?

(c) Arrange the following in increasing order of acidity:

Phenol, ethanol, water [5 marks]

Solution:

Concept:

- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution to the ortho and para positions. Concentrated nitric acid gives extensive nitration.
- Hydroboration followed by oxidation gives an anti-Markovnikov alcohol. Williamson ether synthesis forms an ether by nucleophilic substitution of a primary or methyl halide by an alkoxide ion.
- The iodoform test detects compounds containing the $CH_3CH(OH)-$ group because they are oxidised to methyl ketones. Acid strength increases with the stability of the conjugate base.

Step 1: (a)(i) Nitrate phenol with concentrated nitric acid Phenol reacts with concentrated nitric acid to give 2,4,6-trinitrophenol, also called picric acid. The three nitro groups replace the ring hydrogens at both ortho positions and the para position relative to the hydroxyl group:

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} \underset{\text{2,4,6-trinitrophenol}}{C_6H_2(NO_2)_3OH} + 3H_2O.$$

The hydroxyl group remains on the ring; this is nitration of the ring rather than replacement of the hydroxyl group.

Step 2: (a)(ii) Carry out hydroboration and oxidation of propene Diborane supplies borane for addition across the double bond. Boron attaches predominantly to the less substituted terminal carbon. Oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond by a carbon-oxygen bond, giving propan-1-ol:

$$CH_3CH{=}CH_2 \xrightarrow[\text{2. } H_2O_2/OH^-]{\text{1. } B_2H_6} CH_3CH_2CH_2OH.$$

Thus the hydroxyl group appears on carbon 1. The product is not propan-2-ol, which would correspond to Markovnikov hydration.

Step 3: (a)(iii) React sodium tert-butoxide with methyl chloride The tert-butoxide ion attacks the methyl carbon of methyl chloride and displaces chloride by an S_N2 reaction:

$$(CH_3)_3CONa + CH_3Cl \longrightarrow (CH_3)_3COCH_3 + NaCl.$$

The ether formed is 2-methoxy-2-methylpropane (methyl tert-butyl ether). Although the alkoxide is bulky, the halide is a methyl halide, so nucleophilic substitution gives the ether; methyl chloride has no beta carbon for elimination.

Step 4: (b) Distinguish the two alcohols using the iodoform test Warm separate samples with iodine

Quick Tip to Solve: For the alcohol test, locate the CH3CH(OH) group; for acidity, compare the stability of the anion formed after loss of H+.

and aqueous sodium hydroxide. Butan-2-ol gives a yellow precipitate of iodoform, CHI_3, whereas butan-1-ol gives no yellow precipitate. Butan-2-ol contains the required $CH_3CH(OH)-$ group and is first oxidised to butan-2-one, a methyl ketone. Its overall test reaction is

$$\begin{aligned} &CH_3CH(OH)CH_2CH_3 + 4I_2 + 6NaOH \\ &\longrightarrow CHI_3 \downarrow + CH_3CH_2COONa \\ &\quad + 5NaI + 5H_2O. \end{aligned}$$

Butan-1-ol is oxidised to an aldehyde without a methyl-ketone group and therefore does not give this test.

Step 5: (c) Compare the acidity using conjugate-base stability Removing a proton from ethanol, water and phenol produces ethoxide, hydroxide and phenoxide, respectively. The electron-releasing ethyl group increases electron density on oxygen and destabilises ethoxide relative to hydroxide. Ethanol is therefore less acidic than water. In phenoxide, the negative charge is delocalised by resonance over oxygen and the aromatic ring. This stabilisation makes phenol considerably more acidic than water or ethanol. Hence the increasing order of acidity is

$$\text{ethanol} < \text{water} < \text{phenol}.$$

Step 6: Conclusion (a) The products are (i) 2,4,6-trinitrophenol, (ii) propan-1-ol and (iii) 2-methoxy-2-methylpropane. (b) Butan-2-ol gives yellow iodoform with iodine and alkali; butan-1-ol does not. (c) Increasing acidity: $\text{ethanol} < \text{water} < \text{phenol}$.

Quick Tip to Solve: For the alcohol test, locate the CH3CH(OH) group; for acidity, compare the stability of the anion formed after loss of H+.

OR

26(b). (a) How can you obtain Phenol from (i) Cumene, (ii) Benzene sulphonic acid, (iii) Benzene diazonium chloride?

(b) Write the structure of the major product obtained from dinitration of 3-methylphenol.

(c) Write the reaction involved in Kolbe's reaction. [5 marks]

Solution:

Concept:

- Phenol is obtained by acidic cleavage of cumene hydroperoxide, alkaline fusion of a benzene sulphonate followed by acidification, or hydrolysis of a benzene diazonium salt.
- The $-OH$ group activates the aromatic ring and directs electrophilic substitution to its ortho and

Quick Tip to Solve: For meta-cresol, mark positions 2, 4 and 6 first, then exclude the crowded position 2 to locate the two nitro groups; remember to acidify both phenoxide and salicylate salts.

para positions. In 3-methylphenol, $-CH_3$ also favours positions 2, 4 and 6.

- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure; subsequent acidification gives salicylic acid, with $-COOH$ ortho to $-OH$.

Step 1: (a)(i) Prepare phenol from cumene Oxidise cumene (isopropylbenzene) with air to cumene hydroperoxide. Cleave the hydroperoxide in dilute acid to give phenol and acetone:

$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH,$$
$$C_6H_5C(CH_3)_2OOH \xrightarrow{H^+} C_6H_5OH + CH_3COCH_3.$$

The peroxide intermediate is essential: direct oxidation is followed by acid-catalysed cleavage, and acetone is the coproduct.

Step 2: (a)(ii) Prepare phenol from benzene sulphonic acid Neutralise the acid to sodium benzene sulphonate, fuse it with sodium hydroxide at about $623\,K$, then acidify the sodium phenoxide formed:

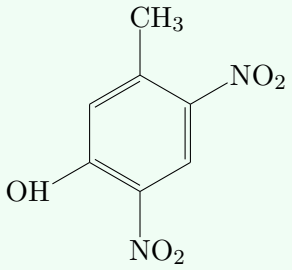
$$C_6H_5SO_3H + NaOH \longrightarrow C_6H_5SO_3Na + H_2O,$$
$$C_6H_5SO_3Na + 2NaOH \xrightarrow{623\,K} C_6H_5ONa + Na_2SO_3 + H_2O,$$
$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl.$$

Acidification is necessary because alkaline fusion produces the phenoxide salt rather than free phenol.

Step 3: (a)(iii) Prepare phenol from benzene diazonium chloride Warm the diazonium salt with water. Hydrolysis replaces the diazonium group by hydroxyl, with evolution of nitrogen:

$$C_6H_5N_2Cl + H_2O \xrightarrow{\text{warm}} C_6H_5OH + N_2\uparrow + HCl.$$

Step 4: (b) Identify the major dinitration product Number the phenol ring with hydroxyl at carbon 1 and methyl at carbon 3. Positions 2, 4 and 6 are favoured by both substituents. Position 2 lies between hydroxyl and methyl and is more sterically hindered; hence the two nitro groups enter positions 4 and 6. The product structure is:



This is $HO-C_6H_2(CH_3)(NO_2)_2$, with OH at 1, CH_3 at 3, and NO_2 at 4 and 6 (4,6-dinitro-3-methylphenol).

Step 5: (c) Write Kolbe's reaction Treat sodium phenoxide with carbon dioxide at about $400\,K$ under

Quick Tip to Solve: For meta-cresol, mark positions 2, 4 and 6 first, then exclude the crowded position 2 to locate the two nitro groups; remember to acidify both phenoxide and salicylate salts.

4–7 atm pressure. Acidify the resulting sodium salicylate:

$$C_6H_5ONa + CO_2 \xrightarrow[\text{pressure}]{400\,K} o\text{-}HOC_6H_4COONa,$$

$$o\text{-}HOC_6H_4COONa + HCl \longrightarrow o\text{-}HOC_6H_4COOH + NaCl.$$

The final product is salicylic acid (2-hydroxybenzoic acid).

Step 6: Conclusion Phenol is obtained through cumene hydroperoxide cleavage, alkaline fusion followed by acidification, and diazonium-salt hydrolysis respectively. Dinitration gives 4,6-dinitro-3-methylphenol. Kolbe's reaction gives salicylic acid after acidification.

Quick Tip to Solve: For meta-cresol, mark positions 2, 4 and 6 first, then exclude the crowded position 2 to locate the two nitro groups; remember to acidify both phenoxide and salicylate salts.

27(a). Account for the following:

(i) Tendency to show -3 oxidation state decreases from N to Bi in group 15.

(ii) Acidic character increases from H_2O to H_2Te.

(iii) F_2 is more reactive than ClF_3, whereas ClF_3 is more reactive than Cl_2.

(b) Draw the structure of (i) XeF_2, (ii) $H_4P_2O_7$. [5 marks]

Solution:

Concept:

- Down a group, atomic size generally increases and electronegativity decreases. These trends affect the tendency to accept electrons and hence to exhibit negative oxidation states.
- The acidity of group 16 hydrides depends strongly on the strength of the $H-E$ bond, where E is the group 16 element. A weaker bond makes proton release easier.
- Molecular reactivity depends on bond strength as well as electronegativity. VSEPR theory predicts molecular shape from the number of bonding pairs and lone pairs around the central atom.

Step 1: (a)(i) Explain the decreasing tendency for the -3 oxidation state Group 15 elements have the valence-shell configuration ns^2np^3. They can complete an octet by gaining three electrons or by sharing electrons with more electropositive atoms. From nitrogen to bismuth, atomic size increases and electronegativity decreases, while metallic character increases. Thus the tendency to attract electrons and form compounds in which the group 15 atom has oxidation state -3 decreases down the group. Nitrogen shows this state readily, for example in NH_3, whereas it is much less characteristic of bismuth.

Step 2: (a)(ii) Explain the increasing acidic character of the hydrides From oxygen to tellurium, the size of the central atom increases. Consequently the $H-E$ bond becomes longer and its bond dissociation enthalpy decreases. Breaking this bond to release a proton therefore becomes easier down the group. This bond-strength effect outweighs the decrease in electronegativity of the central atom, so the acidic character follows

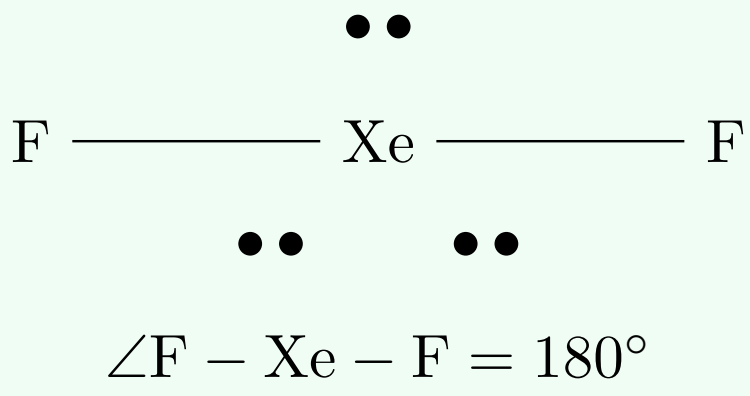
$$H_2O < H_2S < H_2Se < H_2Te.$$

Quick Tip to Solve: For hydride acidity compare H-E bond strengths; for XeF2 count two bonds plus three lone pairs, and for H4P2O7 check that the drawing contains four OH groups and one bridging oxygen.

Water holds its hydrogen atoms most strongly; hydrogen telluride releases a proton most readily among these hydrides.

Step 3: (a)(iii) Compare the reactivities of fluorine, chlorine trifluoride and chlorine Fluorine has the highest electronegativity, and its $F - F$ bond is unusually weak because the small fluorine atoms bring their lone pairs close together, causing strong lone-pair repulsions. Its bond is therefore readily broken, and F_2 is exceptionally reactive, more so than ClF_3. Interhalogens such as ClF_3 are generally more reactive than the constituent halogens other than fluorine: their polar bonds between dissimilar halogen atoms are weaker and more readily broken than the corresponding $Cl - Cl$ bond. Consequently ClF_3 is more reactive than Cl_2, giving the printed comparison $F_2 > ClF_3 > Cl_2$ in reactivity.

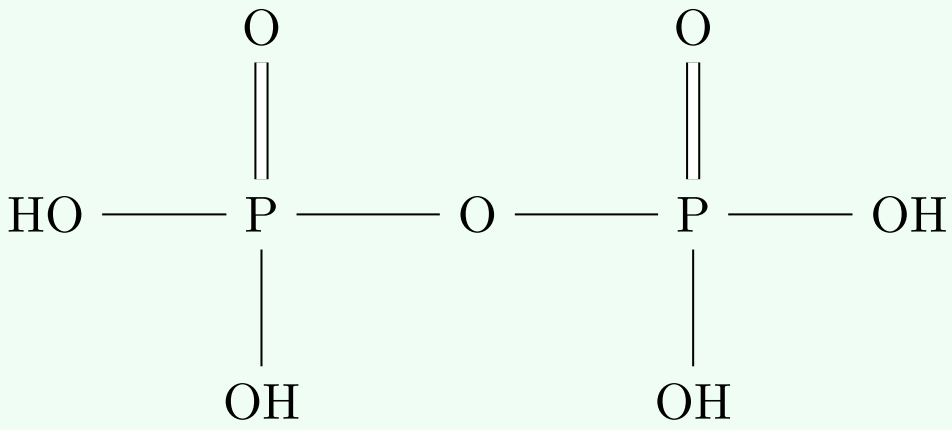
Step 4: (b)(i) Draw the structure of xenon difluoride Xenon has eight valence electrons. In XeF_2, it forms two single bonds and retains three lone pairs, giving five electron-pair domains. The electron-pair arrangement is trigonal bipyramidal. All three lone pairs occupy equatorial positions, where they experience fewer close repulsions, and the two fluorine atoms occupy the axial positions. Hence the molecule is linear with $\angle F - Xe - F = 180°$; its conventional hybridisation description is sp^3d. The diagram shows the three central-atom lone pairs schematically; each terminal fluorine also has three lone pairs.



Linear XeF2; the three xenon lone pairs occupy equatorial sites (schematic).

Step 5: (b)(ii) Draw the structure of pyrophosphoric acid Pyrophosphoric acid, $H_4P_2O_7$, consists of two phosphorus centres connected by one bridging oxygen atom, giving a $P - O - P$ linkage. Each phosphorus has one terminal $P = O$ bond, two $P - OH$ groups and one bond to the bridging oxygen. The four hydrogen atoms are all attached to oxygen, so the acid has four ionisable $O - H$ hydrogens. Each phosphorus has an approximately tetrahedral arrangement of its four oxygen neighbours. The structural formula below displays all seven oxygen atoms and all four hydroxyl groups explicitly.

Quick Tip to Solve: For hydride acidity compare H-E bond strengths; for XeF2 count two bonds plus three lone pairs, and for H4P2O7 check that the drawing contains four OH groups and one bridging oxygen.



Structure of H4P2O7 showing the P-O-P bridge and four hydroxyl groups.

Step 6: Conclusion The -3 oxidation-state tendency decreases because electronegativity decreases down group 15. Hydride acidity increases because the $H-E$ bond weakens down group 16. Weak bonds and fluorine's exceptionally high electronegativity explain $F_2 > ClF_3 > Cl_2$ in reactivity. XeF_2 is linear with three equatorial lone pairs on xenon; $H_4P_2O_7$ has the structure $(HO)_2P(=O)-O-P(=O)(OH)_2$.

Quick Tip to Solve: For hydride acidity compare H-E bond strengths; for XeF2 count two bonds plus three lone pairs, and for H4P2O7 check that the drawing contains four OH groups and one bridging oxygen.

OR

27(b). (a) Give one example to show the anomalous reaction of fluorine.

(b) What is the structural difference between white phosphorus and red phosphorus?

(c) What happens when XeF_6 reacts with NaF?

(d) Why is H_2S a better reducing agent than H_2O?

(e) Arrange the following acids in the increasing order of their acidic character: HF, HCl, HBr and HI [5 marks]

Solution:

Concept:

- Fluorine is the most electronegative element and a powerful oxidising agent. Its small size and unusually weak F–F bond contribute to its anomalous behaviour among the halogens.
- Allotropes differ in the arrangement and bonding of atoms. White phosphorus contains discrete tetrahedral P_4 molecules, whereas red phosphorus has a polymeric network of linked phosphorus units.
- A fluoride-ion acceptor acts as a Lewis acid. The ease of breaking an element–hydrogen bond influences both hydride reducing power and the strength of binary acids in water.

Step 1: (a) An anomalous reaction of fluorine Fluorine oxidises water to oxygen, whereas chlorine

Quick Tip to Solve: For hydride trends down a group, compare bond strengths first: weaker bonds favour both proton release and reducing behaviour.

and bromine react with water to form the corresponding hydrohalic and hypohalous acids. A suitable example is

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2.$$

Here oxygen in water changes from oxidation state -2 to 0; fluorine changes from 0 to -1. Thus fluorine's strong oxidising action gives a reaction different from the usual halogen reaction with water.

Step 2: (b) Structures of white and red phosphorus White phosphorus consists of separate P_4 molecules. In each tetrahedron, a phosphorus atom is bonded to the other three phosphorus atoms; the small bond angles cause considerable strain. Red phosphorus has a polymeric structure in which phosphorus tetrahedral units are linked through P–P bonds to form an extended network. Thus white phosphorus is molecular, while red phosphorus is polymeric rather than a collection of isolated P_4 molecules.

Step 3: (c) Reaction of xenon hexafluoride with sodium fluoride Xenon hexafluoride accepts a fluoride ion from sodium fluoride, forming sodium heptafluoroxenate(VI):

$$XeF_6 + NaF \longrightarrow Na^+[XeF_7]^-.$$

The xenon atom remains in oxidation state $+6$. This is fluoride-ion addition: XeF_6 acts as the Lewis acid and F^- as the Lewis base.

Step 4: (d) Relative reducing power of hydrogen sulphide and water Sulphur is larger than oxygen, so overlap with hydrogen is poorer and the S–H bond is weaker than the O–H bond. Therefore H_2S is less thermally stable and more readily undergoes oxidation than H_2O. Sulphur in H_2S, initially at oxidation state -2, can readily be oxidised to elemental sulphur. For example,

$$H_2S + Cl_2 \longrightarrow 2HCl + S.$$

The easier oxidation of hydrogen sulphide makes it the better reducing agent.

Step 5: (e) Increasing acidic character of the hydrogen halides Down the halogen group, the halogen atom becomes larger, the H–X bond becomes longer and its bond dissociation enthalpy decreases. Release of a proton therefore becomes easier from HF to HI. Although fluorine is the most electronegative halogen, the very strong H–F bond makes HF the weakest acid in this series; bond weakening down the group controls the trend.

Step 6: Conclusion (a) $2F_2 + 2H_2O \rightarrow 4HF + O_2$. (b) White phosphorus has discrete tetrahedral P_4 molecules; red phosphorus is polymeric. (c) $Na[XeF_7]$ is formed. (d) The weaker S–H bond makes H_2S easier to oxidise. (e) The increasing order is $\boxed{HF < HCl < HBr < HI}$.

Quick Tip to Solve: For hydride trends down a group, compare bond strengths first: weaker bonds favour both proton release and reducing behaviour.