CBSE Class 12 Chemistry Question Paper 2019 with Solution PDF-Set 56-2-3

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

Solution:

Concept:

- Nucleophilic substitution replaces a halogen atom by a nucleophile.
- Resonance in an aryl halide gives its carbon–halogen bond partial double-bond character.

Step 1: Compare the carbon–chlorine bonds In chlorobenzene, a lone pair on chlorine interacts with the benzene ring. Consequently, the $\mathrm{C-Cl}$ bond has partial double-bond character and is shorter and stronger than an ordinary single bond.

Step 2: Apply this to substitution Cyclohexyl chloride has chlorine attached to an sp^3-hybridised carbon through an ordinary single bond. This bond is more readily broken than the strong bond to the sp^2-hybridised carbon in chlorobenzene, so replacement of chlorine is easier under comparable conditions.

Step 3: Conclusion Cyclohexyl chloride is more reactive towards nucleophilic substitution because chlorobenzene has a stronger $\mathrm{C-Cl}$ bond with partial double-bond character.

Quick Tip to Solve: Check whether chlorine is bonded directly to an aromatic ring: resonance then makes substitution more difficult.

2. Arrange the following in decreasing order of solubility in water:
$(C_2H_5)_2NH$, $C_2H_5NH_2$, $C_6H_5NH_2$ [1 mark]

Solution:

Concept:

- Water solubility depends on hydrogen bonding with water and on the size of the hydrophobic hydrocarbon group.
- A larger nonpolar group reduces solubility, even when the nitrogen atom can hydrogen-bond.

Step 1: Compare the aliphatic amines Ethylamine, $\mathrm{C_2H_5NH_2}$, has two $\mathrm{N-H}$ bonds and only one ethyl group. Diethylamine, $\mathrm{(C_2H_5)_2NH}$, has one $\mathrm{N-H}$ bond and two ethyl groups. Ethylamine therefore hydrogen-bonds well with water while having the smaller hydrophobic portion.

Step 2: Compare with aniline Aniline, $\mathrm{C_6H_5NH_2}$, contains a large hydrophobic phenyl group. Its solubility in water is lower than that of either of these small aliphatic amines. All three can interact with water, but their hydrocarbon portions differ substantially.

Step 3: Conclusion The decreasing order is

$$\mathrm{C_2H_5NH_2} > \mathrm{(C_2H_5)_2NH} > \mathrm{C_6H_5NH_2}.$$

Quick Tip to Solve: Compare the size of the nonpolar group as well as the number of N–H bonds; the phenyl group makes aniline least soluble here.

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

Solution:

Concept:

- A colloid is classified by the physical states of its dispersed phase and dispersion medium.
- An aerosol has a gas as its dispersion medium; its dispersed particles may be solid or liquid.

Step 1: Identify the two phases The question specifies that the dispersed phase is a solid and that the dispersion medium is a gas. The gas is the continuous phase in which the small solid particles remain dispersed; this is the solid-in-gas class of colloids.

Step 2: Choose an example with matching phases Smoke contains fine solid particles, such as soot, dispersed in air. It is therefore a suitable example. Fog, by contrast, consists of liquid droplets dispersed in air and would not be an example of the solid-in-gas case asked here.

Step 3: Conclusion A solid dispersed in a gas forms a solid aerosol; an example is smoke (solid soot particles dispersed in air).

Quick Tip to Solve: Name both phases before choosing the example: smoke is solid in gas, while fog is liquid in gas.

4(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 missing cations and anions from their normal lattice sites.
- It is favoured in ionic crystals whose cations and anions have comparable sizes and high coordination numbers.

Step 1: Identify the suitable crystal In KCl, the K^+ and Cl^- ions have comparatively similar sizes and the crystal has a high coordination number. These features favour vacancies of both kinds of ions rather than movement of the cation into an interstitial site.

Step 2: Explain the defect and the comparison An equal number of potassium and chloride ions are absent from their lattice sites in a Schottky defect, preserving electrical neutrality. In AgCl, the relatively small silver ion favours a Frenkel defect, in which a cation leaves its site and occupies an interstitial position.

Step 3: Conclusion KCl shows Schottky defect because its oppositely charged ions have comparable sizes and its coordination number is high.

Quick Tip to Solve: Use comparable ion sizes to identify Schottky defects; a small cation moving into an interstitial site indicates a Frenkel defect.

OR

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

Solution:

Concept:

- Heating zinc oxide can produce a metal-excess defect through loss of oxygen.
- Electrons trapped in the solid compensate for the charge imbalance and produce its colour.

Step 1: Explain oxygen loss on heating On heating, ZnO loses a small amount of oxygen and becomes non-stoichiometric. This is represented schematically by

$$\mathrm{ZnO} \xrightarrow{\text{heat}} \mathrm{Zn^{2+}} + \tfrac{1}{2}\mathrm{O_2} + 2\mathrm{e^-}.$$

The equation describes defect formation in the crystal; it does not imply complete decomposition of the sample.

Step 2: Connect the defect to colour The excess zinc ions occupy interstitial sites, with electrons also accommodated in neighbouring interstitial sites to maintain electrical neutrality. These trapped electrons absorb visible light, giving hot zinc oxide its characteristic yellow appearance.

Step 3: Conclusion ZnO appears yellow on heating because oxygen loss produces a metal-excess defect and trapped electrons that absorb visible light.

Quick Tip to Solve: For hot ZnO, connect the colour with oxygen loss and trapped electrons in a metal-excess defect.

5(a). What is the difference between amylose and amylopectin? [1 mark]

Solution:

Concept:

- Amylose and amylopectin are the two glucose polymers that constitute starch.
- The position of glycosidic linkages determines whether the glucose chain remains linear or becomes branched.

Step 1: Describe amylose Amylose is an unbranched polymer of α-D-glucose. Its glucose units are joined mainly through $\alpha(1 \to 4)$ glycosidic linkages, producing a long chain that can adopt a helical form.

Step 2: Describe amylopectin and its branches Amylopectin is a branched polymer of α-D-glucose. Within each chain, the units are linked by $\alpha(1 \to 4)$ bonds, while $\alpha(1 \to 6)$ glycosidic linkages occur at the branching points. Thus the structural difference is the presence of these branch connections in amylopectin.

Step 3: Conclusion Amylose is unbranched with $\alpha(1 \to 4)$ linkages; amylopectin is branched, with additional $\alpha(1 \to 6)$ linkages at branch points.

Quick Tip to Solve: Remember that both have alpha-1,4 links; alpha-1,6 branch links distinguish amylopectin.

OR

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

Solution:

Concept:

- Lactose is a disaccharide composed of one D-galactose unit and one D-glucose unit.
- Hydrolysis adds water across the glycosidic bond, releasing the constituent monosaccharides.

Step 1: Identify the units joined in lactose Lactose contains D-galactose and D-glucose joined by a $\beta(1 \rightarrow 4)$ glycosidic linkage. Hydrolysis cleaves this linkage without changing the identity of the two sugar units.

Step 2: Write the hydrolysis reaction In the presence of an acid catalyst or the enzyme lactase, lactose reacts with water as follows:

$$\underset{\text{lactose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{D-galactose}}{C_6H_{12}O_6} + \underset{\text{D-glucose}}{C_6H_{12}O_6}.$$

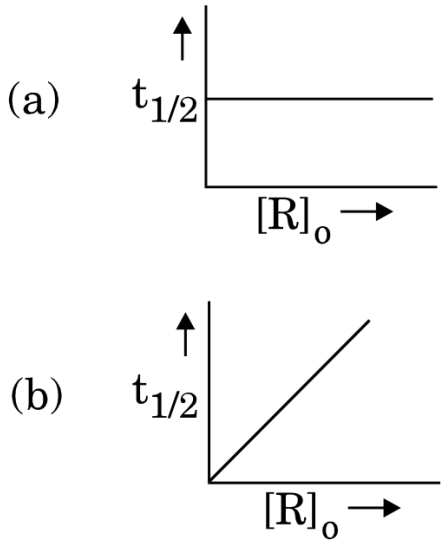
One molecule of each monosaccharide is formed per molecule of lactose hydrolysed.

Step 3: Conclusion The products obtained on hydrolysis of lactose are D-galactose and D-glucose in equimolar amounts.

Quick Tip to Solve: Associate lactose with galactose plus glucose; fructose is a constituent of sucrose, not lactose.

Section B (14 marks)

6. 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:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- For a rate law $r = k[A]^m[B]^n$, the overall order is $m + n$; k is the rate constant. Half-life is the time needed for concentration to fall to half its initial value.

Step 1: Define order and interpret graph (a) Order is determined from the rate law, not from the coefficients of the balanced chemical equation. In graph (a), the horizontal line shows that $t_{1/2}$ remains constant as $[R]_0$ changes. For a first-order reaction,

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

This expression contains no initial-concentration term and therefore matches the horizontal graph.

Step 2: Interpret graph (b) Graph (b) is a straight line through the origin: the half-life is directly proportional to initial concentration. For a zero-order reaction, $[R] = [R]_0 - kt$. Putting $[R] = [R]_0/2$ gives

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

Thus its plot against $[R]_0$ is linear, with positive slope $1/(2k)$, as shown.

Step 3: Conclusion Order is the sum of concentration exponents in the rate law. Graph (a): first order. Graph (b): zero order.

Quick Tip to Solve: Check whether half-life is constant or grows with initial concentration: constant means first order; direct proportionality means zero order.

7. Give reasons:

(a) An increase in temperature is observed on mixing chloroform and acetone.

(b) Aquatic animals are more comfortable in cold water than in warm water. [2 marks]

Solution:

Concept:

- Mixing releases heat when the new intermolecular attractions are stronger than the attractions in the separate liquids; then $\Delta H_{\text{mix}} < 0$.
- The solubility of gases in water generally decreases with increasing temperature. Dissolved oxygen supports respiration of aquatic animals.

Step 1: (a) Explain the temperature increase The hydrogen atom of chloroform, $CHCl_3$, can form a hydrogen bond with the oxygen atom of the carbonyl group of acetone, CH_3COCH_3. These unlike-molecule attractions are stronger than the corresponding attractions in the pure liquids. Energy released on forming the new attractions exceeds the energy needed to separate the original molecules. Mixing is therefore exothermic, so the temperature rises. The mixture also shows negative deviation from Raoultś law.

Step 2: (b) Explain why cold water is more comfortable At the same oxygen partial pressure, cold water dissolves more oxygen than warm water. As temperature increases, the solubility of oxygen decreases. Hence aquatic animals have a greater supply of dissolved oxygen for respiration in cold water, making the environment more comfortable for them.

Step 3: Conclusion (a) Strong hydrogen bonding between chloroform and acetone makes mixing exothermic. (b) Cold water contains more dissolved oxygen for aquatic respiration.

Quick Tip to Solve: Link the two observations to different causes: heat of mixing to stronger attractions, and aquatic comfort to dissolved oxygen solubility.

8. 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:

- Chromite is oxidised in alkaline fusion to yellow chromate, containing chromium in oxidation state $+6$.
- Acidification converts chromate to dichromate: $2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$. Acidified dichromate oxidises sulphite to sulphate.

Step 1: Identify the products of fusion and acidification Fusion of chromite with sodium carbonate in

Quick Tip to Solve: Follow the sequence yellow chromate, orange dichromate, potassium dichromate; an oxidant changes sulphite into sulphate.

air gives sodium chromate, so $A = Na_2CrO_4$, the yellow compound. The balanced fusion equation is

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

Acidification shifts chromate to dichromate, giving sodium dichromate: $B = Na_2Cr_2O_7$.

Step 2: Identify the potassium salt and oxidation product Adding potassium chloride to sodium dichromate gives orange potassium dichromate:

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

Thus $C = K_2Cr_2O_7$. Its acidified solution oxidises sulphite to sulphate, while chromium is reduced from $+6$ to $+3$:

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

Therefore the product derived from sodium sulphite is sodium sulphate, $D = Na_2SO_4$.

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 sequence yellow chromate, orange dichromate, potassium dichromate; an oxidant changes sulphite into sulphate.

9(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, $Ca(OH)_2$, to form bleaching powder, conventionally represented as $CaOCl_2$.
- Sulphur dioxide is a reducing agent: it reduces Fe^{3+} to Fe^{2+}, while sulphur is oxidised from $+4$ to $+6$.

Step 1: (a) Chlorine through slaked lime The balanced equation for the preparation of bleaching powder is

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

The calcium oxychloride formula is the conventional school-level representation of bleaching powder. There is one calcium atom, two chlorine atoms, two oxygen atoms and two hydrogen atoms on each side; no further coefficient is required.

Step 2: (b) Sulphur dioxide through an Fe(III) salt solution The equation can be written in ionic form, since the salt anion is not specified:

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

Quick Tip to Solve: When a salt anion is unspecified, use the balanced ionic equation and check both atoms and total charge.

Each iron(III) ion accepts one electron, and sulphur dioxide loses two electrons on oxidation to sulphate, so two iron(III) ions are needed. The total charge is $+6$ on each side and all atoms are balanced.

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: When a salt anion is unspecified, use the balanced ionic equation and check both atoms and total charge.

OR

9(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 to prepare poisonous compounds such as phosgene and mustard gas.
- Ammonia donates its nitrogen lone pair to Cu^{2+}, acting as a ligand. The copper(II) ammine complex has a characteristic deep blue colour.

Step 1: (a) Name two poisonous gases Two poisonous gases prepared using chlorine are phosgene, $COCl_2$, and mustard gas, $(ClCH_2CH_2)_2S$. Phosgene is carbonyl dichloride; mustard gas is bis(2-chloroethyl) sulphide. These names identify two distinct chlorine-containing poisonous substances.

Step 2: (b) Explain the blue colour with ammonia In aqueous solution copper(II) is present as hydrated copper ions. In excess ammonia, ammonia molecules replace water ligands to produce the intensely blue tetraammine complex, commonly represented in solution as $[Cu(NH_3)_4(H_2O)_2]^{2+}$:

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

Ammonia changes the ligand environment and hence the splitting of copperś partially filled d orbitals. Absorption of visible light by this complex gives its characteristic deep blue appearance.

Step 3: Conclusion (a) Phosgene and mustard gas. (b) Ammonia forms the deep blue tetraamminecopper(II) complex with Cu^{2+}.

Quick Tip to Solve: For copper with excess ammonia, name the deep blue ammine complex and distinguish complex formation from merely mixing coloured solutions.

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

(a) Polydentate ligand

(b) Homoleptic complex [2 marks]

Solution:

Concept:

- A ligand donates an electron pair through a donor atom to a central metal atom or ion. Denticity counts the donor atoms of one ligand that can bind to the same metal.
- A homoleptic complex contains only one kind of ligand; its coordination number may still be greater than one.

Step 1: Define a polydentate ligand and identify its donor sites A polydentate ligand is a ligand capable of coordinating to the same central metal atom or ion through several donor atoms. A suitable example is ethylenediaminetetraacetate, $EDTA^{4-}$, a hexadentate ligand. It can bind through two nitrogen donor atoms and four oxygen donor atoms, forming six coordinate bonds to one metal ion. Thus its denticity is six; the count refers to donor sites, not to the ligand's charge.

Step 2: Define a homoleptic complex and give an example A homoleptic complex is a coordination entity in which the central metal atom or ion is bonded to only one type of ligand. For example, $[Co(NH_3)_6]^{3+}$ is homoleptic because all six ligands are ammonia molecules. The six metal-ligand bonds do not make it heteroleptic: a heteroleptic complex would contain two or more different ligand types.

Step 3: Conclusion (a) A polydentate ligand binds through several donor atoms; $EDTA^{4-}$ is hexadentate. (b) A homoleptic complex has only one ligand type, as in $[Co(NH_3)_6]^{3+}$.

Quick Tip to Solve: Count donor atoms within one ligand for denticity, but count different ligand types in the whole complex for homoleptic character.

OR

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

(a) Potassium tri(oxalato)chromate(III)

(b) Hexaaquamanganese(II) sulphate [2 marks]

Solution:

Concept:

- The formula of a coordination compound must be electrically neutral. Put the coordination entity inside square brackets and counterions outside them.
- Oxalato is $C_2O_4{}^{2-}$; aqua is neutral H_2O. A Roman numeral gives the oxidation state of the metal, rather than the charge on the whole complex.

Step 1: Balance the charge of the trioxalatochromate ion Chromium(III) has oxidation state $+3$. The prefix tri indicates three oxalato ligands, each with charge -2. Therefore the charge of the

Quick Tip to Solve: First calculate the bracketed ion's charge from metal and ligands; then choose the smallest counterion ratio that makes the compound neutral.

coordination anion is

$$+3 + 3(-2) = -3.$$

Three potassium ions, each K^+, are required to neutralise this anion. The formula of potassium tri(oxalato)chromate(III) is consequently $K_3[Cr(C_2O_4)_3]$. The ligand formula is enclosed in parentheses before attaching the subscript three.

Step 2: Combine the hexaaquamanganese cation with sulphate Manganese(II) contributes charge $+2$, while each of the six water ligands is neutral. Thus the coordination entity is $[Mn(H_2O)_6]^{2+}$. Sulphate is ${SO_4}^{2-}$, so one sulphate ion balances one coordination cation. The formula is $[Mn(H_2O)_6]SO_4$; sulphate lies outside the brackets because it is the counterion, not an aqua ligand.

Step 3: Conclusion (a) $K_3[Cr(C_2O_4)_3]$. (b) $[Mn(H_2O)_6]SO_4$.

Quick Tip to Solve: First calculate the bracketed ion's charge from metal and ligands; then choose the smallest counterion ratio that makes the compound neutral.

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:

- Paramagnetism arises from unpaired electrons; an entity with all electrons paired is diamagnetic. Hybridisation describes bonding geometry and alone does not determine magnetic behaviour.
- In an octahedral field, the lower t_{2g} and upper e_g levels are separated by Δ_o. Compare this splitting with pairing energy P to decide whether electrons pair or occupy the higher level.

Step 1: Count the nickel d electrons in each complex Nickel has atomic number 28 and ground-state configuration $[Ar]3d^8 4s^2$. In $[NiCl_4]^{2-}$, four chloride ions contribute charge -4, so nickel is Ni^{2+}, with configuration $3d^8$. Chloride is a weak-field ligand, and the tetrahedral complex retains two unpaired d electrons. It is therefore paramagnetic. In $[Ni(CO)_4]$, neutral CO ligands leave nickel in oxidation state zero. In the carbonyl complex the electrons are paired to give a filled $3d^{10}$ set; the vacant $4s$ and three $4p$ orbitals form sp^3 hybrids. It has no unpaired electrons and is diamagnetic. Both complexes are tetrahedral, although their d-electron populations differ.

Step 2: Fill the octahedral levels for five d electrons For $\Delta_o < P$, promotion costs less energy than pairing, so the five electrons first occupy all five d orbitals singly. The high-spin configuration is

$$t_{2g}^3 e_g^2.$$

For $\Delta_o > P$, pairing in the lower set costs less than occupying the upper set. All five electrons enter

Quick Tip to Solve: Find nickel's oxidation state before counting d electrons; for octahedral d5, weak field gives five unpaired electrons and strong field gives one.

the three t_{2g} orbitals, giving the low-spin configuration

$$t_{2g}^5 e_g^0.$$

The high-spin state has five unpaired electrons; the low-spin state has one.

Step 3: Conclusion (a) $[NiCl_4]^{2-}$ has two unpaired electrons and is paramagnetic, whereas $[Ni(CO)_4]$ has all electrons paired and is diamagnetic. (b) The configurations are $t_{2g}^3 e_g^2$ for $\Delta_o < P$ and $t_{2g}^5 e_g^0$ for $\Delta_o > P$.

Quick Tip to Solve: Find nickel's oxidation state before counting d electrons; for octahedral d5, weak field gives five unpaired electrons and strong field gives one.

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

(a) $CH_3CH_2OH \xrightarrow{PCC} A \xrightarrow{CH_3OH\,/\,\text{dry HCl (g)}} B$

(b) $C_6H_5COCH_3 \xrightarrow{NaOI} A + B$ [2 marks]

Solution:

Concept:

- PCC oxidises a primary alcohol to an aldehyde. In dry acidic medium, an aldehyde reacts with two molecules of an alcohol to form an acetal.
- A methyl ketone, containing the group $-COCH_3$, undergoes the iodoform reaction with sodium hypoiodite, giving a carboxylate salt and CHI_3.

Step 1: Identify the oxidation product and its acetal In part (a), ethanol is a primary alcohol. PCC oxidises its $-CH_2OH$ group to $-CHO$, so compound A is ethanal, with condensed structure $CH_3-CH=O$. PCC stops at the aldehyde under the stated conditions. Methanol and dry hydrogen chloride then convert the carbonyl group into an acetal:

$$CH_3CHO + 2\,CH_3OH \xrightarrow{\text{dry HCl}} CH_3CH(OCH_3)_2 + H_2O.$$

Thus B has structure $CH_3-CH(OCH_3)-OCH_3$, namely 1,1-dimethoxyethane. Both methoxy groups are attached to the former carbonyl carbon.

Step 2: Apply the iodoform reaction to acetophenone In part (b), acetophenone $C_6H_5COCH_3$ is a methyl ketone. Sodium hypoiodite replaces the three hydrogens of its carbonyl-adjacent methyl group by iodine; cleavage then gives the benzoate ion and iodoform. The overall equation is

$$C_6H_5COCH_3 + 3\,NaOI \longrightarrow C_6H_5COONa + CHI_3 + 2\,NaOH.$$

The two products are sodium benzoate, whose condensed structure is $C_6H_5-C(=O)O^-\,Na^+$, and iodoform, $H-C(I)_3$. Since no acidification is specified, the carboxyl product remains the sodium salt rather than benzoic acid. Assign A to sodium benzoate and B to iodoform; the printed A + B denotes these two co-products.

Step 3: Conclusion (a) A: CH_3CHO; B: $CH_3CH(OCH_3)_2$. (b) A: C_6H_5COONa; B: CHI_3.

Quick Tip to Solve: Dry methanol and acid convert an aldehyde into its dimethyl acetal; NaOI cleaves a methyl ketone into a carboxylate salt and iodoform.

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:

- For an empirical rate law, $r = k[A]^m[B]^n$, r is the rate of formation of C, k is the rate constant, and m, n are the orders in A and B. Orders are obtained from experiments, not from stoichiometric coefficients.
- Compare runs with one concentration fixed. A single rate law must give the same k from every experiment at the same temperature.

Step 1: (a) Determine the order in A Compare experiments 3 and 1, where $[B] = 0.3\,\text{M}$ is unchanged. Then

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

Thus the comparison gives $m = 2$. Doubling A quadruples the measured rate.

Step 2: (a) Determine the order in B Compare experiments 4 and 2, where $[A] = 0.1\,\text{M}$ remains fixed:

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

This comparison gives $n = 1$.

Step 3: (b) Write the inferred rate law The two controlled comparisons imply $r = k[A]^2[B]$, whose overall order is $2 + 1 = 3$. The coefficient 2 of B in the reaction does not set its experimental order.

Step 4: (c) Calculate and check the rate constant Using experiment 2,

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

Experiment 4 also gives $6.0\,\text{M}^{-2}\,\text{min}^{-1}$. However, checking the other printed runs gives

$$k_1 = \frac{0.042}{(0.2)^2(0.3)} = 3.5, \qquad k_3 = \frac{0.168}{(0.4)^2(0.3)} = 3.5,$$

in the same units. Therefore the printed table is internally inconsistent with a single rate constant for

Quick Tip to Solve: Use runs 1 and 3 for A and runs 2 and 4 for B, then check k in every run to expose inconsistent rate data.

this rate law; it does not justify reporting one common numerical k for all four experiments.

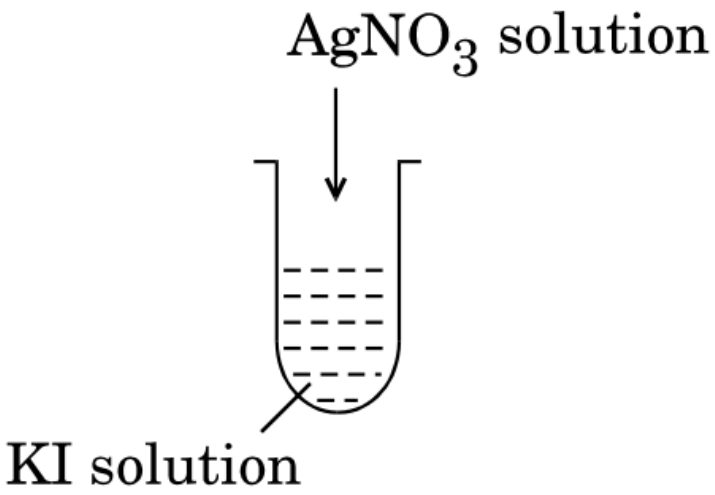
Step 5: Conclusion The comparisons give order 2 in A, order 1 in B and overall order 3, with inferred law $r = k[A]^2[B]$. Runs 2 and 4 give $k = 6.0\,\text{M}^{-2}\,\text{min}^{-1}$, whereas runs 1 and 3 give $3.5\,\text{M}^{-2}\,\text{min}^{-1}$; no single k fits the entire printed table.

Quick Tip to Solve: Use runs 1 and 3 for A and runs 2 and 4 for B, then check k in every run to expose inconsistent rate data.

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

(b) Why does physisorption decrease with increase in temperature?

(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:

- The dispersed phase is the substance distributed as small particles or droplets; the dispersion medium is the continuous phase in which they are distributed.
- Physisorption uses weak van der Waals attractions and is exothermic. A sol preferentially adsorbs the ion common to its particles that is present in excess.

Step 1: (a) Identify the phases in butter Butter has small water droplets dispersed in a continuous fat phase. Therefore its dispersed phase is liquid (water) and its dispersion medium is solid (fat). In the usual school classification it is a gel: liquid dispersed in solid. Identifying the droplets first avoids reversing the two phases.

Step 2: (b) Explain the temperature dependence Physical adsorption releases heat, so it can be represented as gas plus surface in equilibrium with adsorbed gas plus heat. Raising temperature favours the reverse, endothermic process by Le Chatelier's principle. Adsorbed molecules also acquire more kinetic energy and escape the surface more readily, since van der Waals attractions are weak. Consequently the extent of physisorption decreases as temperature increases.

Quick Tip to Solve: Read the solution already in the test tube: KI supplies excess iodide, so the AgI particles acquire a negative charge.

Step 3: (c) Determine the charge and representation of the sol The figure shows $AgNO_3$ solution being added to KI solution already in the test tube. The reaction is

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

Since KI is the surrounding solution in excess, the freshly formed AgI particles preferentially adsorb iodide ions, I^-. Their charge is therefore negative. The charged particle is represented as AgI/I^-, or $[AgI]I^-$; K^+ ions act as counter-ions in the surrounding medium. It is the excess iodide in this arrangement that fixes the sign of the sol.

Step 4: Conclusion (a) Dispersed phase: liquid water; dispersion medium: solid fat. (b) Physisorption is exothermic, so heating favours desorption. (c) The AgI sol is negatively charged and is represented as AgI/I^-, with K^+ counter-ions.

Quick Tip to Solve: Read the solution already in the test tube: KI supplies excess iodide, so the AgI particles acquire a negative charge.

15. 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:

- Osmotic pressure obeys $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature. Isotonic solutions at equal temperature have equal iC.
- Urea is a non-electrolyte with $i = 1$. For $KCl \rightarrow K^+ + Cl^-$, each dissociated formula unit produces two ions, so $i = 1 + \alpha$, where α is the fraction dissociated.

Step 1: Calculate the molar concentrations Each solution occupies $100\,\text{mL} = 0.100\,\text{L}$; the given masses are masses of solute in this volume. Thus

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

Equal volumes do not imply equal osmotic pressures unless the effective number of solute particles is also equal.

Step 2: Use the isotonic condition Equating the two osmotic pressures at the same temperature cancels R and T:

$$i_{KCl}C_{KCl} = C_{urea}, \qquad i_{KCl} = \frac{(3/60)}{(1.9/74.5)} = 1.960526.$$

Urea contributes one particle per molecule, while KCl contributes more particles because it dissociates.

Step 3: Relate the particle factor to dissociation Starting with one mole of KCl, $1 - \alpha$ mole remains undissociated, and α mole each of potassium and chloride ions forms. Total solute particles are

Quick Tip to Solve: With equal 100 mL volumes, divide the urea moles by the KCl moles to find i directly, then use alpha = i - 1.

therefore $(1-\alpha)+\alpha+\alpha = 1+\alpha$ mole. Hence

$$\alpha = i - 1 = 1.960526 - 1 = 0.960526.$$

Multiplication by 100 converts the fraction into percentage dissociation. The value lies between zero and one, as required for a physical fraction.

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

Quick Tip to Solve: With equal 100 mL volumes, divide the urea moles by the KCl moles to find i directly, then use alpha = i - 1.

16. 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:

- The density of a crystalline element is $\rho = ZM/(N_A V)$, where Z is the effective number of atoms per unit cell, M is molar mass, V is unit-cell volume and N_A is Avogadro's constant.
- A simple cubic cell contains one atom, a body-centred cubic cell contains two atoms and a face-centred cubic cell contains four atoms, after accounting for sharing of atoms between neighbouring cells.

Step 1: Express the number of atoms in terms of the data One atom of X has mass M/N_A; therefore a cell containing Z atoms has mass ZM/N_A. Dividing this mass by the cell volume gives the density relation. Rearranging,

$$Z = \frac{\rho V N_A}{M}.$$

The atomic mass $81\,\text{u}$ corresponds to molar mass $M = 81\,\text{g mol}^{-1}$. Use $\rho = 10.2\,\text{g cm}^{-3}$ and $V = 2.7 \times 10^{-23}\,\text{cm}^3$, so the gram and cubic-centimetre units are consistent.

Step 2: Substitute and compare the cubic cell occupancies Substituting the given values,

$$Z = \frac{10.2 \times 2.7 \times 10^{-23} \times 6.022 \times 10^{23}}{81}$$
$$= \frac{165.84588}{81} = 2.04748 \approx 2.$$

The small deviation from an integer reflects the rounded density and volume supplied in the question. In a body-centred cubic cell, the eight corner atoms contribute $8 \times \frac{1}{8} = 1$ atom, and the atom wholly inside the centre contributes one more. Its effective occupancy is thus two atoms. The occupancies of simple cubic and face-centred cubic cells, respectively one and four, do not match the calculated value.

Step 3: Conclusion The element has a $\boxed{\text{body-centred cubic (bcc) unit cell}}$, with approximately two atoms per unit cell.

Quick Tip to Solve: Compute Z directly from density and cell volume; match the nearest integer to 1 (simple cubic), 2 (bcc) or 4 (fcc).

17. Write the principle of the following:

(a) Hydraulic washing

(b) Chromatography

(c) Froth-floatation process [3 marks]

Solution:

Concept:

- Concentration and separation methods exploit a difference in a physical property of the materials to be separated: density, adsorption affinity or wetting behaviour.
- The useful ore particles and unwanted gangue need not respond in the same way to flowing water, an adsorbent or an oil-water interface; this difference allows their separation.

Step 1: (a) Principle of hydraulic washing Hydraulic washing is based on the difference in densities (specific gravities) of ore particles and gangue particles. Powdered ore is washed with a stream of water. The lighter gangue particles are carried away by the flowing water, whereas the heavier ore particles settle and remain behind. Thus the separation is gravitational: water transports the lighter impurities preferentially. This method is also called gravity separation.

Step 2: (b) Principle of chromatography Chromatography is based on the different degrees of adsorption of the components of a mixture on an adsorbent. When a suitable solvent, acting as the mobile phase, passes over the stationary adsorbent, the less strongly adsorbed component moves more readily with the solvent. A more strongly adsorbed component is retained longer and moves more slowly. The unequal rates of movement separate the components into distinct bands, which can then be collected separately.

Step 3: (c) Principle of froth-floatation Froth-floatation is based on the difference in wettability of sulphide ore particles and gangue particles. Sulphide ore particles are preferentially wetted by oil, while gangue is preferentially wetted by water. Air is blown through an agitated mixture of powdered ore, water and suitable oil. The oil-wetted ore particles attach to air bubbles and rise with the froth, which is skimmed off. The water-wetted gangue remains in the water and settles below. The selective wetting, rather than a density difference alone, is the key principle.

Step 4: Conclusion Hydraulic washing uses a density difference; chromatography uses differential adsorption; froth-floatation uses differential wetting of sulphide ore by oil and gangue by water.

Quick Tip to Solve: Associate each process with its distinguishing property: hydraulic washing-density, chromatography-adsorption, froth-floatation-wettability.

18. Give reasons for the following:

(a) Transition metals have high enthalpies of atomization.

(b) Manganese has lower melting point even though it has a higher number of unpaired electrons for bonding.

(c) Ce^{4+} is a strong oxidising agent. [3 marks]

Solution:

Concept:

- Enthalpy of atomization measures the energy needed to form isolated gaseous atoms from an element; strong metallic bonding produces a high value.
- Transition-metal bonding involves outer s and d electrons. However, the stability of a particular electronic configuration can reduce the participation of electrons in metallic bonding.
- An oxidising agent accepts electrons and is itself reduced. The ease of reduction depends on the relative stability of its oxidation states.

Step 1: (a) High enthalpies of atomization Transition metals generally possess several unpaired d electrons. Their d electrons, together with the outer s electrons, participate in metallic bonding, giving strong interatomic attractions in the metal lattice. Considerable energy is therefore needed to separate the metal into individual gaseous atoms. This accounts for their generally high enthalpies of atomization. For a solid metal M, the process represented is $\mathrm{M(s)} \longrightarrow \mathrm{M(g)}$; the stronger the lattice bonding, the larger the energy required for this process.

Step 2: (b) The relatively low melting point of manganese Manganese has the electronic configuration $[\mathrm{Ar}]\,3d^5 4s^2$. Although it has five unpaired d electrons, its half-filled $3d^5$ subshell has extra stability. Consequently these d electrons are less readily involved in the delocalised metallic bonding than a simple count of unpaired electrons would suggest. The resulting metallic bonding is relatively weak compared with the neighbouring transition metals, giving manganese a lower melting point. Thus an unpaired-electron count alone is insufficient; the stability and actual participation of the d electrons must also be considered.

Step 3: (c) Strong oxidising character of cerium(IV) The $+3$ oxidation state is characteristic of lanthanoids. Cerium(IV) readily accepts an electron and is reduced to the more stable cerium(III) state in aqueous solution:

$$\mathrm{Ce^{4+} + e^- \longrightarrow Ce^{3+}}.$$

Its strong tendency to undergo this reduction means that $\mathrm{Ce^{4+}}$ can remove electrons from another substance, oxidising that substance. Hence it acts as a strong oxidising agent. The favourable reduction reflects the overall relative stability of the aqueous ions, rather than the electron configuration of the isolated ion alone.

Step 4: Conclusion Strong metallic bonding explains high atomization enthalpies; the stable half-filled $3d^5$ configuration weakens Mn's metallic bonding; easy reduction to $\mathrm{Ce^{3+}}$ makes $\mathrm{Ce^{4+}}$ a strong oxidising agent.

Quick Tip to Solve: For Mn, mention the stable half-filled d subshell; for Ce(IV), explicitly write electron acceptance to Ce(III) to establish oxidation of another species.

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

(a) Novolac

(b) Neoprene

(c) Buna-S [3 marks]

Solution:

Concept:

- Addition polymers form from unsaturated monomers, whereas condensation polymers form through reactions between functional groups with loss of small molecules.
- Novolac is a phenol-formaldehyde resin; neoprene is a chloroprene homopolymer and Buna-S is a copolymer of butadiene and styrene.

Step 1: Identify the monomers of Novolac Novolac is obtained by condensation of phenol with formaldehyde in an acidic medium. The monomer structures are $C_6H_5 - OH$ (phenol: an OH group directly attached to a benzene ring) and $H - C(= O) - H$ (methanal or formaldehyde). Formaldehyde creates methylene bridges between phenol units, mainly through their ortho and para positions. Novolac is the initially formed linear resin.

Step 2: Write the monomer of Neoprene The monomer is chloroprene, whose structure is

$$CH_2 = C(Cl) - CH = CH_2.$$

Its systematic name is 2-chlorobuta-1,3-diene. Addition polymerisation across the conjugated diene produces neoprene; chlorine is attached to the second carbon of the monomer, not to an end carbon.

Step 3: Write both monomers of Buna-S Buna-S is produced by copolymerisation of two different monomers: buta-1,3-diene, $CH_2 = CH - CH = CH_2$, and styrene, $C_6H_5 - CH = CH_2$. In styrene the vinyl group is attached directly to the benzene ring. Both structures must be given because Buna-S is a copolymer rather than a polymer of only butadiene.

Step 4: Conclusion (a) Novolac: phenol and formaldehyde. (b) Neoprene: chloroprene. (c) Buna-S: buta-1,3-diene and styrene, with the structures written above.

Quick Tip to Solve: Remember S in Buna-S stands for styrene; neoprene requires chlorine on carbon 2 of butadiene.

OR

19(b). **(a) Write one example each of**

(i) Cross-linked polymer

(ii) Natural polymer

(b) Arrange the following in the increasing order of their intermolecular forces:

Terylene, Buna-N, Polystyrene

(c) Define biodegradable polymers with an example. [3 marks]

Solution:

Concept:

- Cross-linked polymers contain covalent connections between chains, forming a three-dimensional network. Natural polymers are produced by living organisms.
- The NCERT classification orders elastomers, thermoplastics and fibres by increasing intermolecular attraction.
- Biodegradable polymers can be decomposed by biological agents such as microorganisms and their enzymes.

Step 1: Give the two examples in part (a) (i) Bakelite is a cross-linked polymer. Its phenol-formaldehyde chains are joined into a rigid three-dimensional network, accounting for its thermosetting behaviour. (ii) Cellulose is a natural polymer. It occurs in plant cell walls and consists of glucose units linked together; it is formed naturally by plants rather than being manufactured by polymerisation in a laboratory.

Step 2: Arrange the polymers in part (b) Buna-N is an elastomer: its relatively weak intermolecular attractions allow its chains to stretch and recover. Polystyrene is a thermoplastic with stronger attractions than those characteristic of elastomers. Terylene is a fibre with strong intermolecular attractions, which support close packing and high tensile strength. Hence the increasing order is

$$\boxed{\text{Buna-N} < \text{Polystyrene} < \text{Terylene.}}$$

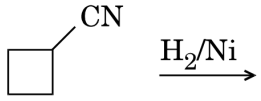
This is the standard polymer-class comparison requested in the question.

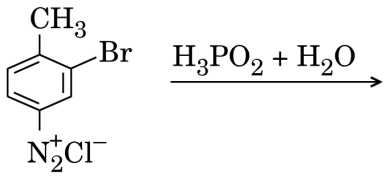
Step 3: Define biodegradable polymers in part (c) Biodegradable polymers are polymers that can be broken down by microorganisms or biological enzymes into simpler products. An example is poly(β-hydroxybutyrate-co-β-hydroxyvalerate), abbreviated PHBV. Its ester linkages allow biological degradation. Thus PHBV supplies a specific example alongside the required definition, rather than merely describing a material as environmentally friendly.

Step 4: Conclusion (a) (i) Bakelite; (ii) cellulose. (b) Buna-N < Polystyrene < Terylene. (c) Polymers decomposed by biological agents are biodegradable; PHBV is an example.

Quick Tip to Solve: For the force-order question, classify the materials first: elastomer < thermoplastic < fibre.

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

(a) 

(b) 

(c) 

Solution:

Concept:

- Catalytic reduction converts a nitrile group, $R-C\equiv N$, into $R-CH_2NH_2$; its carbon is retained.
- Hypophosphorous acid replaces an aromatic diazonium group by hydrogen without removing other ring substituents.
- The carbylamine reaction converts primary amines into isocyanides using chloroform and alcoholic potassium hydroxide.

Step 1: Reduce the nitrile in part (a) The printed starting compound is cyclobutanecarbonitrile: the nitrile carbon lies outside the four-membered ring. Hydrogen with nickel reduces the nitrile to a primary amine, without increasing the ring size. Writing $c-C_4H_7$ for the cyclobutyl group,

$$(c-C_4H_7)-CN+2H_2 \xrightarrow{Ni} (c-C_4H_7)-CH_2NH_2.$$

The product is cyclobutylmethanamine. The extra methylene carbon comes from the original nitrile carbon.

Step 2: Replace the diazonium group in part (b) In the printed ring, the methyl group is para to the diazonium group and bromine is meta to it. Treatment with $H_3PO_2+H_2O$ removes the diazonium group as nitrogen and places hydrogen at that position. Bromine and methyl remain on adjacent carbons, so the organic product is 2-bromotoluene (1-bromo-2-methylbenzene). The overall change is

$$ArN_2Cl+H_3PO_2+H_2O \rightarrow ArH+N_2+H_3PO_3+HCl,$$

where Ar retains the printed bromine and methyl substituents.

Step 3: Apply the carbylamine reaction in part (c) The starting amine is benzylamine, $C_6H_5CH_2NH_2$, not aniline. As a primary amine it gives benzyl isocyanide with chloroform and ethanolic potassium hydroxide:

$$C_6H_5CH_2NH_2+CHCl_3+3KOH \xrightarrow{\text{ethanol}} C_6H_5CH_2N\equiv C+3KCl+3H_2O.$$

In the isocyanide group the benzyl carbon is bonded to nitrogen; the terminal carbon is bonded triply

Quick Tip to Solve: Track the carbon next to nitrogen: nitrile reduction retains it as CH2, and benzylamine retains its benzyl CH2 group.

to that nitrogen. The original benzyl methylene group is retained.

Step 4: Conclusion (a) Cyclobutylmethanamine, $(c-C_4H_7)CH_2NH_2$. (b) 2-bromotoluene. (c) Benzyl isocyanide, $C_6H_5CH_2N \equiv C$.

Quick Tip to Solve: Track the carbon next to nitrogen: nitrile reduction retains it as CH2, and benzylamine retains its benzyl CH2 group.

OR

20(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:

- The acetamido group in acetanilide is ortho/para directing. Protection of the amino group limits bromination, and hydrolysis subsequently restores the amino group.
- An aromatic diazonium group can be replaced by a nitro group through the diazonium tetrafluoroborate using sodium nitrite and copper.
- Hofmann bromamide degradation converts an amide to a primary amine with one fewer carbon atom; the carbonyl carbon is lost.

Step 1: (a) Brominate the protected amine and hydrolyse N-Phenylethanamide is acetanilide, $C_6H_5NHCOCH_3$. Treat it with bromine in glacial acetic acid. The acetamido group directs bromination mainly to the para position; hydrolysis of the resulting p-bromoacetanilide with aqueous acid on heating yields p-bromoaniline.

$$C_6H_5NHCOCH_3 \xrightarrow{Br_2/CH_3COOH} p-BrC_6H_4NHCOCH_3 \xrightarrow{H_3O^+,\ heat} p-BrC_6H_4NH_2.$$

Step 2: (b) Replace the diazonium group by a nitro group First treat benzene diazonium chloride with fluoroboric acid to precipitate benzene diazonium tetrafluoroborate. Heat this salt with aqueous sodium nitrite in the presence of copper to form nitrobenzene, with nitrogen gas evolving.

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

Step 3: (c) Form benzamide and carry out Hofmann degradation React benzoic acid with ammonia to form ammonium benzoate, which gives benzamide on heating. Treat benzamide with bromine and aqueous sodium hydroxide:

$$C_6H_5COOH \xrightarrow{NH_3,\ then\ heat} C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} C_6H_5NH_2.$$

Quick Tip to Solve: For benzoic acid to aniline, first make the amide: Hofmann degradation removes its carbonyl carbon while retaining the phenyl group.

The balanced final reaction is

$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

Step 4: Conclusion (a) Brominate acetanilide, then hydrolyse. (b) Form the diazonium tetrafluoroborate, then use $NaNO_2/Cu$. (c) Prepare benzamide, then use $Br_2/NaOH$.

Quick Tip to Solve: For benzoic acid to aniline, first make the amide: Hofmann degradation removes its carbonyl carbon while retaining the phenyl group.

21(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 by medicinal action: tranquillisers act on the nervous system, whereas antiseptics inhibit microorganisms on living tissues.
- Detergents can be anionic, cationic or non-ionic according to the charge of their active surface species; non-ionic detergents have no charged head group.
- An artificial sweetener must remain chemically stable under the conditions in which a food is prepared and served.

Step 1: (a) Compare the medicinal properties Equanil, Seconal and Luminal belong to the group of tranquillisers or sedative drugs acting on the central nervous system. They are used to reduce anxiety or produce a calming or sedative effect. Bithional is an antiseptic, used to inhibit microbial growth; it is also added to soaps to impart antiseptic properties. Thus, Bithional differs from the other three in its medicinal action. The basis of the selection is the drug's action, rather than its spelling or chemical structure.

Step 2: (b) Identify the detergents in dishwashing liquids Non-ionic detergents are used in dishwashing liquids. Their molecules possess a hydrophobic portion that associates with grease and a hydrophilic portion that interacts with water, but they do not produce a charged detergent ion in solution. A common class is made by reacting a long-chain alcohol with ethylene oxide. The polyoxyethylene portion provides the water-attracting end, allowing oily food residues to be dispersed and washed away. The required classification is therefore non-ionic, rather than anionic or cationic.

Step 3: (c) Explain the temperature limitation of aspartame Aspartame is the methyl ester of a dipeptide formed from aspartic acid and phenylalanine. It is a sweetening agent, but it is not stable at cooking temperatures. On heating it decomposes and consequently loses its sweetness. Therefore it is suitable for cold foods and drinks, where its sweet taste is retained. It is unsuitable for foods requiring substantial heating or baking because the sweetening molecule does not survive those conditions unchanged.

Quick Tip to Solve: Classify the four drugs by their medicinal action, and link aspartame's cold-food use directly to its instability on heating.

Step 4: Conclusion (a) Bithional is the odd one because it is an antiseptic. (b) Dishwashing liquids use non-ionic detergents. (c) Aspartame is limited to cold foods because it decomposes on heating and loses sweetness.

Quick Tip to Solve: Classify the four drugs by their medicinal action, and link aspartame's cold-food use directly to its instability on heating.

OR

21(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 responsible for infections by killing them or inhibiting their growth.
- Antiseptics inhibit or kill microorganisms and can be applied to living tissues at their recommended concentrations.
- In an anionic detergent, the negatively charged part of the molecule is responsible for its cleansing action.

Step 1: (a) Define antibiotics and give an example Antibiotics are chemical substances produced by microorganisms, or their synthetic or semisynthetic analogues, which in low concentrations inhibit the growth of or destroy other microorganisms. They are used to treat susceptible microbial infections. Penicillin is a suitable example. It is effective against susceptible bacteria by interfering with bacterial cell-wall formation. The definition concerns action against microorganisms; it does not mean that an antibiotic is a general painkiller or a medicine for every illness.

Step 2: (b) Define antiseptics and give an example Antiseptics are chemical substances which kill microorganisms or prevent their growth and are applied to living tissues such as skin, wounds and cuts at suitable concentrations. Their purpose is to prevent or control infection on these tissues. Dettol is an example; its antiseptic components include chloroxylenol and terpineol. Antiseptics are distinguished from disinfectants, which are generally used on non-living objects such as floors and instruments. The concentration and site of use matter when classifying an antimicrobial preparation.

Step 3: (c) Define anionic detergents and give an example Anionic detergents are synthetic cleansing agents in which the active cleansing part is a negatively charged ion. They are commonly sodium salts of long-chain alkyl sulphates or alkylbenzene sulphonates. Sodium lauryl sulphate is a suitable example:

$$CH_3(CH_2)_{11}OSO_3^-Na^+.$$

The long hydrocarbon chain forms the hydrophobic tail, while the negatively charged sulphate group forms the hydrophilic head. The anion helps disperse grease in water; the sodium ion is the counterion

Quick Tip to Solve: Pair each definition with one named example, and identify the negative detergent head group to justify the term anionic.

and does not give this class its name.

Step 4: Conclusion Antibiotics inhibit or kill susceptible microorganisms, for example penicillin. Antiseptics prevent microbial growth on living tissues, for example Dettol. Anionic detergents cleanse through their negatively charged active ion, for example sodium lauryl sulphate.

Quick Tip to Solve: Pair each definition with one named example, and identify the negative detergent head group to justify the term anionic.

22. 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 carbon bonded to four different groups; an individual enantiomer rotates plane-polarised light.
- In an S_N2 reaction, the nucleophile attacks from the side opposite the leaving group. Less steric crowding favours this one-step substitution.
- Alcoholic KOH removes a hydrogen from a carbon adjacent to the carbon bearing bromine, eliminating HBr and forming an alkene.

Step 1: List the constitutional isomers The four isomers are 1-bromobutane, $CH_3CH_2CH_2CH_2Br$; 2-bromobutane, $CH_3CH(Br)CH_2CH_3$; 1-bromo-2-methylpropane, $(CH_3)_2CHCH_2Br$; and 2-bromo-2-methylpropane, $(CH_3)_3CBr$. Comparing all four avoids confusing the straight-chain and branched primary bromides.

Step 2: (a) Identify the optically active isomer In 2-bromobutane, carbon 2 is attached to Br, H, CH_3, and CH_2CH_3. All four groups differ, so this carbon is chiral and the isomer can exist as optically active enantiomers. None of the other three constitutional isomers has such a carbon. A racemic mixture of the enantiomers itself has zero net rotation.

Step 3: (b) Compare substitution reactivity 1-Bromobutane is primary and has an unbranched chain near the reaction centre, so backside approach is least hindered. The other primary isomer, 1-bromo-2-methylpropane, has branching at the adjacent carbon. The secondary and tertiary bromides are more crowded. Thus 1-bromobutane is the most reactive of these isomers towards S_N2.

Step 4: (c) Compare elimination products Both branched bromides yield 2-methylpropene on heating with alcoholic KOH:

$$(CH_3)_2CHCH_2Br \longrightarrow CH_2 = C(CH_3)_2,$$
$$(CH_3)_3CBr \longrightarrow CH_2 = C(CH_3)_2.$$

In the first, the adjacent methine carbon supplies the hydrogen; in the second, all three methyl groups are equivalent, so elimination at any one produces the same alkene.

Step 5: Conclusion (a) 2-Bromobutane; (b) 1-bromobutane; (c) 1-bromo-2-methylpropane and

Quick Tip to Solve: Write all four bromides first: check four different groups for chirality, crowding for substitution, and the carbon skeleton for elimination.

2-bromo-2-methylpropane, both giving 2-methylpropene.

Quick Tip to Solve: Write all four bromides first: check four different groups for chirality, crowding for substitution, and the carbon skeleton for elimination.

23(a). Write the product when D-glucose reacts with Br_2(aq).

(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:

- Bromine water is a mild oxidising agent: it oxidises the aldehyde group of glucose to a carboxylic acid without oxidising its terminal primary alcohol group.
- The secondary structure of a protein is stabilised by hydrogen bonding between peptide backbone groups.
- Vitamin deficiency diseases can be identified by matching the disease to the relevant vitamin.

Step 1: (a) Oxidation of D-glucose The open-chain form of D-glucose contains an aldehyde group at carbon 1. Bromine water converts this $-\mathrm{CHO}$ group into $-\mathrm{COOH}$, giving D-gluconic acid:

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O \longrightarrow COOH(CHOH)_4CH_2OH + 2HBr.}$$

The $-\mathrm{CH_2OH}$ end remains unchanged because bromine water is a mild oxidant. Thus the product is the monocarboxylic acid, not the dicarboxylic acid formed using a stronger oxidising agent.

Step 2: (b) Stability of the alpha-helix The α-helix is stabilised by intramolecular hydrogen bonds between the carbonyl oxygen, $\mathrm{C=O}$, of one peptide unit and the $\mathrm{N-H}$ group of another peptide unit in the same polypeptide chain. These regularly repeated hydrogen bonds hold the chain in its helical arrangement; peptide covalent bonds form the backbone itself.

Step 3: (c) Vitamin deficiency Deficiency of vitamin $\mathrm{B_{12}}$, also called cobalamin, causes pernicious anaemia in the standard CBSE vitamin-deficiency association. The requested answer is the vitamin name: it should not be confused with vitamin C, whose deficiency causes scurvy, or vitamin D, whose deficiency causes rickets.

Step 4: Conclusion (a) D-Gluconic acid; (b) intramolecular hydrogen bonding between peptide backbone groups; (c) vitamin $\mathrm{B_{12}}$ (cobalamin).

Quick Tip to Solve: For bromine water change only glucoseś aldehyde end to COOH; associate the alpha-helix with backbone hydrogen bonds and pernicious anaemia with B12.

OR

23(b). Define the following terms:

(a) Invert sugar

(b) Native protein

(c) Nucleotide [3 marks]

Solution:

Concept:

- Hydrolysis of sucrose yields one molecule each of glucose and fructose; the resulting mixture has a different direction of optical rotation from sucrose.
- A proteiṅs biological activity depends on its characteristic folded conformation in its natural environment.
- A nucleotide is a nucleoside with an attached phosphate group and is a building unit of nucleic acids.

Step 1: (a) Define invert sugar Invert sugar is the equimolar mixture of D-glucose and D-fructose obtained by hydrolysis of sucrose:

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

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, or inversion, in the direction of optical rotation gives invert sugar its name.

Step 2: (b) Define native protein A native protein is a protein in its natural, biologically active state, possessing its characteristic three-dimensional conformation. Its specific folding enables it to carry out its normal function. Denaturation disturbs this conformation and usually destroys biological activity; therefore a denatured protein is no longer in its native state even if its primary sequence remains intact.

Step 3: (c) Define nucleotide A nucleotide is a compound made of a nitrogenous base, a pentose sugar and a phosphate group. The base joined to the sugar forms a nucleoside; addition of phosphate produces a nucleotide. The sugar is ribose in RNA nucleotides and 2-deoxyribose in DNA nucleotides. Nucleotides join through phosphodiester linkages to form the nucleic-acid chain, so phosphate must be included in the definition.

Step 4: Conclusion Invert sugar: equimolar glucose-fructose mixture from sucrose hydrolysis with inverted optical rotation. Native protein: naturally folded, biologically active protein. Nucleotide: nitrogenous base + pentose sugar + phosphate.

Quick Tip to Solve: Distinguish nucleotide from nucleoside by the phosphate group, and native protein from denatured protein by its natural fold and activity.

24. (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 base: a more stable carboxylate ion corresponds to a stronger carboxylic acid.
- Nucleophilic addition is favoured by greater positive character at the carbonyl carbon and less steric hindrance. Aldehydes reduce Tollens' reagent, whereas ordinary ketones do not.

Step 1: (a)(i) Compare the conjugate bases In acetic acid, the methyl group has a positive inductive effect and releases electron density towards the carboxyl group. This increases the electron density of the acetate ion and makes it less stable. The phenyl group in benzoic acid has an electron-withdrawing inductive effect relative to methyl, which stabilises the benzoate ion. Consequently, loss of a proton is easier from benzoic acid. The approximate pK_a values, 4.2 for benzoic acid and 4.76 for acetic acid, agree with this ordering.

Step 2: (a)(ii) Compare the carbonyl groups Methanal, HCHO, has two small hydrogen atoms attached to its carbonyl carbon. Ethanal, $\mathrm{CH_3CHO}$, has a methyl group that donates electron density by its positive inductive effect, reducing the electrophilic character of the carbonyl carbon. The methyl group also offers more steric hindrance to the approaching nucleophile than hydrogen. Methanal is therefore more reactive by both electronic and steric considerations.

Step 3: (b) Apply Tollens' test Warm separate samples with freshly prepared Tollens' reagent in a water bath. Propanal produces a silver mirror as it is oxidised to propanoate; propanone produces no silver mirror under these conditions.

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

Thus, deposition of metallic silver identifies propanal, while the negative test identifies propanone.

Step 4: Conclusion Benzoic acid is stronger because its conjugate base is more stable; methanal is more reactive because it has greater carbonyl electrophilicity and less steric hindrance. Propanal gives a silver mirror with Tollens' reagent, while propanone does not.

Quick Tip to Solve: Compare conjugate-base stability for acidity, and check both electron donation and steric hindrance for carbonyl addition.

Section D (15 marks)

25(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 increases and electronegativity generally decreases. Bond strength and the ease of releasing a proton govern the acidity of group 16 hydrides.
- Molecular reactivity depends on bond dissociation energies as well as oxidising power. VSEPR predicts molecular geometry from bonding pairs and lone pairs around the central atom.

Step 1: (a)(i) Trend in the negative oxidation state Group 15 atoms have the valence-shell configuration ns^2np^3. They can attain an octet by gaining or formally acquiring three electrons, giving the oxidation state -3. From nitrogen to bismuth, atomic size increases and electronegativity decreases. The attraction for additional electrons therefore becomes weaker and metallic character increases. Hence, the tendency to exhibit the -3 oxidation state decreases down the group.

Step 2: (a)(ii) Acidity of group 16 hydrides The size of the central atom increases from oxygen to tellurium, so the $E-H$ bond becomes longer and weaker. The bond dissociation enthalpy decreases, making release of H^+ progressively easier. This weakening of the bond dominates the trend despite decreasing electronegativity. Therefore,

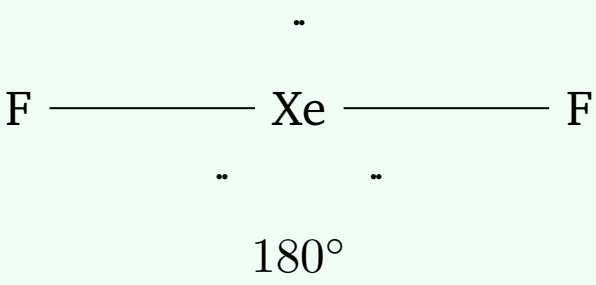
$$H_2O < H_2S < H_2Se < H_2Te$$

is the increasing order of acidic character.

Step 3: (a)(iii) Relative reactivity of the halogen species Fluorine is exceptionally reactive because the $F-F$ bond is weak owing to strong repulsion between lone pairs on the small fluorine atoms, and fluorine has very high oxidising power. It is therefore more reactive than ClF_3. In general, the bonds between unlike halogen atoms in interhalogen compounds are weaker than those in the corresponding halogen molecule, apart from the special case of F_2. The $Cl-F$ bonds in ClF_3 are more readily broken than the $Cl-Cl$ bond in Cl_2. Thus, the required order is $F_2 > ClF_3 > Cl_2$.

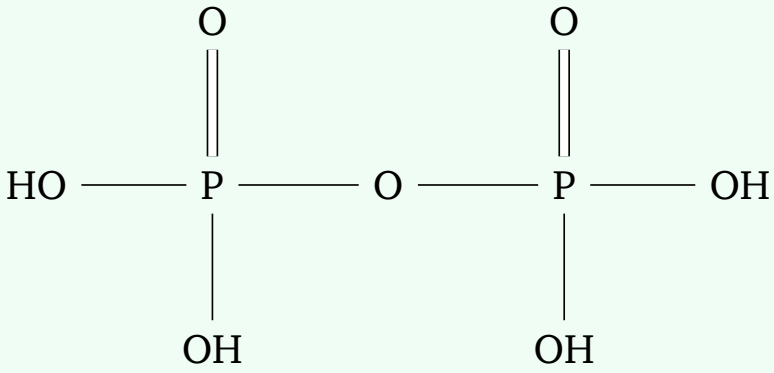
Step 4: (b)(i) Structure of xenon difluoride Xenon has five electron pairs around it: two bonding pairs and three lone pairs. The electron-pair arrangement is trigonal bipyramidal. The three lone pairs occupy equatorial positions to minimise repulsion, leaving the two fluorine atoms at the axial positions. Consequently, XeF_2 is linear, with an $F-Xe-F$ angle of 180°. The dots in the drawing show the three lone pairs on xenon.

Quick Tip to Solve: For XeF2 place all three lone pairs equatorially; for H4P2O7 join two phosphorus centres by oxygen and attach two OH groups to each.



Linear XeF2 with three equatorial lone pairs on Xe

Step 5: (b)(ii) Structure of pyrophosphoric acid Pyrophosphoric acid consists of two phosphorus centres joined through one bridging oxygen, giving a $\mathrm{P-O-P}$ linkage. Each phosphorus is bonded to one terminal oxygen by a double bond, two hydroxyl groups, and the bridging oxygen. Each phosphorus centre has an approximately tetrahedral arrangement of oxygen atoms. The displayed structure contains four OH groups and has the molecular formula $\mathrm{H_4P_2O_7}$.



Structure of pyrophosphoric acid, H4P2O7

Step 6: Conclusion The -3 state becomes less favoured down group 15; hydride acidity increases as the $\mathrm{E-H}$ bond weakens. Reactivity follows $\mathrm{F_2 > ClF_3 > Cl_2}$. $\mathrm{XeF_2}$ is linear, and $\mathrm{H_4P_2O_7}$ contains two tetrahedral phosphorus centres joined by a bridging oxygen.

Quick Tip to Solve: For XeF2 place all three lone pairs equatorially; for H4P2O7 join two phosphorus centres by oxygen and attach two OH groups to each.

OR

25(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 exhibits only the oxidation state -1 in its compounds; its reaction with oxygen therefore differs from that of other halogens.
- White phosphorus contains discrete P_4 tetrahedra, whereas red phosphorus has a polymeric network of phosphorus atoms.
- A weaker hydrogen-element bond favours reducing behaviour and, for hydrogen halides in aqueous solution, easier release of H^+.

Step 1: (a) An anomalous reaction of fluorine Fluorine reacts with cold, dilute sodium hydroxide to form oxygen difluoride:

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O.$$

In OF_2, fluorine has oxidation state -1, so oxygen has oxidation state $+2$. Other halogens react with cold dilute alkali to form a halide and a hypohalite, with the halogen showing both negative and positive oxidation states. Fluorine's formation of an oxygen fluoride illustrates its anomalous behaviour.

Step 2: (b) Compare the phosphorus structures White phosphorus consists of separate tetrahedral P_4 molecules. Each phosphorus atom is bonded to the other three atoms of the tetrahedron, giving strained bond angles of about $60°$. Red phosphorus has a polymeric structure: phosphorus tetrahedra are linked together into an extended network. Thus white phosphorus is molecular, while red phosphorus is polymeric; the less strained network also explains the greater stability of red phosphorus.

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

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

Here XeF_6 acts as a Lewis acid and F^- acts as a Lewis base. The product contains the complex anion $[XeF_7]^-$, and xenon's oxidation state remains $+6$.

Step 4: (d) Compare the reducing powers of the hydrides Sulfur is larger than oxygen, so overlap in an S–H bond is poorer than in an O–H bond. The S–H bond is therefore weaker and H_2S is more readily oxidised than H_2O. Since a reducing agent is itself oxidised, hydrogen sulfide is the better reducing agent. For example,

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

Sulfur changes from -2 to 0, supplying electrons to chlorine.

Quick Tip to Solve: For both hydride reducing power and hydrohalic acidity, compare H–element bond strength down the group before comparing electronegativity.

Step 5: (e) Compare the hydrohalic acids Down the halogen group the atomic size increases, the H–X bond length increases and its bond dissociation enthalpy decreases. Consequently ionisation of the hydrogen halide in water becomes easier. Although fluorine is most electronegative, the exceptionally strong H–F bond makes HF the weakest acid in this series; bond strength controls the trend down the group.

Step 6: Conclusion (a) Fluorine forms OF_2 with cold dilute NaOH. (b) White phosphorus has discrete P_4 tetrahedra; red phosphorus is polymeric. (c) $Na[XeF_7]$ is formed. (d) The weaker S–H bond makes H_2S more readily oxidised. (e) Increasing acidic strength: $\boxed{HF < HCl < HBr < HI}$.

Quick Tip to Solve: For both hydride reducing power and hydrohalic acidity, compare H–element bond strength down the group before comparing electronegativity.

26(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 monoprotic acid, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, and $K_a = c\alpha^2/(1-\alpha)$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log_{10} Q$, where n is the number of electrons transferred and Q is the reaction quotient.

Step 1: (a) Calculate molar conductivity and dissociation Acetic acid is a weak electrolyte, so its degree of dissociation is obtained by comparing its molar conductivity with the limiting value. With $c = 0.001\,\mathrm{mol\,L^{-1}}$ and $\kappa = 4.95 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$,

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

Hence

$$\alpha = \frac{49.5}{390.5} = 0.12676.$$

Thus approximately 12.68% of the acid is dissociated at the stated concentration. The factor 1000 converts concentration per litre into concentration per cubic centimetre.

Step 2: (a) Use the acid dissociation equilibrium For $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$, the equilibrium

Quick Tip to Solve: Compute molar conductivity before using Ostwald's law; for the Nernst equation count six electrons from the balanced Al/Cu reaction and omit pure solids.

concentrations are $c(1-\alpha)$ for the undissociated acid and $c\alpha$ for each ion. Therefore,

$$\begin{aligned} K_a &= \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} \\ &= \frac{c\alpha^2}{1-\alpha} \\ &= \frac{0.001(0.12676)^2}{1-0.12676} \\ &= 1.84 \times 10^{-5}\,\mathrm{mol\,L^{-1}}. \end{aligned}$$

The denominator must be retained here because the calculated dissociation is appreciable; replacing $1-\alpha$ by unity would lower the calculated value.

Step 3: (b) Determine electron transfer and the reaction quotient The oxidation and reduction half-reactions are

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

Thus $n = 6$, rather than the sum of the two electron counts. Pure solid aluminium and copper have unit activity and are omitted from Q. Approximating dissolved-ion activities by their concentrations relative to the standard concentration gives

$$Q = \frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}.$$

Consequently the required equation at $25^\circ\mathrm{C}$ is

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

The coefficients of the balanced overall reaction become the powers in the reaction quotient.

Step 4: (c) Explain secondary batteries Secondary batteries are rechargeable electrochemical batteries. During discharge they operate as galvanic cells and convert chemical energy into electrical energy. Passing an external current in the opposite direction reverses the discharge reactions and regenerates the active materials, allowing repeated use. A lead storage battery is an example: its electrodes are lead and lead dioxide in sulfuric acid. On discharge both electrodes form lead sulfate; charging restores the original electrode materials.

Step 5: Conclusion (a) $\boxed{K_a = 1.84 \times 10^{-5}\,\mathrm{mol\,L^{-1}}}$. (b) $E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0591}{6}\log_{10}\left(\frac{[\mathrm{Al^{3+}}]^2}{[\mathrm{Cu^{2+}}]^3}\right)$. (c) Secondary batteries can be recharged by reversing their discharge reactions; a lead storage battery is an example.

Quick Tip to Solve: Compute molar conductivity before using Ostwald's law; for the Nernst equation count six electrons from the balanced Al/Cu reaction and omit pure solids.

OR

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

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

Calculate its emf if $E^\circ_{cell} = 1.41$ 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:

- Oxidation occurs at the anode and reduction at the cathode. Cell notation places the anode on the left and uses a double vertical line for the salt bridge.
- At 298 K, the Nernst equation is $E = E^\circ - (0.0591/n)\log Q$, 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 conducting ability per mole of electrolyte. Its limiting value Λ°_m corresponds to infinite dilution; Kohlrausch's law expresses it as the sum of independent ionic contributions.

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

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

Thus aluminium is the anode, nickel is the cathode and $n = 6$. The cell representation is

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

The salt bridge completes the internal circuit and maintains electrical neutrality in the two half-cells.

Step 2: (a) Calculate the cell emf Taking concentrations in the usual dilute-solution approximation, the quotient for the stated reaction is

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

Using the standard Nernst coefficient at 298 K,

$$E_{\mathrm{cell}} = 1.41 - \frac{0.0591}{6}\log(0.1)$$
$$= 1.41 + 0.00985 = 1.41985\,\mathrm{V}.$$

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 essentially completely ionised; increasing concentration strengthens interionic interactions and reduces ionic mobility. Its

Quick Tip to Solve: Balance electrons before using Nernst: the aluminium/nickel reaction transfers six electrons, not two or three; omit the solids from its reaction quotient.

decrease is comparatively gradual and, at low concentrations, follows

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

where A is a positive constant for the given electrolyte and solvent at fixed temperature. For a weak electrolyte, increasing concentration also reduces the degree of ionisation, so fewer free ions are available per mole. Consequently its molar conductivity decreases much more sharply. Conversely, dilution increases ionisation and causes a pronounced rise in Λ_m.

Step 4: (b) Obtain the limiting value for a weak electrolyte The strongly curved variation for a weak electrolyte prevents reliable direct extrapolation of its Λ_m versus $\sqrt{c}$ plot. Instead use Kohlrausch's law with limiting conductivities of suitable strong electrolytes. For example, for acetic acid,

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

Substitution of the independent ionic contributions cancels Na^+ and Cl^-, leaving those of H^+ and CH_3COO^-, as required.

Step 5: Conclusion The cell is $Al \mid Al^{3+}(0.01\,M) \parallel Ni^{2+}(0.1\,M) \mid Ni$, with emf approximately $1.420\,V$. Increasing concentration lowers molar conductivity for both types of electrolyte, more sharply for weak electrolytes. Their limiting conductivity is obtained using Kohlrausch's law.

Quick Tip to Solve: Balance electrons before using Nernst: the aluminium/nickel reaction transfers six electrons, not two or three; omit the solids from its reaction quotient.

27(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 phenol ring and directs electrophilic substitution to the ortho and para positions.
- Hydroboration followed by oxidation adds water across an alkene in anti-Markovnikov orientation. Williamson synthesis forms an ether by nucleophilic substitution of a primary alkyl halide with an alkoxide.
- A secondary alcohol containing the $CH_3CH(OH)-$ group gives the iodoform test. Acidity increases

Quick Tip to Solve: For the iodoform test, locate the CH3-CH(OH)- group; for Williamson synthesis, check the alkyl halide carbon, which is methyl here.

when the conjugate base is better stabilised.

Step 1: (a)(i) Nitrate phenol with concentrated nitric acid The strongly activating hydroxyl group allows nitration at both ortho positions and at the para position. Concentrated nitric acid produces 2,4,6-trinitrophenol, commonly called picric acid:

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} C_6H_2(NO_2)_3OH + 3H_2O.$$

In the product, the three nitro groups occupy positions 2, 4 and 6 relative to the hydroxyl group at position 1.

Step 2: (a)(ii) Carry out hydroboration and oxidation of propene Diborane provides borane for hydroboration. Boron attaches preferentially to the less substituted terminal carbon; oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond by a carbon-oxygen bond. Thus the net transformation is

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

The product is propan-1-ol. The hydroxyl group is on the terminal carbon, consistent with anti-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 in an S_N2 reaction:

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

This Williamson synthesis gives methyl tert-butyl ether, also named 2-methoxy-2-methylpropane. Although the alkoxide is bulky, the halide is methyl chloride and offers minimal steric hindrance; it also has no beta carbon for elimination.

Step 4: (b) Distinguish the two butanols by the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Butan-2-ol gives a yellow precipitate of iodoform, CHI_3, because its $CH_3CH(OH)-$ group is first oxidised to a methyl ketone, which undergoes the haloform reaction. The overall equation is

$$CH_3CH(OH)CH_2CH_3 + 4I_2 + 6NaOH \longrightarrow CHI_3 \downarrow + CH_3CH_2COONa + 5NaI + 5H_2O.$$

Butan-1-ol gives no yellow precipitate: it lacks the required methyl-carbinol group and is oxidised to butanal, which does not give this test. The contrasting precipitate provides a clear distinction.

Step 5: (c) Compare the stability of the conjugate bases Ethanol forms ethoxide, water forms hydroxide, and phenol forms phenoxide on losing a proton. The electron-releasing ethyl group increases electron density on the negatively charged oxygen of ethoxide and destabilises it relative to hydroxide. Ethanol is therefore less acidic than water. In phenoxide, the negative charge is delocalised by resonance into the aromatic ring, whereas ethoxide and hydroxide lack such resonance stabilisation. Phenol is consequently the strongest acid of the three.

Step 6: Conclusion The reaction products are (i) 2,4,6-trinitrophenol, (ii) propan-1-ol and (iii) methyl tert-butyl ether. Butan-2-ol gives a yellow iodoform precipitate, while butan-1-ol does not. The increasing order of acidity is ethanol $<$ water $<$ phenol.

Quick Tip to Solve: For the iodoform test, locate the CH3-CH(OH)- group; for Williamson synthesis, check the alkyl halide carbon, which is methyl here.

OR

27(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 prepared by cleavage of cumene hydroperoxide, alkaline fusion of benzene sulphonic acid followed by acidification, or hydrolysis of benzene diazonium chloride.
- The $-OH$ group strongly activates a benzene ring and directs electrophilic substitution to its ortho and para positions. A methyl group also directs substitution to ortho and para positions.
- In Kolbe's reaction, sodium phenoxide reacts with CO_2 under pressure; acidification of the resulting sodium salicylate gives salicylic acid.

Step 1: (a)(i) Oxidise cumene and cleave its hydroperoxide Pass air through cumene (isopropylbenzene) to form cumene hydroperoxide. Acid-catalysed cleavage of this intermediate produces phenol and acetone:

$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH$$

$$C_6H_5C(CH_3)_2OOH \xrightarrow{H^+} C_6H_5OH + CH_3COCH_3$$

Thus, the hydroperoxide is the essential intermediate, and acetone is obtained as a useful coproduct.

Step 2: (a)(ii) Fuse the sulphonate with alkali and acidify First neutralise benzene sulphonic acid to obtain sodium benzene sulphonate. Fuse it with sodium hydroxide at about $623\,K$, then acidify the sodium phenoxide:

$$C_6H_5SO_3H + NaOH \longrightarrow C_6H_5SO_3Na + H_2O$$

$$C_6H_5SO_3Na + 2\,NaOH \xrightarrow{623\,K} C_6H_5ONa + Na_2SO_3 + H_2O$$

$$C_6H_5ONa + HCl \longrightarrow C_6H_5OH + NaCl$$

Acidification is necessary because alkaline fusion initially gives the phenoxide salt, rather than free phenol.

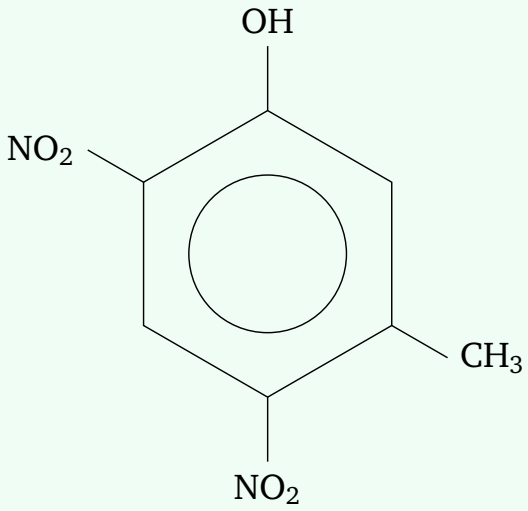
Step 3: (a)(iii) Warm the diazonium salt with water Benzene diazonium chloride undergoes hydrolysis on warming with water. The diazonium group is replaced by a hydroxyl group, with nitrogen gas liberated:

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

This conversion uses the ready loss of the diazonium group as stable molecular nitrogen.

Step 4: (b) Identify the favoured positions for dinitration Number the carbon bearing $-OH$ as 1 and the carbon bearing $-CH_3$ as 3. Both groups favour positions 2, 4 and 6. Position 2 lies between the two existing substituents and is more sterically hindered. Nitration therefore occurs mainly at positions 4 and 6, giving 3-methyl-4,6-dinitrophenol. Its structure is shown below; the nitro groups occupy one para and one ortho position relative to $-OH$.

Quick Tip to Solve: For dinitration of 3-methylphenol, mark positions directed by both substituents and avoid the crowded carbon between them. Remember to acidify phenoxide or salicylate salts to obtain the free phenol or acid.



Major dinitration product: 3-methyl-4,6-dinitrophenol

Step 5: (c) Carboxylate sodium phenoxide by Kolbe's reaction Treat sodium phenoxide with carbon dioxide at about $400\,\mathrm{K}$ under pressure (about 4–7 atm), then acidify. The major product is the ortho hydroxy acid, salicylic acid:

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

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

The phenoxide group activates the ring toward carboxylation; the product's $-\mathrm{COOH}$ group is ortho to its phenolic $-\mathrm{OH}$ group.

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

Quick Tip to Solve: For dinitration of 3-methylphenol, mark positions directed by both substituents and avoid the crowded carbon between them. Remember to acidify phenoxide or salicylate salts to obtain the free phenol or acid.