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

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). Write IUPAC name of the complex $K_3[Cr(C_2O_4)_3]$. [1 mark]

Solution:

Concept:

- An oxalato ligand, $C_2O_4^{2-}$, carries charge -2; potassium is present as K^+.
- An anionic chromium coordination entity uses the metal name chromate. The oxidation state follows the metal name in Roman numerals.

Step 1: Find the oxidation state Three potassium ions give a total charge of $+3$, so the complex ion has charge -3. If chromium has oxidation state x, then $x + 3(-2) = -3$, giving $x = +3$.

Step 2: Name the ligand and complex The three oxalato ligands are indicated by tris(oxalato). Name the cation first, followed by the anionic complex; retain (III) to show the oxidation state of chromium.

Step 3: Conclusion The IUPAC name is **potassium tris(oxalato)chromate(III)**.

Quick Tip to Solve: First use the three potassium ions to determine the complex charge; do not equate that charge with the metal oxidation state.

OR

1(b). Using IUPAC norms write the formula of Hexaamminecobalt(III) sulphate. [1 mark]

Solution:

Concept:

- Ammine means a coordinated neutral NH_3 ligand; hexaammine denotes six such ligands.
- Cobalt(III) has oxidation state $+3$, while sulphate is SO_4^{2-}. A salt formula must have zero total charge.

Step 1: Write the complex cation Because all six ammonia ligands are neutral, the charge on the coordination entity equals the cobalt oxidation state. The complex cation is therefore $[Co(NH_3)_6]^{3+}$; sulphate stays outside the coordination brackets.

Step 2: Balance the ionic charges The smallest common total charge is six. Two complex cations contribute $+6$, while three sulphate ions contribute -6. Hence combine them in the ratio $2 : 3$, without altering the six ligands inside each complex.

Step 3: Conclusion The formula is $\boxed{[Co(NH_3)_6]_2(SO_4)_3}$.

Quick Tip to Solve: Keep the six ammonia molecules inside each bracket and balance the external cation and sulphate charges separately.

2. Why is $CH_2=CH-CH_2-Cl$ more easily hydrolysed than $CH_3-CH_2-CH_2-Cl$? [1 mark]

Solution:

Concept:

- Hydrolysis replaces a halogen by a hydroxyl group through nucleophilic substitution.
- An allylic carbocation is stabilised by resonance because its positive charge can be delocalised over the adjacent double bond.

Step 1: Identify the allylic halide In $CH_2=CH-CH_2Cl$, chlorine is attached to the saturated carbon next to a double bond. On ionisation, the allylic cation is resonance stabilised:

$$CH_2=CH-CH_2^+ \leftrightarrow {}^+CH_2-CH=CH_2.$$

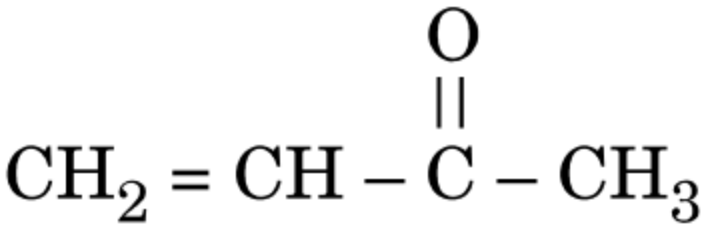
Step 2: Compare with propyl chloride Ionisation of $CH_3CH_2CH_2Cl$ would produce a primary propyl cation with no adjacent double bond and hence no corresponding resonance stabilisation. Resonance lowers the energy barrier for substitution in the allylic compound, making its hydrolysis easier.

Step 3: Conclusion $CH_2=CH-CH_2Cl$ is hydrolysed more easily because the allylic intermediate is resonance stabilised, whereas the propyl intermediate is not.

Quick Tip to Solve: Look for a double bond next to the carbon bearing chlorine; allylic stabilisation applies even though that carbon is saturated.

3. Write the IUPAC name of the following compound:

$CH_2=CH-CO-CH_3$ [1 mark]



Solution:

Concept:

- Choose the longest chain containing the ketone carbonyl carbon and the carbon-carbon double bond.
- The ketone suffix has priority over the alkene locant; number the chain to give the carbonyl group the lowest number.

Step 1: Choose and number the parent chain The structure $CH_2=CH-CO-CH_3$ contains four carbons. Number from the CH_3 end: the carbonyl carbon is carbon 2 and the double bond lies between carbons 3 and 4. Numbering from the opposite end would incorrectly give the ketone locant 3.

Quick Tip to Solve: For an unsaturated ketone, give the carbonyl carbon its lowest locant before considering the double-bond locant.

Step 2: Construct the name The four-carbon parent is but-. The double bond supplies the infix -3-en-, and the ketone supplies the suffix -2-one. Combine these descriptors, retaining the carbonyl locant and omitting the final e of ene before one.

Step 3: Conclusion The IUPAC name is **but-3-en-2-one**.

Quick Tip to Solve: For an unsaturated ketone, give the carbonyl carbon its lowest locant before considering the double-bond locant.

4(a). What is the difference between a glycosidic linkage and a peptide linkage? [1 mark]

Solution:

Concept:

- A glycosidic linkage joins monosaccharide units through an oxygen atom.
- A peptide linkage is an amide bond, $-CO-NH-$, joining amino-acid residues.

Step 1: Describe the glycosidic linkage A glycosidic linkage is formed when the anomeric hydroxyl group of one monosaccharide reacts with a hydroxyl group of another, eliminating water. The resulting $C-O-C$ bridge links sugar units, as in disaccharides and polysaccharides.

Step 2: Describe the peptide linkage A peptide linkage forms when the carboxyl group of one amino acid reacts with the amino group of another, eliminating water. Its characteristic group is $-CO-NH-$, and it links amino-acid residues in peptides and proteins.

Step 3: Conclusion A **glycosidic linkage** joins sugar units through oxygen, whereas a **peptide linkage** joins amino-acid residues through $-CO-NH-$.

Quick Tip to Solve: Identify the units joined: sugars indicate a glycosidic bond; amino acids indicate a peptide bond.

OR

4(b). What is the difference between Nucleotide and Nucleoside? [1 mark]

Solution:

Concept:

- A nucleoside consists of a nitrogenous base linked to a pentose sugar.
- A nucleotide contains a nitrogenous base, a pentose sugar and a phosphate group.

Step 1: Identify the nucleoside components The nitrogenous base is attached to the pentose sugar by an N-glycosidic linkage. A nucleoside therefore has two constituent types, base and sugar, and does not include phosphate. For example, adenosine consists of adenine and ribose.

Step 2: Identify the extra nucleotide component A nucleotide is obtained when a phosphate group is attached to a hydroxyl group of the sugar of a nucleoside by a phosphate ester linkage. Thus it contains the same base-sugar unit plus phosphate; adenosine monophosphate is an example.

Quick Tip to Solve: Check for phosphate: its presence distinguishes a nucleotide from the corresponding nucleoside.

Step 3: Conclusion **Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.**

Quick Tip to Solve: Check for phosphate: its presence distinguishes a nucleotide from the corresponding nucleoside.

5. Arrange the following in increasing order of their boiling point:
CH_3CH_2OH, CH_3CHO, CH_3-O-CH_3 [1 mark]

Solution:

Concept:

- For compounds of comparable molecular mass, stronger intermolecular attractions generally give a higher boiling point.
- Alcohols form intermolecular hydrogen bonds; aldehydes have substantial carbonyl dipole-dipole attractions, whereas ethers have weaker dipolar attractions.

Step 1: Compare ether and aldehyde Dimethyl ether, CH_3OCH_3, and ethanal, CH_3CHO, cannot hydrogen-bond to themselves because neither has an O-H bond. Ethanal has a strongly polar carbonyl group, so its intermolecular attractions are stronger and its boiling point is higher.

Step 2: Place the alcohol Ethanol, CH_3CH_2OH, has an O-H group and forms intermolecular hydrogen bonds. More energy is needed to separate its molecules during boiling. With the molecular masses comparable here, this makes ethanol the highest-boiling compound.

Step 3: Conclusion The increasing order is

$$\boxed{CH_3-O-CH_3 < CH_3CHO < CH_3CH_2OH}.$$

Quick Tip to Solve: For these similar-sized molecules, rank the attractions: ether dipoles, carbonyl dipoles, then alcohol hydrogen bonding.

Section B (14 marks)

6(a). What happens when AgCl is doped with $CdCl_2$? What is the name of this defect? [2 marks]

Solution:

Concept:

- A foreign ion of different charge produces an impurity defect when it replaces a host ion in an ionic crystal.
- Electrical neutrality requires the total positive charge to equal the total negative charge; a divalent ion cannot replace a monovalent ion without compensation.

Step 1: Identify the substituted ion AgCl contains Ag^+ and Cl^- ions. On doping with $CdCl_2$, some Cd^{2+} ions occupy silver-ion sites in the crystal lattice. Each cadmium ion contributes twice the positive charge of the silver ion that originally occupied that site.

Quick Tip to Solve: Compare dopant and host cation charges: a $+2$ dopant on a $+1$ site needs one additional vacant $+1$ site.

Step 2: Account for charge compensation One Cd^{2+} ion replaces the charge of two Ag^{+} ions. It occupies only one cation site, so the other silver-ion site must remain vacant. Thus, for every cadmium ion introduced, one cation vacancy is produced. The chloride-ion framework remains electrically balanced; the compensation is by a vacant silver site, rather than by adding an extra silver ion.

Step 3: Conclusion Doping AgCl with $CdCl_2$ produces one Ag^{+}-site vacancy per Cd^{2+} ion. This is an impurity defect with cation vacancies.

Quick Tip to Solve: Compare dopant and host cation charges: a $+2$ dopant on a $+1$ site needs one additional vacant $+1$ site.

OR

6(b). What type of defect is shown by NaCl in
(a) stoichiometric defects, and
(b) non-stoichiometric defects? [2 marks]

Solution:

Concept:

- Stoichiometric defects preserve the cation-to-anion ratio of an ionic crystal.
- A non-stoichiometric defect changes the ratio of ions; electrons may compensate for missing negative ions.

Step 1: Classify the stoichiometric defect NaCl shows the Schottky defect. Equal numbers of Na^{+} and Cl^{-} ions are missing from their normal lattice sites. The equal loss of positive and negative charges maintains electrical neutrality, and the ratio of sodium to chloride ions remains $1:1$. Since ions leave the crystal while its volume is approximately unchanged, its density decreases.

Step 2: Classify the non-stoichiometric defect NaCl can show a metal-excess defect due to anion vacancies. When heated in sodium vapour, some chloride-ion sites become vacant and an electron occupies each such site. These trapped electrons compensate the charge and form F-centres. The crystal therefore has excess sodium relative to chlorine. F-centres absorb visible light and impart a yellow colour to sodium chloride.

Step 3: Conclusion (a) Schottky defect. (b) Metal-excess defect due to anion vacancies occupied by electrons (F-centres).

Quick Tip to Solve: For NaCl distinguish paired missing ions (Schottky) from a missing chloride ion with a trapped electron (F-centre).

7. Account for the following:

(a) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.

(b) On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali. [2 marks]

Solution:

Concept:

- Gabriel synthesis uses nucleophilic substitution of a halide by the phthalimide anion, followed by hydrolysis to a primary amine.
- In the Hinsberg test, an acidic N–H bond in the sulphonamide permits formation of an alkali-soluble salt.

Step 1: Explain the limitation of Gabriel synthesis An aromatic primary amine would require the phthalimide anion to displace halide from an aryl halide. Ordinary aryl halides do not undergo this nucleophilic substitution readily: resonance gives the aryl carbon–halogen bond partial double-bond character, making it shorter and stronger. Consequently the required N-aryl phthalimide is not readily formed, so Gabriel synthesis is unsuitable for preparing aromatic primary amines.

Step 2: Compare the sulphonamide products A primary amine forms $C_6H_5SO_2NHR$ on reaction with benzene sulphonyl chloride. Its remaining N–H hydrogen is acidic because of the electron-withdrawing sulphonyl group; alkali removes it to give an ionic, soluble salt. A secondary amine forms $C_6H_5SO_2NR_2$, which has no N–H hydrogen. It cannot form this salt with alkali and remains insoluble.

Step 3: Conclusion (a) Aryl halides resist the nucleophilic substitution required for Gabriel synthesis. (b) The primary-amine sulphonamide has an acidic N–H bond and forms an alkali-soluble salt; the secondary-amine product has no N–H bond.

Quick Tip to Solve: After the Hinsberg reaction count hydrogens on nitrogen: an N–H bond allows salt formation in alkali.

8(a). Complete and balance the following equations:

(a) $S + H_2SO_4\ (\text{conc.}) \rightarrow$

(b) $PCl_3 + H_2O \rightarrow$ [2 marks]

Solution:

Concept:

- Hot concentrated sulphuric acid acts as an oxidising agent and is reduced to sulphur dioxide.
- Phosphorus trichloride undergoes hydrolysis to phosphorous acid and hydrogen chloride; balance every element in the final equation.

Step 1: Balance sulphur with concentrated sulphuric acid Sulphur is oxidised from oxidation state 0 to $+4$, losing four electrons. Sulphur in each acid molecule is reduced from $+6$ to $+4$, gaining two electrons. Hence two acid molecules are required for one sulphur atom. Balancing hydrogen and

Quick Tip to Solve: Use the two-electron reduction of each acid sulphur to balance (a); PCl3 hydrolysis produces H3PO3.

oxygen then gives

$$S + 2H_2SO_4\ (\text{conc.}) \longrightarrow 3SO_2 + 2H_2O.$$

Both sides contain three sulphur atoms, four hydrogen atoms and eight oxygen atoms.

Step 2: Balance hydrolysis of phosphorus trichloride All three P–Cl bonds are hydrolysed by water, producing phosphorous acid and hydrochloric acid. The balanced equation is

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl.$$

The three chlorine atoms require three HCl molecules. Three water molecules provide the three oxygen atoms of phosphorous acid and the six hydrogen atoms in the products. The acid formed is H_3PO_3, not phosphoric acid.

Step 3: Conclusion (a) $S + 2H_2SO_4\ (\text{conc.}) \rightarrow 3SO_2 + 2H_2O$.
(b) $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$.

Quick Tip to Solve: Use the two-electron reduction of each acid sulphur to balance (a); PCl3 hydrolysis produces H3PO3.

OR

8(b). Write balanced chemical equations involved in the following reactions:
(a) Chlorine gas reacts with cold and dilute NaOH.
(b) Calcium phosphide is dissolved in water. [2 marks]

Solution:

Concept:

- Chlorine disproportionates in cold dilute alkali, forming chloride and hypochlorite.
- Metal phosphides react with water to produce phosphine and the corresponding metal hydroxide.

Step 1: Balance chlorine with cold dilute sodium hydroxide Chlorine starts at oxidation state 0. One chlorine atom is reduced to -1 in chloride, while the other is oxidised to $+1$ in hypochlorite. Thus equal quantities of these products form:

$$Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O.$$

This is the reaction for cold, dilute alkali; the chlorate product belongs to the different hot, concentrated condition. Sodium, oxygen and hydrogen are balanced by two NaOH molecules and one water molecule.

Step 2: Balance calcium phosphide with water Calcium phosphide has formula Ca_3P_2. Its three calcium atoms give three calcium hydroxide units, and its two phosphorus atoms give two phosphine molecules:

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3.$$

Six water molecules supply six oxygen atoms for the hydroxide groups and twelve hydrogen atoms.

Quick Tip to Solve: Cold dilute alkali gives hypochlorite; in phosphide hydrolysis match Ca and P first, then balance water.

Six hydrogen atoms occur in the hydroxide and six in phosphine, confirming that the equation is balanced.

Step 3: Conclusion (a) $Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$.
(b) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$.

Quick Tip to Solve: Cold dilute alkali gives hypochlorite; in phosphide hydrolysis match Ca and P first, then balance water.

9. Draw structures of the following:

(a) XeF_4

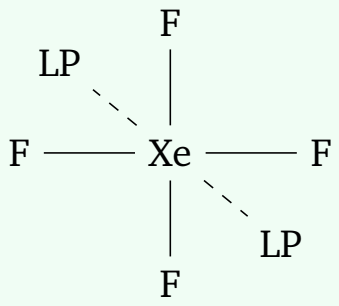
(b) $S_2O_8^{2-}$ [2 marks]

Solution:

Concept:

- VSEPR theory determines the molecular shape from bonding and lone electron pairs. In XeF_4, xenon has four bond pairs and two lone pairs.
- Peroxodisulphate, $S_2O_8^{2-}$, contains a peroxide linkage, $-O-O-$, connecting two tetrahedral sulphur centres.

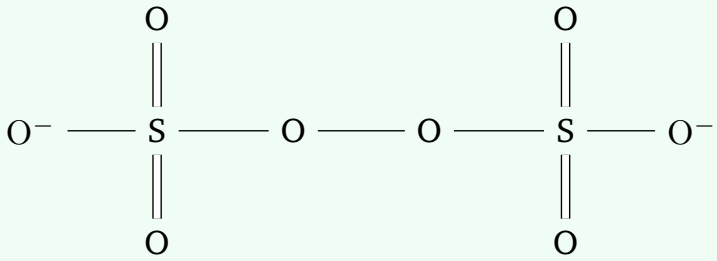
Step 1: (a) Structure of xenon tetrafluoride Six electron pairs around xenon have an octahedral arrangement. The two lone pairs occupy opposite positions to minimise their repulsion. The four fluorine atoms lie in one plane, giving a square-planar molecular shape, with adjacent $F-Xe-F$ angles of $90°$. In the drawing, LP denotes a lone pair; the axial lone pairs lie above and below the fluorine plane.



Square-planar XeF4; axial lone pairs shown schematically

Step 2: (b) Structure of peroxodisulphate Each sulphur atom is bonded to two terminal oxygen atoms by double bonds, one terminal O^- by a single bond, and one oxygen of the peroxide bridge by a single bond. Thus the connectivity is $^-O-S(=O)_2-O-O-S(=O)_2-O^-$. Each sulphur centre is approximately tetrahedral; the schematic below displays its connectivity. The two terminal negative charges give the overall charge $2-$.

Quick Tip to Solve: Count both lone pairs on Xe, and retain the O–O bridge when drawing peroxodisulphate.



Peroxodisulphate ion: the peroxide linkage is central

Step 3: Conclusion XeF_4 is square planar with two opposite axial lone pairs. $S_2O_8^{2-}$ has two sulphur centres joined by an $S-O-O-S$ peroxide bridge, as drawn.

Quick Tip to Solve: Count both lone pairs on Xe, and retain the O–O bridge when drawing peroxodisulphate.

10. (a) Write the reaction that occurs at anode on electrolysis of concentrated H_2SO_4 using platinum electrodes.

(b) What is the effect of temperature on ionic conductance? [2 marks]

Solution:

Concept:

- Oxidation takes place at the anode. In concentrated sulphuric acid, sulphate or hydrogen sulphate ions undergo oxidation to form peroxodisulphate or peroxodisulphuric acid.
- Ionic conductance depends on the mobility of ions in solution. Lower solvent viscosity permits ions to move more readily under an electric field.

Step 1: (a) Write the anodic oxidation With platinum electrodes and concentrated H_2SO_4, the anodic half-reaction may be written as

$$2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-.$$

Equivalently, in sulphate-ion form it is

$$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-.$$

Both expressions represent formation of a peroxide bond by oxidation. The electrons occur on the product side because anode oxidation releases electrons; atoms and net charge are balanced in each form.

Step 2: (b) Explain the temperature effect Ionic conductance increases as temperature rises. Heating reduces the viscosity of the solvent and increases ionic mobility, so ions carry electric charge more easily. For a weak electrolyte, increased ionisation can also contribute to the rise in conductance. This behaviour concerns electrolytic conduction by moving ions in solution.

Step 3: Conclusion At the anode, $2HSO_4^- \rightarrow H_2S_2O_8 + 2e^-$. Ionic conductance increases with increasing temperature because ionic mobility increases.

Quick Tip to Solve: For concentrated sulphuric acid at a platinum anode, write peroxide formation and put electrons on the right.

11. (a) Out of 0.1 molal aqueous solution of glucose and 0.1 molal aqueous solution of KCl, which one will have higher boiling point and why?

(b) Predict whether van't Hoff factor, (i) is less than one or greater than one in the following:

(i) CH_3COOH dissolved in water

(ii) CH_3COOH dissolved in benzene [2 marks]

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_bm$, where i is the van't Hoff factor, K_b is the solvent's ebullioscopic constant and m is molality.
- Dissociation increases the number of solute particles and gives $i > 1$. Association reduces their number and gives $i < 1$.

Step 1: (a) Compare the boiling points Both solutions have the same solvent and molality, so their K_b and m are equal. Glucose is a nonelectrolyte and remains as molecules, giving $i = 1$. Potassium chloride dissociates as

$$\mathrm{KCl(aq)} \longrightarrow \mathrm{K^+(aq) + Cl^-(aq)}.$$

Its van't Hoff factor is greater than one, approaching two for ideal complete dissociation. Consequently, iK_bm is larger for KCl, and its solution has the higher boiling point.

Step 2: (b)(i) Acetic acid in water Acetic acid partially ionises in water:

$$\mathrm{CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+}.$$

Each ionised acid molecule produces two solute ions. The number of solute particles therefore increases, and $i = 1 + \alpha > 1$, where α is the fraction ionised.

Step 3: (b)(ii) Acetic acid in benzene In benzene, acetic acid molecules associate into hydrogen-bonded dimers:

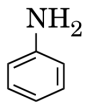
$$\mathrm{2CH_3COOH \rightleftharpoons (CH_3COOH)_2}.$$

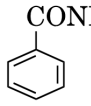
Two molecules become one solute particle, reducing the particle count. Thus $i = 1 - \alpha/2 < 1$, where here α is the fraction of acid molecules associated into dimers.

Step 4: Conclusion The 0.1-molal KCl solution has the higher boiling point. For acetic acid, $i > 1$ in water and $i < 1$ in benzene.

Quick Tip to Solve: At equal molality in the same solvent, compare particle counts: ions raise i, while dimers lower it.

12. Write structures of compounds A and B in each of the following reactions: [2 marks]

(a)  $\xrightarrow{\text{conc. } H_2SO_4}$ A $\xrightarrow{\text{heat, } 453-473 \text{ K}}$ B

(b)  $\xrightarrow{Br_2/NaOH}$ A $\xrightarrow{(CH_3CO)_2O/\text{pyridine}}$ B

Solution:

Concept:

- Aniline forms an anilinium salt with a strong acid. Heating anilinium hydrogen sulphate produces sulphanilic acid, with the sulphonic acid group para to the amino group.
- Hofmann bromamide degradation converts a primary amide into a primary amine containing one carbon atom fewer. Acetic anhydride acetylates the amino group of aniline.

Step 1: (a) Identify the salt A and sulphonation product B The basic nitrogen of aniline accepts a proton from concentrated sulphuric acid. Therefore A is anilinium hydrogen sulphate, with structure

$$[C_6H_5 - NH_3]^+[HSO_4]^-.$$

On heating at 453–$473\,\text{K}$, this salt yields sulphanilic acid. Thus B has the para-substituted structure

$$p - H_2N - C_6H_4 - S(=O)_2 - OH.$$

The $-NH_2$ and $-SO_3H$ groups occupy positions 1 and 4 of the benzene ring. Sulphanilic acid commonly exists as the zwitterion $p - {}^+H_3N - C_6H_4 - SO_3^-$.

Step 2: (b) Identify the Hofmann product A and acetylated product B Benzamide reacts with $Br_2/NaOH$ by Hofmann degradation. Its carbonyl carbon is lost, while the phenyl group remains attached to nitrogen. Hence A is aniline:

$$A = C_6H_5 - NH_2.$$

Acetic anhydride in pyridine acetylates the nitrogen of aniline, yielding acetanilide. Hence B has the structure

$$B = C_6H_5 - NH - C(=O) - CH_3.$$

The acetyl group replaces one hydrogen on the amino nitrogen; the benzene ring is unchanged.

Step 3: Conclusion (a) A: $[C_6H_5NH_3]^+[HSO_4]^-$; B: $p - H_2N - C_6H_4 - SO_3H$ (sulphanilic acid).
(b) A: $C_6H_5NH_2$; B: $C_6H_5NHCOCH_3$ (acetanilide).

Quick Tip to Solve: Separate salt formation from hot sulphonation; in the second sequence remove the amide carbonyl carbon before acetylating nitrogen.

Section C (36 marks)

13(a). Define the following with a suitable example, of each:

(a) Coagulation

(b) Multimolecular colloid

(c) Gel [3 marks]

Solution:

Concept:

- Colloidal particles remain dispersed because of stabilising factors such as electrical charge or solvation. Coagulation removes their stability and produces larger aggregates.
- Colloids are classified by how their particles are formed and by the physical states of the dispersed phase and dispersion medium. A gel has liquid dispersed in a solid medium.

Step 1: Define coagulation and give an example Coagulation is the aggregation of colloidal particles to form larger particles which separate out as a precipitate. Addition of an electrolyte can neutralise the charge on a sol, reducing repulsion between its particles. For example, adding sodium chloride solution to a ferric hydroxide sol causes its coagulation: the oppositely charged chloride ions discharge the positively charged colloidal particles.

Step 2: Define a multimolecular colloid and give an example A multimolecular colloid is one in which a large number of small atoms or molecules aggregate to form particles of colloidal dimensions, generally held together by van der Waals forces. For example, a gold sol contains colloidal particles made from aggregates of many gold atoms. Each individual gold atom is much smaller than a colloidal particle; it is the aggregate that constitutes the dispersed particle.

Step 3: Define a gel and give an example A gel is a colloidal system in which the dispersed phase is a liquid and the dispersion medium is a solid. The solid forms a network that holds the liquid, giving the system a semisolid character. Jelly is a suitable example. Thus its classification refers to the physical states of its two phases, rather than to the manner in which its particles are formed.

Step 4: Conclusion Coagulation: aggregation and precipitation of colloidal particles, e.g. ferric hydroxide sol with sodium chloride. Multimolecular colloid: aggregates of atoms or small molecules, e.g. gold sol. Gel: liquid dispersed in solid, e.g. jelly.

Quick Tip to Solve: For a gel, write the phase order explicitly: liquid is dispersed and solid is the medium.

OR

13(b). (a) Out of starch and ferric hydroxide sol, which one can easily be coagulated and why?
(b) What is observed when an emulsion is centrifuged?
(c) What is the role of promoters and poisons in catalysis? [3 marks]

Solution:

Concept:

- Lyophobic sols have little affinity for their dispersion medium and are stabilised mainly by particle charge; lyophilic sols additionally have strong solvation.
- Centrifugation separates phases with different densities. A promoter increases a catalyst's activity, while a poison reduces it.

Step 1: Compare the coagulation of the two sols Ferric hydroxide sol can be coagulated more easily. It is a lyophobic sol, whose particles have little affinity for water and are stabilised mainly by their electrical charge. A small amount of a suitable electrolyte neutralises that charge, allowing aggregation. Starch is lyophilic: its particles have considerable affinity for water and a protective hydration layer. Both charge and hydration contribute to its stability, so simple charge neutralisation is less effective.

Step 2: State the effect of centrifuging an emulsion An emulsion separates into its constituent liquid phases on centrifugation; this is demulsification. Centrifugation accelerates separation because the dispersed droplets and the surrounding liquid generally have different densities. The droplets concentrate and coalesce, ultimately producing separate liquid layers, such as the oil and water layers of an oil–water emulsion.

Step 3: Explain promoters and poisons in catalysis Promoters are substances which enhance the activity of a catalyst. For example, molybdenum acts as a promoter for the iron catalyst in the Haber process. Catalyst poisons decrease or destroy catalytic activity, often by occupying active sites and preventing reactant adsorption. For example, arsenic compounds poison the platinum catalyst used in the oxidation of sulphur dioxide. These terms describe their effect on the catalyst rather than their role as reactants in the overall reaction.

Step 4: Conclusion (a) Ferric hydroxide sol coagulates more readily because it is lyophobic. (b) The emulsion separates into its constituent liquid phases. (c) Promoters enhance catalytic activity; poisons suppress or destroy it.

Quick Tip to Solve: Compare starch and ferric hydroxide by hydration as well as charge; hydration makes starch harder to coagulate.

14. (a) Following reaction takes place in the cell:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Calculate $\Delta_r G^\circ$ of the reaction.

[Given: $E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V, $E^\circ_{(Ag^+/Ag)} = 0.80$ V, 1 F = 96,500 C mol^{-1}]

(b) How can you determine limiting molar conductivity, (Λ_m°) for strong electrolyte and weak electrolyte? [3 marks]

Solution:

Concept:

- For a cell reaction, $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant. Cell emf is cathode reduction potential minus anode reduction potential.
- For strong electrolytes, $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$ at low concentration. Kohlrauschś law gives Λ_m° as the stoichiometric sum of limiting ionic conductivities.

Step 1: Electron transfer and emf Zinc is oxidised from zero to $+2$, releasing two electrons; two silver atoms are reduced from $+1$ to zero. Hence $n = 2$. Using the reduction potentials supplied, the intended calculation is

$$E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56\,\text{V}.$$

Subtract the zinc reduction potential from the silver reduction potential.

Step 2: Standard Gibbs energy Using these supplied potentials,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(1.56)\\ &= -301080\,\text{J mol}^{-1}\\ &= -301.08\,\text{kJ mol}^{-1}.\end{aligned}$$

Strictly, the printed reaction contains Ag_2O, but the given potential is for Ag^+/Ag. The exact oxide-reaction value requires the $Ag_2O/Ag, OH^-$ potential or equivalent thermodynamic data; the result above is the intended supplied-potential calculation.

Step 3: Strong electrolyte Measure Λ_m at several low concentrations and plot it against $\sqrt{c}$. The dilute-solution plot is linear. Extrapolate the line to $\sqrt{c} = 0$; its conductivity-axis intercept is Λ_m°, the molar conductivity at infinite dilution.

Step 4: Weak electrolyte A weak electrolyte dissociates increasingly on dilution, so direct straight-line extrapolation is unreliable. Apply Kohlrauschś law using suitable strong electrolytes. For example,

$$\Lambda_m^\circ(CH_3COOH) = \Lambda_m^\circ(HCl) + \Lambda_m^\circ(CH_3COONa) - \Lambda_m^\circ(NaCl).$$

The sodium and chloride contributions cancel.

Step 5: Conclusion (a) The supplied potentials give the intended value $\Delta_r G^\circ = -301.08\,\text{kJ mol}^{-1}$; the literal oxide reaction requires oxide-electrode data. (b) Use extrapolation of Λ_m versus $\sqrt{c}$ for a strong electrolyte, and Kohlrauschś law for a weak electrolyte.

Quick Tip to Solve: Count two electrons from zinc, subtract the anode reduction potential, and convert joules to kilojoules only at the end.

15(a). Write down the reactions taking place in blast furnace related to the metallurgy of iron in the temperature range 500 K – 800 K. What is the role of limestone in the metallurgy of iron? [3 marks]

Solution:

Concept:

- In the blast furnace, carbon monoxide acts as the reducing agent: it removes oxygen from iron oxides and is itself oxidised to CO_2.
- Limestone, $CaCO_3$, supplies a basic flux, CaO, which combines with acidic silica gangue to form fusible slag.

Step 1: Reduction reactions in the 500–800 K region The reactions associated with the lower-temperature reduction zone are

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2,$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2,$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2.$$

Thus hematite is reduced to magnetite or ferrous oxide, and reduction of magnetite gives iron. In each equation, CO accepts oxygen from the ore; no carbon monoxide is merely a catalyst. These are the specified reactions for the stated temperature region.

Step 2: Formation of the basic flux Limestone decomposes in the hotter part of the furnace:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2.$$

The calcium oxide produced is basic and serves as the flux. Limestone is added to remove gangue, rather than to reduce the iron oxide.

Step 3: Removal of silica as slag Calcium oxide reacts with the acidic silica impurity present in the ore:

$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

Calcium silicate is a fusible slag. It floats over molten iron and can be removed separately, thereby separating silica gangue from the metal.

Step 4: Conclusion CO reduces the iron oxides through the reactions shown above. Limestone supplies CaO, which removes SiO_2 as calcium silicate slag, $CaSiO_3$.

Quick Tip to Solve: For limestone, write both steps: carbonate decomposition, followed by CaO reacting with silica to form slag.

OR

15(b). What happens when

(a) Silver is leached with NaCN in the presence of air?

(b) Copper matte is charged into silica lined converter and hot air blast is blown?

(c) NaCN is added in an ore containing PbS and ZnS during concentration by froth floatation method?

[3 marks]

Solution:

Concept:

- Leaching selectively dissolves a metal as a soluble complex; oxidation and complex formation enable cyanide leaching of silver.
- In copper extraction, air oxidises sulphides and silica removes iron oxide as slag; the copper compounds then undergo self-reduction.
- A depressant prevents a selected sulphide from entering the froth, permitting separation of mixed sulphide ores.

Step 1: (a) Silver leached with sodium cyanide in air Silver dissolves as the soluble dicyanidoargentate(I) complex. Oxygen from air enables its oxidation:

$$4Ag + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Ag(CN)_2] + 4NaOH.$$

Thus silver passes into the leach solution as $[Ag(CN)_2]^-$, while insoluble gangue can be separated. Air is essential to the oxidative leaching process.

Step 2: (b) Copper matte in a silica-lined converter Copper matte contains mainly Cu_2S and FeS. Hot air oxidises iron sulphide; the resulting iron oxide combines with silica:

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2,$$
$$FeO + SiO_2 \longrightarrow FeSiO_3.$$

Iron is removed as iron silicate slag. Part of the copper sulphide is oxidised to copper(I) oxide, which reacts with remaining sulphide:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2,$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2.$$

This self-reduction yields blister copper; escaping sulphur dioxide accounts for its blistered appearance.

Step 3: (c) Sodium cyanide in a mixture of PbS and ZnS NaCN acts as a depressant for ZnS. It selectively prevents ZnS from being collected in the froth, so ZnS remains in the aqueous pulp while PbS is carried into the froth. The two sulphide ores can therefore be separated by selective froth flotation.

Step 4: Conclusion (a) Silver forms soluble $Na[Ag(CN)_2]$. (b) Iron is removed as slag and blister copper is formed. (c) NaCN depresses ZnS, allowing PbS to enter the froth selectively.

Quick Tip to Solve: Remember the selective depressant pair: NaCN holds back ZnS, so PbS is the sulphide collected in the froth.

16. A solution 0.1 M of Na_2SO_4 is dissolved to the extent of 95%. What would be its osmotic pressure at 27°C? (R = 0.0821 L atm K^{-1} mol^{-1}) [3 marks]

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT$, where i is the van't Hoff factor, C is formula-unit molarity, R is the gas constant and T is absolute temperature.
- For dissociation of one formula unit into n ions with fractional dissociation α, the particle-count factor is $i = 1 + (n-1)\alpha$.

Step 1: Count the ions formed by sodium sulphate The given 95% extent is used as the extent of dissociation of this electrolyte in solution. Sodium sulphate dissociates as

$$\mathrm{Na_2SO_4} \longrightarrow 2\mathrm{Na^+} + \mathrm{SO_4^{2-}}.$$

Each dissociated formula unit produces three ions, so $n = 3$ and $\alpha = 95/100 = 0.95$. Starting with one mole of formula units, the undissociated amount is $1 - \alpha$ and the ions contribute 3α moles of particles. Therefore

$$i = (1-\alpha) + 3\alpha = 1 + 2(0.95) = 2.90.$$

Incomplete dissociation makes this factor slightly smaller than the fully dissociated value of 3.

Step 2: Convert temperature and calculate osmotic pressure The absolute temperature is $T = 27 + 273 = 300\,\mathrm{K}$. With $C = 0.1\,\mathrm{mol\ L^{-1}}$ and $R = 0.0821\,\mathrm{L\ atm\ K^{-1}mol^{-1}}$, substitution gives

$$\begin{aligned}\pi &= iCRT \\ &= 2.90 \times 0.1 \times 0.0821 \times 300 \\ &= 7.1427\,\mathrm{atm}.\end{aligned}$$

The litre, mole and kelvin units cancel to leave atmospheres. Equivalently, the effective particle concentration is $iC = 0.290\,\mathrm{mol\ L^{-1}}$, rather than the original formula-unit concentration of $0.1\,\mathrm{mol\ L^{-1}}$.

Step 3: Conclusion The osmotic pressure of the solution is $\boxed{\pi \approx 7.14\,\mathrm{atm}}$.

Quick Tip to Solve: Count all three ions of Na2SO4, use i = 1 + 2 alpha, and convert Celsius to kelvin before substituting.

17. (a) An element crystallises in bcc lattice with a cell edge of 3×10^{-8} cm. The density of the element is 6.89 g cm^{-3}. Calculate the molar mass of the element. ($N_A = 6.022 \times 10^{23}$ mol^{-1})

(b) What type of semiconductor is obtained when

(i) Ge is doped with In?

(ii) Si is doped with P? [3 marks]

Solution:

Concept:

- Unit-cell density is $\rho = ZM/(N_A a^3)$, where Z is the number of atoms per cell, M is molar mass, a is cell edge and N_A is Avogadro's constant.
- In a bcc cell, eight corner atoms contribute one atom altogether and the body-centred atom contributes one, so $Z = 2$.
- A trivalent dopant in a group-14 crystal produces holes (p-type); a pentavalent dopant supplies extra electrons (n-type).

Step 1: (a) Calculate the cell volume and molar mass Retaining centimetres is convenient because the density is in g cm^{-3}. The cell volume is

$$a^3 = (3 \times 10^{-8})^3 = 2.7 \times 10^{-23}\,\text{cm}^3.$$

Rearranging the density relation gives

$$\begin{aligned} M &= \frac{\rho N_A a^3}{Z} \\ &= \frac{6.89 \times 6.022 \times 10^{23} \times 2.7 \times 10^{-23}}{2} \\ &= 56.014\,\text{g mol}^{-1} \approx 56.0\,\text{g mol}^{-1}. \end{aligned}$$

The factors 10^{23} and 10^{-23} cancel. Dimensionally, density times cell volume gives grams, and multiplication by N_A/Z converts this to grams per mole.

Step 2: (b)(i) Identify the carriers in Ge doped with In Germanium has four valence electrons, whereas indium has three. Substitutional In leaves one neighbouring covalent bond deficient in an electron. This deficiency is a hole; holes become the majority carriers, giving a p-type semiconductor.

Step 3: (b)(ii) Identify the carriers in Si doped with P Silicon has four valence electrons and phosphorus has five. Four P electrons participate in covalent bonding, leaving one extra electron that can conduct. Electrons are the majority carriers, giving an n-type semiconductor.

Step 4: Conclusion (a) $M \approx 56.0\,\text{g mol}^{-1}$. (b)(i) Ge doped with In is p-type; (ii) Si doped with P is n-type.

Quick Tip to Solve: First set Z = 2 for bcc, cube the entire cell-edge expression, and compare the dopant's valence with four to identify the carrier.

18. Give reasons for the following:

(a) O−O single bond is weaker than S−S single bond.

(b) Tendency to show −3 oxidation state decreases from Nitrogen (N) to Bismuth (Bi).

(c) Cl_2 acts as a bleaching agent. [3 marks]

Solution:

Concept:

- Bond strength reflects both bonding attraction and electron-pair repulsions. Small atoms can bring nonbonding electron pairs very close together.
- The tendency to gain electrons decreases as atomic size and metallic character increase down group 15.
- Chlorine bleaches in the presence of moisture by oxidation of coloured substances; hypochlorous acid is formed in water.

Step 1: (a) Compare O–O and S–S single bonds Each atom in an O–O single bond has two lone pairs. Oxygen's small size brings the lone pairs on the two bonded atoms close together, producing strong lone-pair–lone-pair repulsion. This repulsion weakens the single bond. Sulphur atoms are larger, so their nonbonding electron pairs are farther apart and repel one another less strongly. Consequently, the S–S single bond is stronger than the O–O single bond. The effect concerns single bonds and should not be confused with the strength of the O=O double bond.

Step 2: (b) Explain the decreasing tendency for the -3 state Group-15 atoms have the valence configuration ns^2np^3 and need three additional electrons to complete an octet. From N to Bi, atomic size and shielding increase, while electronegativity decreases and metallic character increases. The attraction for incoming electrons therefore becomes weaker. Hence the tendency to exhibit the -3 oxidation state decreases down the group.

Step 3: (c) Explain chlorine's bleaching action In moist conditions, chlorine reacts with water to form hydrochloric acid and hypochlorous acid:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl.$$

The standard school-level representation of hypochlorous acid's oxidising action is

$$HOCl \longrightarrow HCl + [O].$$

Here $[O]$ denotes oxidising oxygen. It oxidises a coloured substance to a colourless product:

$$\text{Coloured substance} + [O] \longrightarrow \text{colourless product.}$$

The oxidation changes the colouring material chemically, so chlorine's bleaching is permanent. Dry chlorine does not bleach dry litmus because water is needed to generate the bleaching species.

Step 4: Conclusion (a) Stronger lone-pair repulsion weakens O–O. (b) Decreasing electronegativity reduces the tendency for the -3 state. (c) Moist chlorine bleaches by oxidation through hypochlorous acid.

Quick Tip to Solve: Link each reason to its cause: small oxygen means lone-pair repulsion, increasing group-15 size means weaker electron attraction, and moist chlorine means oxidation.

19(a). Write the structures of monomers used to obtain the following polymers:

(a) Buna-S

(b) Glyptal

(c) Nylon-6 [3 marks]

Solution:

Concept:

- Monomers are the small molecules from which a polymer is formed; their reactive groups determine the polymerisation process.
- Buna-S is an addition copolymer of a conjugated diene and styrene. Glyptal is a condensation polyester, while Nylon-6 is obtained by ring-opening polymerisation of a cyclic amide.

Step 1: (a) Monomers of Buna-S Buna-S is formed by copolymerising 1,3-butadiene and styrene. Their structures are

$$\underbrace{CH_2{=}CH{-}CH{=}CH_2}_{\text{1,3-butadiene}} \qquad \underbrace{C_6H_5{-}CH{=}CH_2}_{\text{styrene}}.$$

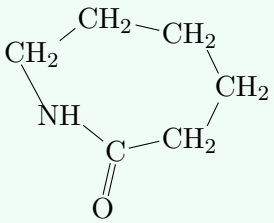
In styrene, C_6H_5 is the phenyl group, a benzene ring attached to the vinyl group. Both monomers contain carbon–carbon double bonds that participate in addition polymerisation; the S in Buna-S refers to styrene.

Step 2: (b) Monomers of Glyptal Glyptal is obtained from ethane-1,2-diol (ethylene glycol) and benzene-1,2-dicarboxylic acid (phthalic acid):

$$\underbrace{HO{-}CH_2{-}CH_2{-}OH}_{\text{ethylene glycol}} \qquad \underbrace{1{,}2{-}C_6H_4(COOH)_2}_{\text{phthalic acid}}.$$

The two carboxyl groups in phthalic acid occupy adjacent positions on the benzene ring (the ortho arrangement). Hydroxyl groups of the diol react with carboxyl groups of the diacid, forming ester links with elimination of water. This identifies Glyptal as a polyester.

Step 3: (c) Monomer of Nylon-6 The monomer is ε-caprolactam, a seven-membered cyclic amide. Its structure is



The ring contains one nitrogen atom, one carbonyl carbon and five methylene groups. Ring opening produces the polyamide chain with repeating unit $[-NH-(CH_2)_5-CO-]_n$. Thus the single monomer contains six carbon atoms, accounting for the name Nylon-6.

Step 4: Conclusion Buna-S: 1,3-butadiene and styrene. Glyptal: ethylene glycol and phthalic acid. Nylon-6: ε-caprolactam, with the structures shown above.

Quick Tip to Solve: Remember Buna-S as butadiene plus styrene; for Glyptal use the ortho diacid, and for Nylon-6 count six carbons in the caprolactam ring.

OR

19(b). (a) Arrange the following polymers in increasing order of their intermolecular forces: Polyvinylchloride, Neoprene, Terylene

(b) Write one example each of

(i) Natural polymer

(ii) Thermosetting polymer

(c) What is the significance of numbers 6,6 in the polymer Nylon-6,6? [3 marks]

Solution:

Concept:

- In the school classification, elastomers have the weakest intermolecular attractions, thermoplastics have intermediate attractions and fibres have stronger attractions that permit close packing and high tensile strength.
- Natural polymers occur in living organisms; thermosetting polymers form a permanent cross-linked network on heating. Nylon nomenclature identifies the carbon counts of its monomers.

Step 1: (a) Classify the polymers and compare their attractions Neoprene is an elastomer: its chains have relatively weak intermolecular attractions, so they can stretch and recover. Polyvinylchloride (PVC) is a thermoplastic, with stronger attractions than an elastomer. Terylene is a polyester fibre; its chains have strong intermolecular attractions, including dipole interactions associated with ester groups, giving high tensile strength. Thus the increasing order is

$$\text{Neoprene} < \text{Polyvinylchloride} < \text{Terylene}.$$

This is an order of attractions between chains, not of the covalent bond strength within an individual chain.

Step 2: (b) Give examples of the two polymer classes (i) Cellulose is a natural polymer. It is a polysaccharide produced by plants and is a major constituent of their cell walls. (ii) Bakelite is a thermosetting polymer. Its phenol-formaldehyde chains form a cross-linked network on curing, so the hardened material cannot be repeatedly softened and remoulded like a thermoplastic.

Step 3: (c) Interpret the two numbers in Nylon-6,6 Nylon-6,6 is formed by condensation of hexamethylenediamine, $H_2N(CH_2)_6NH_2$, and adipic acid, $HOOC(CH_2)_4COOH$. The first 6 denotes the six carbon atoms in the diamine; the second 6 denotes the six carbon atoms in the dicarboxylic acid. Adipic acid has four methylene carbons plus two carboxyl carbons, so its total is six.

Step 4: Conclusion (a) Neoprene $<$ Polyvinylchloride $<$ Terylene. (b) Natural polymer: cellulose; thermosetting polymer: Bakelite. (c) Each monomer used in Nylon-6,6 contains six carbon atoms.

Quick Tip to Solve: Use elastomer $<$ thermoplastic $<$ fibre, and count the carboxyl carbons when interpreting the second 6 in Nylon-6,6.

20(a). Which one of the following is a disinfectant?

0.2% solution of phenol or 1% solution of phenol

(b) What is the difference between agonists and antagonists?

(c) Write one example each of

(i) Artificial sweetener

(ii) Antacids [3 marks]

Solution:

Concept:

- A disinfectant destroys microorganisms on non-living objects. Whether a chemical is suitable as an antiseptic or disinfectant can depend on its concentration.
- Receptor-binding drugs may either activate a receptor and reproduce its natural response or block receptor action. Sweeteners impart sweetness, whereas antacids neutralise excess stomach acid.

Step 1: (a) Select the disinfectant concentration The 1% solution of phenol is a disinfectant. The more dilute 0.2% phenol solution is used as an antiseptic. Thus the same compound has different uses at the two concentrations: the stronger solution is used on non-living objects, while the dilute solution is suitable for antiseptic use. The required choice depends on the stated concentration rather than the name phenol alone.

Step 2: (b) Distinguish agonists from antagonists Agonists bind to a receptor and activate it, mimicking the action of the body's natural chemical messenger. They therefore produce the normal receptor-mediated response. Antagonists also bind to receptors, but block their action instead of activating them. By occupying the receptor they prevent the natural messenger from producing its usual response. The key distinction is activation versus blocking; receptor binding by itself does not make a drug an agonist.

Step 3: (c) Give suitable examples (i) Saccharin is an artificial sweetener: it provides a sweet taste and is used as a sugar substitute. (ii) Magnesium hydroxide, $\mathrm{Mg(OH)_2}$, is an antacid, commonly used as milk of magnesia. It neutralises excess hydrochloric acid in the stomach according to

$$\mathrm{Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O}.$$

These examples distinguish the food-additive role of a sweetener from the acid-neutralising role of an antacid.

Step 4: Conclusion (a) 1% phenol solution. (b) Agonists activate receptors and mimic natural messengers; antagonists block receptor action. (c) Artificial sweetener: saccharin; antacid: magnesium hydroxide.

Quick Tip to Solve: Remember phenol at 0.2 percent as antiseptic and at 1 percent as disinfectant; distinguish receptor activation from receptor blocking.

OR

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

(a) Antiseptics

(b) Bactericidal antibiotics

(c) Cationic detergents [3 marks]

Solution:

Concept:

- Antimicrobial substances are distinguished by their use and action: antiseptics are applied to living tissue, while bactericidal antibiotics kill bacteria rather than merely inhibiting their growth.
- A detergent contains a hydrophobic hydrocarbon region and a hydrophilic ionic region. Cationic detergents have a positively charged organic detergent ion, usually a quaternary ammonium ion.

Step 1: (a) Define antiseptics and give an example Antiseptics are chemical substances that kill microorganisms or inhibit their growth and can be applied to living tissues, such as wounds and cuts, without harming those tissues at the suitable concentration. A suitable example is tincture of iodine, a solution of iodine in an alcohol-water mixture, used on wounds. Their application to living tissue distinguishes antiseptics from disinfectants used on non-living surfaces.

Step 2: (b) Define bactericidal antibiotics and give an example Bactericidal antibiotics are antibiotics that kill bacteria. Penicillin is a suitable example; it interferes with bacterial cell-wall formation and can cause the death of susceptible bacteria. This killing action distinguishes a bactericidal antibiotic from a bacteriostatic antibiotic, which inhibits bacterial growth without directly killing the bacteria. Thus the defining property is bacterial death, not simply slowing multiplication.

Step 3: (c) Define cationic detergents and give an example Cationic detergents are detergents in which the organic surface-active ion is positively charged. They are commonly quaternary ammonium salts containing a long hydrocarbon chain. A suitable example is cetyltrimethylammonium bromide:

$$[CH_3(CH_2)_{15}N(CH_3)_3]^+Br^-.$$

Its long hydrocarbon chain is the hydrophobic part, while the positively charged ammonium group is the hydrophilic part. Bromide is the counterion; the positive organic ion gives this detergent its cationic classification.

Step 4: Conclusion (a) Antiseptics act against microorganisms on living tissue; example: tincture of iodine. (b) Bactericidal antibiotics kill bacteria; example: penicillin. (c) Cationic detergents have a positively charged organic surface-active ion; example: cetyltrimethylammonium bromide.

Quick Tip to Solve: Link each definition to its deciding feature: living tissue, bacterial killing, or a positively charged organic detergent ion.

21. What happens when

(a) Salicylic acid is treated with $(CH_3CO)_2O/H^+$?

(b) Phenol is oxidised with $Na_2Cr_2O_7/H^+$?

(c) Anisole is treated with CH_3Cl/anhydrous $AlCl_3$?

Write chemical equation in support of your answer. [3 marks]

Solution:

Concept:

- Acetic anhydride acetylates the phenolic $-OH$ group of salicylic acid, forming an ester while retaining its carboxyl group.
- Acidified sodium dichromate oxidises phenol to a quinone. The methoxy group of anisole activates the aromatic ring and directs electrophilic substitution to the ortho and para positions.

Step 1: (a) Acetylation of salicylic acid Salicylic acid is 2-hydroxybenzoic acid. In the presence of acid, its phenolic hydrogen is replaced by an acetyl group, CH_3CO-. The product is acetylsalicylic acid, commonly called aspirin; ethanoic acid is the coproduct.

$$o\text{-}HOC_6H_4COOH + (CH_3CO)_2O \xrightarrow{H^+} o\text{-}CH_3COOC_6H_4COOH + CH_3COOH.$$

The $-COOH$ substituent remains intact; acetylation occurs at the phenolic oxygen.

Step 2: (b) Oxidation of phenol Phenol is oxidised to benzene-1,4-dione (p-benzoquinone), which has two carbonyl groups at opposite ring positions. Writing $[O]$ for oxygen supplied by the oxidising reagent gives

$$C_6H_5OH + 2[O] \xrightarrow{Na_2Cr_2O_7/H^+} C_6H_4O_2 + H_2O.$$

The product is a quinone, rather than an alcohol or an aromatic carboxylic acid.

Step 3: (c) Friedel–Crafts methylation of anisole Anisole undergoes electrophilic substitution with chloromethane in the presence of anhydrous aluminium chloride. Electron donation by $-OCH_3$ favours attack at the ortho and para ring positions, producing a mixture of 2-methylanisole and 4-methylanisole. The para product is the major product because it is less sterically crowded.

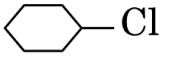
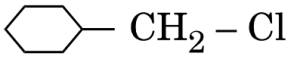
$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhydrous } AlCl_3} o\text{- or } p\text{-}CH_3C_6H_4OCH_3 + HCl.$$

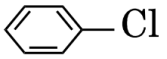
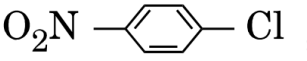
This equation represents each substitution product; methylation occurs on the ring.

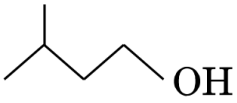
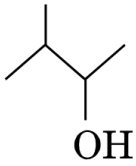
Step 4: Conclusion (a) Aspirin is formed. (b) Phenol gives p-benzoquinone. (c) Anisole gives ortho- and para-methylanisole, with the para isomer as the major product.

Quick Tip to Solve: Track the reactive group: phenolic oxygen is acetylated, phenol is oxidised to quinone, and anisole undergoes ortho/para ring methylation.

22. [3 marks]

(a) Out of  and , which one is more reactive towards S_N2 reaction and why ?

(b) Out of  and , which one is more reactive towards nucleophilic substitution reaction and why ?

(c) Out of  and , which one is optically active and why ?

Solution:

Concept:

- An S_N2 substitution occurs by simultaneous backside attack and departure of the leaving group. Lower steric hindrance at the carbon bearing the leaving group increases its rate.
- A nitro group ortho or para to an aryl halide stabilises the negatively charged intermediate in nucleophilic aromatic substitution through resonance.
- A tetrahedral carbon bonded to four different groups is a stereogenic centre; an individual enantiomer of such a chiral molecule is optically active.

Step 1: (a) Compare the saturated chlorides Cyclohexylmethyl chloride, $C_6H_{11}CH_2Cl$, is more reactive towards S_N2 substitution than cyclohexyl chloride, $C_6H_{11}Cl$. In the former, chlorine is attached to the external $-CH_2-$ carbon, a primary carbon bonded to only one other carbon. The nucleophile can approach this centre from the side opposite the C–Cl bond with less obstruction. In cyclohexyl chloride, the carbon bearing chlorine is a secondary ring carbon bonded to two carbon neighbours. The ring and neighbouring carbon groups hinder backside attack. Both compounds contain saturated rings, so the distinction here is steric hindrance at a primary versus a secondary carbon, rather than aromatic resonance.

Step 2: (b) Compare the aromatic chlorides p-Nitrochlorobenzene is more reactive than chlorobenzene towards nucleophilic substitution. The electron-withdrawing $-NO_2$ group at the para position makes the carbon bearing chlorine more susceptible to nucleophilic attack. After addition of the nucleophile, the negative charge of the intermediate can delocalise into the nitro group, stabilising that intermediate and facilitating subsequent loss of chloride. Chlorobenzene lacks this additional stabilisation. Its C–Cl bond also has partial double-bond character from resonance, so ordinary nucleophilic substitution is difficult. The comparison concerns activated nucleophilic aromatic substitution, rather than a direct S_N2 attack on an aromatic carbon.

Step 3: (c) Identify the stereogenic centre The second alcohol, $CH_3CH(OH)CH(CH_3)CH_3$, is 3-methylbutan-2-ol. Its carbon numbered 2 is attached to four different groups: $-H$, $-OH$, $-CH_3$, and $-CH(CH_3)_2$. It is therefore chiral and its individual enantiomers are optically active. The first alcohol,

Quick Tip to Solve: For substitution, inspect the carbon bonded to chlorine; for optical activity, list all four groups on the carbon bearing OH.

$(CH_3)_2CHCH_2CH_2OH$, is 3-methylbutan-1-ol. Its branched carbon bears two identical methyl groups, and each other saturated carbon has repeated hydrogen atoms. Thus it has no stereogenic centre and is optically inactive. A racemic mixture of the second alcohol would also show no net optical rotation, but the structural comparison identifies the second molecule as the optically active one.

Step 4: Conclusion (a) Cyclohexylmethyl chloride is more reactive by the S_N2 mechanism. (b) p-Nitrochlorobenzene is more reactive towards nucleophilic substitution. (c) 3-Methylbutan-2-ol is chiral and has optically active enantiomers.

Quick Tip to Solve: For substitution, inspect the carbon bonded to chlorine; for optical activity, list all four groups on the carbon bearing OH.

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23. (a) Give one chemical test as an evidence to show that $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$ are ionisation isomers.

(b) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why? (Atomic no. of Ni = 28)

(c) Write the electronic configuration of Fe(III) on the basis of crystal field theory when it forms an octahedral complex in the presence of (i) strong field ligand, and (ii) weak field ligand. (Atomic no. of Fe = 26) [3 marks]

Solution:

Concept:

- Ionisation isomers exchange a coordinated ligand with a counter-ion. A precipitation test detects the ion outside the coordination sphere, which dissociates in aqueous solution.
- Unpaired electrons cause paramagnetism. The oxidation state of the metal determines its d-electron count; molecular geometry alone does not determine magnetic behaviour.
- In an octahedral field, the lower t_{2g} set contains three orbitals and the upper e_g set contains two. Strong fields favour pairing, whereas weak fields favour maximum unpaired occupation.

Step 1: (a) Test the freely ionisable sulphate Add aqueous barium chloride to separate aqueous solutions of the complexes. $[Co(NH_3)_5Cl]SO_4$ gives a white precipitate of barium sulphate because sulphate is its counter-ion outside the coordination sphere:

$$[Co(NH_3)_5Cl]SO_4 \longrightarrow [Co(NH_3)_5Cl]^{2+} + SO_4^{2-},$$

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow .$$

$[Co(NH_3)_5(SO_4)]Cl$ does not give this immediate sulphate precipitate, since sulphate is coordinated to cobalt rather than freely ionisable. Its counter-ion is chloride. This difference establishes that the two complexes release different ions despite having the same overall composition.

Step 2: (b) Explain the nickel complexes In $[NiCl_4]^{2-}$, the four chloride ligands contribute a total charge of -4, so nickel is in the $+2$ state. Neutral Ni has configuration $[Ar]3d^8 4s^2$; hence Ni^{2+} is $3d^8$. In a tetrahedral field this gives $e^4t_2^4$, with two unpaired electrons, making the complex paramagnetic. Chloride is a weak-field ligand. In $[Ni(CO)_4]$, CO is neutral and nickel is in oxidation state zero.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons, and test only the ions written outside the square brackets.

Strong-field CO causes the two $4s$ electrons to enter the $3d$ subshell, giving a filled $3d^{10}$ configuration in the standard valence-bond account. All electrons are paired, so the tetrahedral sp^3 complex is diamagnetic. Thus the two tetrahedral complexes differ in oxidation state and electron occupation.

Step 3: (c) Distribute the electrons of Fe(III) Fe has configuration $[\mathrm{Ar}]3d^6 4s^2$. Removing the two $4s$ electrons and one $3d$ electron gives $\mathrm{Fe}^{3+} = [\mathrm{Ar}]3d^5$. With a strong-field ligand, the octahedral splitting Δ_o exceeds the pairing energy P, so the five electrons occupy the lower set as $\boxed{t_{2g}^5 e_g^0}$. There are two paired orbitals and one unpaired electron: this is the low-spin configuration. With a weak-field ligand, $\Delta_o < P$, so electrons occupy all five d orbitals singly before pairing. The configuration is $\boxed{t_{2g}^3 e_g^2}$, with five unpaired electrons: this is the high-spin configuration.

Step 4: Conclusion (a) Only $[\mathrm{Co(NH_3)_5Cl}]\mathrm{SO_4}$ gives an immediate white $\mathrm{BaSO_4}$ precipitate. (b) The nickel chloride complex has two unpaired electrons, whereas the carbonyl has none. (c) Strong field: $t_{2g}^5 e_g^0$; weak field: $t_{2g}^3 e_g^2$.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons, and test only the ions written outside the square brackets.

24. Differentiate between the following:

(a) Fibrous protein and Globular protein

(b) Essential amino acids and Non-essential amino acids

(c) Amylose and Amylopectin [3 marks]

Solution:

Concept:

- Protein shape and solubility depend on how polypeptide chains fold and associate; these features also relate to their biological roles.
- Essentiality of an amino acid refers to whether the human body can synthesise enough of it. It does not refer to whether the amino acid is important.
- Amylose and amylopectin are both components of starch made from α-D-glucose; their glycosidic linkages determine their chain architecture.

Step 1: (a) Fibrous proteins and globular proteins Fibrous proteins have polypeptide chains arranged in long, fibre-like structures, commonly held together by hydrogen bonds and disulphide bonds. They are generally insoluble in water and serve structural roles. Examples are keratin in hair and wool, and myosin in muscles. Globular proteins have chains folded into compact, approximately spherical structures. They are usually water-soluble and commonly perform metabolic or regulatory functions; examples are insulin and albumin.

Step 2: (b) Essential and non-essential amino acids Essential amino acids cannot be synthesised by the human body in the required amounts, so they must be supplied through the diet. Valine and leucine are examples. Non-essential amino acids can be synthesised by the body and therefore need not necessarily be obtained directly from food. Glycine and alanine are examples. Both categories are needed for normal protein synthesis; only their dietary requirement differs.

Quick Tip to Solve: Compare each pair on the same basis: protein shape and solubility, amino-acid synthesis, and starch-chain branching.

Step 3: (c) Amylose and amylopectin Amylose is a predominantly unbranched polymer of α-D-glucose with $\alpha(1 \rightarrow 4)$ glycosidic linkages; its chain can coil into a helix. It forms about 15–20% of starch and is water-soluble. Amylopectin is a branched polymer: the main chains have $\alpha(1 \rightarrow 4)$ linkages, while branches occur through $\alpha(1 \rightarrow 6)$ linkages. It forms about 80–85% of starch and is insoluble in water.

Step 4: Conclusion Fibrous and globular proteins differ in shape and solubility; essential and non-essential amino acids differ in the need for dietary supply; amylose is unbranched whereas amylopectin contains branch linkages.

Quick Tip to Solve: Compare each pair on the same basis: protein shape and solubility, amino-acid synthesis, and starch-chain branching.

Section D (15 marks)

25(a). Account for the following:

(i) Manganese shows maximum number of oxidation states in 3d series.

(ii) E° value for Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+}.

(iii) Ti^{4+} is colourless whereas V^{4+} is coloured in an aqueous solution.

(b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2. Why does purple colour of acidified permanganate solution decolourise when it oxidises Fe^{2+} to Fe^{3+}? [5 marks]

Solution:

Concept:

- The small energy difference between $3d$ and $4s$ orbitals allows both sets of electrons to participate in bonding in transition elements.
- A standard reduction potential measures the tendency for reduction. Particularly stable electronic configurations influence the relative stability of the two oxidation states.
- Visible-light absorption through d-d transitions requires occupied and vacant levels within the split d orbitals of a complex.
- Preparation of permanganate proceeds through manganate, and acidified permanganate is reduced from Mn(VII) to Mn(II) while oxidising iron(II).

Step 1: (a)(i) Variable oxidation states of manganese Manganese has the configuration $[\mathrm{Ar}]\,3d^5 4s^2$. Its five $3d$ electrons and two $4s$ electrons can participate in bonding because these orbitals have comparable energies. Consequently, different numbers of these seven electrons can be involved, giving oxidation states from $+2$ to $+7$. This provides manganese with the maximum number of oxidation states among the $3d$-series elements.

Step 2: (a)(ii) Compare the reduction potentials Reduction of Mn^{3+}, which is $3d^4$, gives Mn^{2+} with the especially stable half-filled $3d^5$ configuration. Thus, Mn^{3+} has a strong tendency to accept an electron. By contrast, Cr^{3+} has a stable $3d^3$ configuration (t_{2g}^3 in its octahedral aqueous complex), whereas Cr^{2+} is $3d^4$. Reduction of chromium(III) therefore loses this relative stability. Hence the standard reduction potential for Mn^{3+}/Mn^{2+} is much more positive than that for Cr^{3+}/Cr^{2+}.

Step 3: (a)(iii) Explain the colours Titanium has configuration $[\mathrm{Ar}]\,3d^2 4s^2$, so Ti^{4+} is $3d^0$. It has

Quick Tip to Solve: First write the ionic d-electron counts; for permanganate in acid, remember that one ion consumes five iron(II) ions.

no d electron for a d-d transition and is colourless in aqueous solution. Vanadium has configuration $[\mathrm{Ar}]\,3d^3 4s^2$, so V^{4+} is $3d^1$. In its aqueous complex, the d orbitals split into different energy levels. The electron absorbs visible light to move to a higher level, so the solution appears coloured.

Step 4: (b) Prepare potassium permanganate Fuse manganese dioxide with potassium hydroxide in the presence of oxygen (air). Oxidation produces green potassium manganate:

$$2\mathrm{MnO_2} + 4\mathrm{KOH} + \mathrm{O_2} \longrightarrow 2\mathrm{K_2MnO_4} + 2\mathrm{H_2O}.$$

Oxidise the manganate electrolytically in alkaline solution to obtain potassium permanganate. The anode reaction is

$$\mathrm{MnO_4^{2-}} \longrightarrow \mathrm{MnO_4^-} + e^-.$$

With hydrogen evolution at the cathode, the overall preparation step can be written as

$$2\mathrm{K_2MnO_4} + 2\mathrm{H_2O} \xrightarrow{\text{electrolysis}} 2\mathrm{KMnO_4} + 2\mathrm{KOH} + \mathrm{H_2}.$$

Step 5: (b) Explain decolourisation during iron(II) oxidation In acidic medium each permanganate ion accepts five electrons and is reduced to $\mathrm{Mn^{2+}}$, while five iron(II) ions each lose one electron:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5e^- \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O},$$
$$5\mathrm{Fe^{2+}} \longrightarrow 5\mathrm{Fe^{3+}} + 5e^-.$$

Adding these gives

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{Fe^{2+}} \longrightarrow \mathrm{Mn^{2+}} + 4\mathrm{H_2O} + 5\mathrm{Fe^{3+}}.$$

Purple $\mathrm{MnO_4^-}$ is consumed and replaced by very pale pink $\mathrm{Mn^{2+}}$, which is practically colourless in dilute solution. Therefore the purple colour disappears while sufficient iron(II) remains.

Step 6: Conclusion Manganese uses its seven valence electrons to show many oxidation states; the stability of $\mathrm{Mn^{2+}}$ and $\mathrm{Cr^{3+}}$ explains their potential difference. The d^0 and d^1 configurations explain the titanium and vanadium colours. Permanganate is prepared through manganate and loses its purple colour on reduction to $\mathrm{Mn^{2+}}$ during iron(II) oxidation.

Quick Tip to Solve: First write the ionic d-electron counts; for permanganate in acid, remember that one ion consumes five iron(II) ions.

OR

25(b). (a) Write one difference between transition elements and p-block elements with reference to variability of oxidation states.

(b) Why do transition metals exhibit higher enthalpies of atomization?

(c) Name an element of lanthanoid series which is well known to shown +4 oxidation state. Is it a strong oxidising agent or reducing agent?

(d) What is lanthanoid contraction? Write its one consequence.

(e) Write the ionic equation showing the oxidation of Fe(II) salt by acidified dichromate solution.

[5 marks]

Solution:

Concept:

- Transition-metal oxidation states involve electrons from both the $(n-1)d$ and ns subshells, whose energies are comparable.
- Strong metallic bonding gives a large enthalpy of atomization. Poor shielding by $4f$ electrons causes the lanthanoid contraction.
- An oxidising agent accepts electrons. Ionic redox equations conserve both atoms and total charge.

Step 1: (a) Compare the variability of oxidation states Transition elements commonly show several oxidation states differing by one unit, because both outer ns and inner $(n-1)d$ electrons can participate in bonding. For example, manganese exhibits $+2, +3, +4, +5, +6$ and $+7$ states. In p-block elements, the common variable oxidation states generally differ by two units, owing to participation or nonparticipation of the outer ns^2 pair. For example, tin shows $+2$ and $+4$, while lead also shows $+2$ and $+4$.

Step 2: (b) Explain the high enthalpies of atomization Transition metals possess a considerable number of unpaired d electrons, along with s electrons, available for metallic bonding. This produces strong attraction between the metal atoms in the lattice. Separating the solid metal into individual gaseous atoms therefore requires considerable energy, so their enthalpies of atomization are generally high. The relevant process is $\mathrm{M(s)} \rightarrow \mathrm{M(g)}$; it breaks metallic bonding rather than removing an electron from an atom.

Step 3: (c) Identify the lanthanoid and its redox character Cerium, Ce, is well known for the $+4$ oxidation state. Cerium(IV) is a strong oxidising agent because it readily accepts an electron to form the more stable, usual lanthanoid $+3$ state:

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

Thus it oxidises another substance while itself being reduced.

Step 4: (d) Define lanthanoid contraction and state a consequence Lanthanoid contraction is the gradual decrease in atomic size and, particularly, the radii of $\mathrm{Ln^{3+}}$ ions from lanthanum to lutetium as atomic number increases. Added $4f$ electrons shield the increasing nuclear charge poorly, so effective nuclear attraction increases and draws the electron cloud inward. One consequence is that zirconium and hafnium have nearly equal atomic radii and consequently very similar chemical properties, making their separation difficult.

Quick Tip to Solve: In acidic dichromate reactions, balance the dichromate half-reaction first: its six-electron requirement fixes the coefficient of iron(II) as six.

Step 5: (e) Balance the oxidation of iron(II) by dichromate Each iron(II) ion loses one electron, whereas one dichromate ion accepts six electrons in acidic solution:

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-},$$
$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O}.$$

Multiply the iron half-reaction by six and add, cancelling the electrons. The resulting equation has two chromium atoms, seven oxygen atoms and fourteen hydrogen atoms on each side; the net charge on each side is $+24$.

Step 6: Conclusion Transition-metal oxidation states commonly differ by one, while p-block states generally differ by two. Strong metallic bonding explains high atomization enthalpy. Cerium(IV) is a strong oxidising agent; lanthanoid contraction gives nearly equal Zr and Hf radii. The required ionic equation is

$$\boxed{\mathrm{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}}}.$$

Quick Tip to Solve: In acidic dichromate reactions, balance the dichromate half-reaction first: its six-electron requirement fixes the coefficient of iron(II) as six.

26(a). Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction?

(b) A first order reaction is 50% complete in 25 minutes. Calculate the time for 80% completion of the reaction. [5 marks]

Solution:

Concept:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- Molecularity counts the reacting species participating simultaneously in a single elementary step; it does not describe an overall complex reaction.
- For a first-order reaction, $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$ and $t_{1/2} = \dfrac{0.693}{k}$, where k is the rate constant and $[A]_t$ is the concentration remaining at time t.

Step 1: (a) Define order and distinguish it from molecularity If the observed rate law is $r = k[A]^m[B]^n$, the order of reaction is $m + n$. The exponents must be determined experimentally; they need not equal the stoichiometric coefficients in the balanced overall equation. Order may be zero, integral or fractional, and it applies to the experimentally observed rate of an overall complex reaction. Molecularity is the number of reacting atoms, ions or molecules taking part in an elementary reaction step. It is always a positive integer, usually one, two or three, and cannot be zero or fractional. A complex reaction proceeds through several elementary steps, so molecularity is assigned to each individual step and is not defined for the overall complex reaction. Its observed order follows its rate law and mechanism, often involving the slow step; it cannot be obtained simply by counting species in the overall equation.

Quick Tip to Solve: Convert percent completion into the fraction remaining before using the logarithm: eighty percent completion gives an initial-to-remaining concentration ratio of five.

Step 2: (b) Obtain the rate constant from the half-life At 50% completion, half the initial reactant remains. The given time is therefore the first-order half-life:

$$t_{1/2} = 25\,\text{min}.$$

Hence

$$k = \frac{0.693}{25} = 0.02772\,\text{min}^{-1}.$$

The unit is inverse minutes because the supplied time is in minutes. For a first-order reaction this half-life is independent of the initial concentration, so no starting concentration is needed.

Step 3: Calculate the time for eighty percent completion At 80% completion, 20% remains unreacted. Thus $[A]_t = 0.20[A]_0$, giving $[A]_0/[A]_t = 5$. Substitution in the integrated first-order rate law gives

$$\begin{aligned} t_{80\%} &= \frac{2.303}{0.02772}\log 5 \\ &= \frac{2.303 \times 0.6990}{0.02772}\,\text{min} \\ &\approx 58.1\,\text{min}. \end{aligned}$$

As a check, the same result follows from $t_{80\%}/t_{1/2} = \log 5/\log 2 \approx 2.322$. After two half-lives, namely $50\,\text{min}$, the completion is only 75%, so the required time must exceed $50\,\text{min}$. The calculation is consistent with that check. Completion must not be treated as proportional to elapsed time because the reaction rate decreases as reactant concentration falls.

Step 4: Conclusion Order is the sum of the experimentally determined concentration exponents in the rate law. Molecularity is defined only for an elementary step, not an overall complex reaction. The time required for 80% completion is $\boxed{58.1\,\text{min}}$.

Quick Tip to Solve: Convert percent completion into the fraction remaining before using the logarithm: eighty percent completion gives an initial-to-remaining concentration ratio of five.

OR

26(b). (a) The decomposition of a hydrocarbon has value of rate constant as 2.5 $\times$ 10^4 s^{-1} at 27°C. At what temperature would rate constant be 7.5 $\times$ 10^4 s^{-1} if energy of activation is 19.147 $\times$ 10^3 J mol^{-1}?

(b) Write a condition under which a bimolecular reaction is kinetically first order. Give an example of such a reaction.

(Given: log 2 = 0.3010, log 3 = 0.4771, log 5 = 0.6990) [5 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy and $R = 8.314\,\text{J mol}^{-1}\text{K}^{-1}$.

Quick Tip to Solve: Divide the rate constants first: their common power of ten cancels, leaving the supplied log 3; convert Celsius to kelvin before using Arrhenius.

- For the same reaction at two temperatures, $\log(k_2/k_1) = \dfrac{E_a}{2.303R}(1/T_1 - 1/T_2)$. Temperatures must be in kelvin.
- A bimolecular reaction with rate $r = k[A][B]$ becomes pseudo first order when one reactant is in such large excess that its concentration remains practically constant.

Step 1: (a) Form the ratio and convert the temperature The given constants have the same units, so their ratio is dimensionless:

$$\frac{k_2}{k_1} = \frac{7.5 \times 10^4}{2.5 \times 10^4} = 3, \qquad T_1 = 27 + 273 = 300\,\text{K}.$$

Use $E_a = 19.147 \times 10^3\,\text{J mol}^{-1}$ with the gas constant in joules. The frequency factor cancels when the two Arrhenius equations are divided.

Step 2: (a) Calculate the higher temperature Substituting the supplied $\log 3 = 0.4771$,

$$\begin{aligned} 0.4771 &= \frac{19147}{2.303 \times 8.314}\left(\frac{1}{300} - \frac{1}{T_2}\right), \\ \frac{1}{T_2} &= \frac{1}{300} - \frac{0.4771 \times 2.303 \times 8.314}{19147} \\ &\simeq 0.0028562\,\text{K}^{-1}, \\ T_2 &\simeq 350.1\,\text{K}. \end{aligned}$$

Thus the corresponding Celsius temperature is approximately $350.1 - 273 = 77.1\,^\circ\text{C}$. It is higher than the initial temperature, as expected because an increased temperature increases the rate constant for positive activation energy.

Step 3: (b) State the condition and illustrate it Keep one reactant in large excess. Its concentration changes negligibly during the reaction, and it can be absorbed into an effective rate constant:

$$r = k[A][B] = k'[A], \qquad k' = k[B]_{\text{excess}}.$$

An example is acid-catalysed hydrolysis of ethyl acetate in excess water, with the catalyst concentration kept fixed:

$$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}.$$

Water is the solvent and is present in very large excess, so its concentration is nearly constant. The observed rate is consequently proportional to the ester concentration alone. The reaction is therefore kinetically first order under these conditions, although two reacting species occur in the hydrolysis reaction.

Step 4: Conclusion (a) The required temperature is approximately $350\,\text{K}$, or $77\,^\circ\text{C}$. (b) A large excess of one reactant gives pseudo first-order kinetics; hydrolysis of ethyl acetate in excess water is an example.

Quick Tip to Solve: Divide the rate constants first: their common power of ten cancels, leaving the supplied log 3; convert Celsius to kelvin before using Arrhenius.

27(a). Predict the main product of the following reactions:

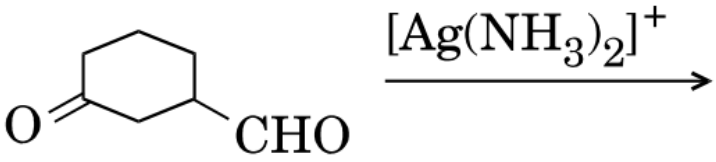
(i) 3-Oxocyclohexane-1-carbaldehyde with $[Ag(NH_3)_2]^+$, as shown in the figure.

(ii) $CH_3COCH_2COOCH_3$ with (i) $NaBH_4$, (ii) H^+.

(iii) $C_6H_5CHO + CH_3CHO$ with dilute $NaOH$.

(b) Give a simple chemical test to distinguish between acetophenone $C_6H_5COCH_3$ and benzophenone $C_6H_5COC_6H_5$.

(c) Why is alpha (α) hydrogen of carbonyl compounds acidic in nature? [5 marks]



Solution:

Concept:

- Tollens' reagent oxidises an aldehyde group to a carboxylate ion in its alkaline medium while reducing silver(I) to metallic silver. An ordinary ketone group remains unchanged.
- Sodium borohydride reduces aldehydes and ketones to alcohols, but normally does not reduce an ester group under these conditions.
- Carbonyl compounds containing alpha hydrogen form resonance-stabilised enolate ions. These undergo aldol reactions; methyl ketones also give the iodoform test.

Step 1: (a)(i) Oxidise the aldehyde selectively The printed structure contains both a ring ketone and a side-chain $-CHO$ group. Tollens' reagent oxidises only the aldehyde. Replace $-CHO$ by $-COO^-$ at the same position on the ring, leaving the ring $C = O$ intact. The product is 3-oxocyclohexane-1-carboxylate in the alkaline reaction mixture; acidification would give 3-oxocyclohexane-1-carboxylic acid.

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

Here R denotes the ketone-containing ring shown in the question. The deposited silver is the positive Tollens' test.

Step 2: (a)(ii) Reduce the ketone in the keto ester In methyl acetoacetate, $CH_3COCH_2COOCH_3$, the first carbonyl is a ketone and the second belongs to an ester. $NaBH_4$, followed by acidic work-up, reduces the ketone to a secondary alcohol while retaining the ester:

$$CH_3COCH_2COOCH_3 \xrightarrow[\text{then } H^+]{NaBH_4} CH_3CH(OH)CH_2COOCH_3.$$

The product is methyl 3-hydroxybutanoate. The reagent does not convert the ester group into a primary alcohol here.

Step 3: (a)(iii) Carry out crossed aldol condensation Benzaldehyde has no alpha hydrogen, whereas acetaldehyde has alpha hydrogens. Dilute hydroxide forms the acetaldehyde enolate, which attacks the carbonyl carbon of benzaldehyde. Protonation first gives the crossed aldol $C_6H_5CH(OH)CH_2CHO$.

Quick Tip to Solve: Identify each carbonyl group separately: Tollens oxidises CHO, borohydride reduces the ketone, and the iodoform test requires a COCH3 group.

Its dehydration gives the conjugated main condensation product, cinnamaldehyde:

$$\mathrm{C_6H_5CHO + CH_3CHO \xrightarrow{dil.\ NaOH} C_6H_5CH(OH)CH_2CHO}$$
$$\longrightarrow \mathrm{C_6H_5CH{=}CHCHO + H_2O.}$$

The newly formed carbon-carbon bond comes from the alpha carbon of acetaldehyde. Conjugation of the double bond with the phenyl ring and aldehyde group stabilises the condensation product.

Step 4: (b) Use the iodoform test Warm each compound with iodine and aqueous sodium hydroxide. Acetophenone, $\mathrm{C_6H_5COCH_3}$, contains the methyl-ketone group and gives a yellow precipitate of iodoform, $\mathrm{CHI_3}$:

$$\mathrm{C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 + 3NaI + 3H_2O.}$$

Benzophenone, $\mathrm{C_6H_5COC_6H_5}$, has no $-\mathrm{COCH_3}$ group and gives no yellow iodoform precipitate. These contrasting observations distinguish the two ketones.

Step 5: (c) Explain alpha-hydrogen acidity An alpha hydrogen is attached to the carbon adjacent to the carbonyl carbon. The electron-withdrawing carbonyl group polarises the alpha carbon-hydrogen bond. More decisively, removal of this proton produces an enolate ion in which the negative charge is delocalised between carbon and oxygen:

$$\mathrm{RCOCH_2R' \xrightarrow{base} RCOCH^-R' \longleftrightarrow RC(O^-){=}CHR'.}$$

Resonance stabilises this conjugate base, including a contributor with charge on electronegative oxygen. Formation of a stabilised conjugate base makes alpha hydrogens more acidic than ordinary alkane hydrogens, whose removal gives an unstabilised carbanion.

Step 6: Conclusion (a) The products are (i) the ring-ketone carboxylate, or the corresponding acid after acidification; (ii) $\mathrm{CH_3CH(OH)CH_2COOCH_3}$; (iii) cinnamaldehyde, $\mathrm{C_6H_5CH{=}CHCHO}$. (b) Acetophenone gives yellow iodoform; benzophenone does not. (c) Alpha hydrogens are acidic because the conjugate enolate ion is resonance stabilised.

Quick Tip to Solve: Identify each carbonyl group separately: Tollens oxidises CHO, borohydride reduces the ketone, and the iodoform test requires a COCH3 group.

OR

27(b). (a) Write the main product formed when propanal reacts with the following reagents:

(i) 2 moles of CH_3OH in presence of dry HCl

(ii) Dilute NaOH

(iii) H_2N-NH_2 followed by heating with KOH in ethylene glycol

(b) Arrange the following compounds in increasing order of their property as indicated:

(i) $F-CH_2COOH$, O_2N-CH_2COOH, CH_3COOH, HCOOH — acid character

(ii) Acetone, Acetaldehyde, Benzaldehyde, Acetophenone — reactivity towards addition of HCN

[5 marks]

Solution:

Concept:

- An aldehyde reacts with two equivalents of an alcohol in dry acid to form an acetal, in which the carbonyl oxygen is replaced by two alkoxy groups.
- Aldehydes having an α-hydrogen undergo aldol addition with dilute alkali to form a β-hydroxy aldehyde. Wolff–Kishner reduction converts $-CHO$ into $-CH_3$.
- Acid strength increases when an electron-withdrawing group stabilises the conjugate carboxylate ion. Carbonyl addition is favoured by greater electrophilicity and less steric hindrance at the carbonyl carbon.

Step 1: (a)(i) Formation of the acetal Propanal first forms a hemiacetal with methanol. Reaction with the second molecule of methanol, catalysed by dry HCl, gives the acetal:

$$CH_3CH_2CHO + 2CH_3OH \xrightarrow{\text{dry HCl}} CH_3CH_2CH(OCH_3)_2 + H_2O.$$

The main product is 1,1-dimethoxypropane. Both methoxy groups are attached to the carbon that originally carried the carbonyl oxygen.

Step 2: (a)(ii) Aldol addition with dilute NaOH Propanal contains α-hydrogens on the carbon adjacent to $-CHO$. Hydroxide removes one of these to generate an enolate, which attacks the carbonyl carbon of another propanal molecule. Protonation gives the aldol:

$$2CH_3CH_2CHO \xrightarrow{\text{dilute NaOH}} CH_3CH_2CH(OH)CH(CH_3)CHO.$$

This product is 3-hydroxy-2-methylpentanal, a β-hydroxy aldehyde. The question specifies dilute alkali without heating, so the main product is the aldol addition product, before dehydration.

Step 3: (a)(iii) Wolff–Kishner reduction Hydrazine first converts propanal into its hydrazone. Heating the hydrazone with KOH in ethylene glycol removes the oxygen functionality, with liberation of nitrogen:

$$CH_3CH_2CHO + H_2NNH_2 \longrightarrow CH_3CH_2CH{=}NNH_2 + H_2O,$$

$$CH_3CH_2CH{=}NNH_2 \xrightarrow[\Delta]{\text{KOH, ethylene glycol}} CH_3CH_2CH_3 + N_2.$$

Thus the carbon skeleton is retained, and the aldehyde group is reduced to a terminal methyl group; the organic product is propane.

Quick Tip to Solve: For propanal's aldol, keep one aldehyde group, join two three-carbon units through their alpha and carbonyl carbons, and place OH on the former carbonyl carbon.

Step 4: (b)(i) Increasing acid character The methyl group has a $+I$ effect, which destabilises the carboxylate ion relative to formate. Hence acetic acid is weaker than formic acid. The fluorine and nitro substituents withdraw electron density by the $-I$ effect and stabilise the conjugate bases. The nitro substituent produces the stronger acid in this pair. Therefore,

$$\boxed{CH_3COOH < HCOOH < FCH_2COOH < O_2NCH_2COOH}.$$

This is an increasing order of acidity, so the weakest acid is written first.

Step 5: (b)(ii) Increasing reactivity towards HCN Cyanide attacks the electrophilic carbonyl carbon and the resulting alkoxide is protonated to form a cyanohydrin. Aldehydes are more reactive than ketones because they have less steric hindrance and fewer electron-releasing alkyl groups. Conjugation with the phenyl ring reduces carbonyl electrophilicity, making an aromatic carbonyl compound less reactive than the corresponding aliphatic compound. Thus acetophenone is less reactive than acetone, and benzaldehyde is less reactive than acetaldehyde. The required increasing order is

$$\boxed{\text{Acetophenone} < \text{Acetone} < \text{Benzaldehyde} < \text{Acetaldehyde}}.$$

Step 6: Conclusion (a) The products are (i) $CH_3CH_2CH(OCH_3)_2$, (ii) $CH_3CH_2CH(OH)CH(CH_3)CHO$, and (iii) $CH_3CH_2CH_3$. (b) Acid character: $CH_3COOH < HCOOH < FCH_2COOH < O_2NCH_2COOH$. HCN addition: acetophenone $<$ acetone $<$ benzaldehyde $<$ acetaldehyde.

Quick Tip to Solve: For propanal's aldol, keep one aldehyde group, join two three-carbon units through their alpha and carbonyl carbons, and place OH on the former carbonyl carbon.