CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/3 (Delhi)

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) **All questions are compulsory.**
(ii) **Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.**
(iii) **Question numbers 9 to 18 are short-answer questions and carry 2 marks each.**
(iv) **Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.**
(v) **Question numbers 28 to 30 are long-answer questions and carry 5 marks each.**
(vi) **Use Log Tables, if necessary. Use of calculators is not allowed.**

1. Give one example each of lyophobic sol and lyophilic sol. [1 mark]

Solution:

Concept:

- A lyophobic sol has little affinity between its dispersed particles and the dispersion medium.
- A lyophilic sol has strong affinity between the dispersed substance and the dispersion medium.

Step 1: Identify a lyophobic sol Gold sol in water is a lyophobic sol. The dispersed gold particles do not interact strongly with water; a suitable preparation and stabilisation method is needed to keep the particles dispersed.

Step 2: Identify a lyophilic sol Starch sol in water is a lyophilic sol. Starch interacts with water through its polar hydroxyl groups and forms a hydrated dispersion. Thus the classification concerns affinity for the medium, rather than simply the size of the particles.

Step 3: Conclusion Lyophobic sol: gold sol in water. Lyophilic sol: starch sol in water.

Quick Tip to Solve: Use gold for low affinity and starch for strong affinity towards water.

2. Write the IUPAC name of the compound.

$CH_3-CH(OH)-CH_2-CO-CH_3$ [1 mark]

Solution:

Concept:

- The ketone group has higher naming priority than the alcohol group, so the suffix is $-\text{one}$.
- Number the longest chain containing the carbonyl carbon so that this principal functional group receives the lowest locant.

Step 1: Choose and number the parent chain The structure contains a continuous chain of five carbon atoms. Numbering from the end nearer the carbonyl group puts the ketone carbon at position 2 and the hydroxyl-bearing carbon at position 4. Thus the parent is pentan-2-one.

Step 2: Locate the hydroxyl substituent The hydroxyl group is attached to carbon 4 with this numbering, and is named by the prefix hydroxy. Numbering from the opposite end would place the ketone at carbon 4, so that direction is rejected even though it gives the hydroxyl group a lower number.

Step 3: Conclusion The IUPAC name is $\boxed{\text{4-hydroxypentan-2-one}}$.

Quick Tip to Solve: Give the carbonyl group its lowest number before locating the hydroxy prefix.

3. What type of intermolecular attractive interaction exists in the pair of methanol and acetone?

[1 mark]

Solution:

Concept:

- Hydrogen bonding occurs when hydrogen bonded to an electronegative atom interacts with a lone pair on another electronegative atom.
- Methanol has an $O-H$ hydrogen-bond donor; acetone has a carbonyl oxygen that acts as a hydrogen-bond acceptor.

Step 1: Identify the donor In methanol, CH_3OH, the oxygen withdraws electron density from the hydrogen of its hydroxyl group. This leaves that hydrogen partially positive and able to participate in an intermolecular hydrogen bond.

Step 2: Identify the acceptor The carbonyl oxygen of acetone, CH_3COCH_3, has lone pairs that attract the hydroxyl hydrogen of methanol. The interaction is represented as $CH_3O-H\cdots O=C(CH_3)_2$, where the dots denote a hydrogen bond between the two molecules.

Step 3: Conclusion The characteristic intermolecular attractive interaction is hydrogen bonding.

Quick Tip to Solve: Look for an O-H donor in methanol and the carbonyl oxygen acceptor in acetone.

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4. Which of the following is more stable complex and why?

$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$

[1 mark]

Solution:

Concept:

- Ethylenediamine, en, is bidentate: both nitrogen atoms can coordinate to the same metal ion.
- The chelate effect gives complexes of multidentate ligands greater stability than comparable complexes with monodentate ligands.

Step 1: Compare ligand attachment Both complexes contain cobalt in the $+3$ oxidation state and six coordinated nitrogen donor atoms. In $[Co(NH_3)_6]^{3+}$, each ammonia molecule binds through just one nitrogen atom; ammonia is monodentate.

Step 2: Apply the chelate effect In $[Co(en)_3]^{3+}$, each ethylenediamine ligand binds at two sites and forms a five-membered chelate ring with cobalt. The three chelate rings give additional stability. This is the chelate effect, so comparing only the oxidation state or coordination number would miss the distinguishing feature.

Step 3: Conclusion $[Co(en)_3]^{3+}$ is more stable because of the chelate effect.

Quick Tip to Solve: When metal and coordination number match, check whether the ligand forms chelate rings.

5. Arrange the following compounds in increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$ [1 mark]

Solution:

Concept:

- Basic strength depends on the availability of the nitrogen lone pair for accepting a proton.
- Methyl groups exert an electron-releasing inductive effect, increasing electron density on nitrogen in these aniline derivatives.

Step 1: Compare with aniline In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring and is less available for protonation. An N-methyl group supplies electron density through its positive inductive effect, so N-methylaniline is more basic than aniline.

Step 2: Compare the substituted anilines N,N-Dimethylaniline has two electron-releasing methyl groups attached to nitrogen, whereas N-methylaniline has one. For the given aromatic amines, their net effect increases the availability of the nitrogen lone pair and hence basic strength in the order aniline, N-methylaniline, N,N-dimethylaniline.

Step 3: Conclusion Increasing basic strength:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2.$$

Quick Tip to Solve: For this aniline series, increasing N-methyl substitution increases basic strength.

6. Name the products of hydrolysis of sucrose. [1 mark]

Solution:

Concept:

- Sucrose is a disaccharide made from one glucose unit and one fructose unit.
- Hydrolysis cleaves its glycosidic linkage by the addition of one molecule of water.

Step 1: Identify the monosaccharides The glycosidic linkage in sucrose joins a glucose unit to a fructose unit. Hydrolysis with dilute acid or the enzyme invertase breaks this linkage and releases both constituent monosaccharides.

Step 2: State the products and proportion The reaction is

$$\underbrace{C_{12}H_{22}O_{11}}_{\text{sucrose}} + H_2O \longrightarrow \underbrace{C_6H_{12}O_6}_{\text{D-glucose}} + \underbrace{C_6H_{12}O_6}_{\text{D-fructose}}.$$

One mole of sucrose therefore gives one mole each of D-glucose and D-fructose, an equimolar mixture also called invert sugar.

Step 3: Conclusion The products are D-glucose and D-fructose in equimolar amounts.

Quick Tip to Solve: Remember sucrose as glucose plus fructose; maltose instead gives only glucose.

7. Which of the following isomers is more volatile: o-nitrophenol or p-nitrophenol? [1 mark]

Solution:

Concept:

- Volatility is the tendency of a substance to enter the vapour phase; weaker intermolecular attraction gives greater volatility.
- Hydrogen bonding within one molecule is intramolecular, whereas bonding between separate molecules is intermolecular.

Step 1: Examine o-nitrophenol In o-nitrophenol, the adjacent $-\mathrm{OH}$ and $-\mathrm{NO_2}$ groups form intramolecular hydrogen bonds. This reduces hydrogen bonding between different molecules and hence reduces molecular association.

Step 2: Compare p-nitrophenol In p-nitrophenol, these groups are too far apart for such intramolecular bonding. It forms intermolecular hydrogen bonds, so more energy is required to separate its associated molecules into vapour.

Step 3: Conclusion o-Nitrophenol is more volatile than p-nitrophenol.

Quick Tip to Solve: For nitrophenol isomers, identify whether hydrogen bonding is within a molecule or between molecules before comparing volatility.

8. Which reducing agent is employed to get copper from the leached low grade copper ore? [1 mark]

Solution:

Concept:

- A metal more reactive than copper can displace copper from its aqueous salt solution.
- Reduction converts copper ions to metallic copper by electron gain: $\mathrm{Cu^{2+}} + 2\mathrm{e^-} \rightarrow \mathrm{Cu}$.

Step 1: Choose the reducing agent Iron, generally used as scrap iron, is employed to recover copper from the leach solution of low-grade copper ore. Iron is more reactive than copper and is oxidised as copper ions are reduced.

Step 2: Write the displacement reaction The ionic equation is

$$\mathrm{Cu^{2+}(aq)} + \mathrm{Fe(s)} \rightarrow \mathrm{Cu(s)} + \mathrm{Fe^{2+}(aq)}.$$

Each iron atom supplies two electrons, causing metallic copper to be deposited from the solution.

Step 3: Conclusion Scrap iron (Fe) is the reducing agent used to obtain copper from the leached ore.

Quick Tip to Solve: Remember leached copper recovery as a displacement: iron dissolves as iron(II) ions while copper is deposited.

9. State Raoult's law for the solution containing volatile components. What is the similarity between Raoult's law and Henry's law? [2 marks]

Solution:

Concept:

- For component i, x_i denotes its mole fraction in the liquid solution and p_i its partial pressure above the solution.
- At fixed temperature, Raoult's law uses the pure-component vapour pressure p_i°, while Henry's law uses the Henry constant K_H.

Step 1: State Raoult's law For a solution containing volatile components, the partial vapour pressure of each component equals the product of its mole fraction in the solution and its vapour pressure in the pure state at the same temperature:

$$p_i = x_i p_i^\circ.$$

Thus, for two components, $p_A = x_A p_A^\circ$, $p_B = x_B p_B^\circ$, and the total vapour pressure is $p = p_A + p_B$.

Step 2: Compare with Henry's law Henry's law for a dissolved gas is $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution. Both laws state that the partial pressure of a component is directly proportional to its mole fraction at a fixed temperature. Their proportionality constants are different: p_i° for Raoult's law and K_H for Henry's law.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^\circ$. Its similarity to Henry's law, $p = K_H x$, is the direct proportionality between partial pressure and mole fraction.

Quick Tip to Solve: Write both laws in the form pressure = constant times mole fraction; the common dependence is then immediately visible.

10. Explain the following terms:

(i) Rate constant (k)

(ii) Half life period of a reaction ($t_{1/2}$) [2 marks]

Solution:

Concept:

- A rate law relates reaction rate to reactant concentrations: $r = k[A]^m[B]^n$, where m, n are the reaction orders.
- A half-life describes the time for a reactant concentration to fall to half its initial value; its concentration dependence depends on reaction order.

Step 1: Define the rate constant The rate constant k is the proportionality constant in the experimentally determined rate law:

$$k = \frac{r}{[A]^m[B]^n}.$$

Numerically, it equals the reaction rate when the concentration of each reactant appearing in the rate law is unity in the chosen concentration units. For a given reaction it is constant at a fixed temperature, but changes with temperature and can change when a catalyst is introduced. Its units

Quick Tip to Solve: Do not define half-life as the time for completion; it describes a fall from the initial concentration to exactly one-half of it.

depend on the overall reaction order.

Step 2: Define the half-life period The half-life period, $t_{1/2}$, is the time required for the concentration (or amount, at constant volume) of a reactant to decrease to one-half of its initial value:

$$[A]_{t_{1/2}} = \frac{[A]_0}{2}.$$

For example, for a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, so its half-life is independent of the initial concentration.

Step 3: Conclusion k is the constant of proportionality in the rate law; $t_{1/2}$ is the time in which the reactant concentration becomes half its initial value.

Quick Tip to Solve: Do not define half-life as the time for completion; it describes a fall from the initial concentration to exactly one-half of it.

11. Write the principles of the following methods:

(i) Froth floatation method

(ii) Electrolytic refining [2 marks]

Solution:

Concept:

- Froth flotation concentrates sulphide ores by exploiting differences in wetting by oil and water.
- Electrolytic refining purifies a metal through selective anodic dissolution and cathodic deposition in an electrolyte containing its ions.

Step 1: Principle of froth flotation Sulphide ore particles are preferentially wetted by oil, while gangue particles are wetted by water. Air is blown through the aqueous ore pulp containing a suitable oil/frothing agent. The oil-wetted ore particles attach to air bubbles and rise with the froth, which is skimmed off. The water-wetted gangue remains behind. Thus, the separation rests on the different wetting properties of ore and gangue.

Step 2: Principle of electrolytic refining The impure metal is made the anode and a thin sheet of pure metal the cathode in a suitable solution of a salt of the metal. On passing current, metal dissolves from the anode as ions and deposits as pure metal at the cathode:

$$\text{Anode: } \mathrm{M} \rightarrow \mathrm{M^{n+}} + \mathrm{ne^-},$$
$$\text{Cathode: } \mathrm{M^{n+}} + \mathrm{ne^-} \rightarrow \mathrm{M}.$$

Insoluble impurities collect below the anode as anode mud, while suitable soluble impurities remain in solution.

Step 3: Conclusion Froth flotation uses preferential wetting of sulphide ore by oil and gangue by water. Electrolytic refining uses dissolution of impure metal at the anode and deposition of pure metal at the cathode.

Quick Tip to Solve: In electrolytic refining, remember that the impure anode loses metal and the pure cathode gains metal as current passes.

12. An element with density 11.2 g cm^{-3} forms a f.c.c. lattice with edge length of 4×10^{-8} cm. Calculate the atomic mass of the element.

(Given: $N_A = 6.022 \times 10^{23}$ mol^{-1}) [2 marks]

Solution:

Concept:

- The density of a cubic unit cell is $\rho = ZM/(N_A a^3)$, where Z is the number of atoms per cell, M is molar mass, N_A is Avogadro's constant and a is the edge length.
- An f.c.c. cell contains $8(1/8) + 6(1/2) = 4$ atoms: corner atoms are shared by eight cells and face atoms by two cells.

Step 1: Determine the unit-cell volume The edge length is $a = 4 \times 10^{-8}$ cm. Thus

$$a^3 = (4 \times 10^{-8})^3 = 64 \times 10^{-24} = 6.4 \times 10^{-23}\,\text{cm}^3.$$

Since the density is in g cm^{-3}, retaining centimetres makes the units consistent.

Step 2: Calculate the molar mass Rearranging the density relation and using $Z = 4$,

$$\begin{aligned} M &= \frac{\rho N_A a^3}{Z} \\ &= \frac{11.2 \times 6.022 \times 10^{23} \times 6.4 \times 10^{-23}}{4} \\ &= 107.91424\,\text{g mol}^{-1}. \end{aligned}$$

The powers of ten cancel. The atomic mass in unified atomic mass units has the same numerical value as this molar mass in grams per mole.

Step 3: Conclusion The atomic mass of the element is approximately $\boxed{108\,\text{u}}$, corresponding to a molar mass of $107.9\,\text{g mol}^{-1}$.

Quick Tip to Solve: For an f.c.c. density calculation use four atoms per cell and cube both the numerical edge length and its power of ten.

13. Examine the given defective crystal. Answer the following questions:

(i) What type of stoichiometric defect is shown by the crystal?

(ii) How is the density of the crystal affected by this defect?

(iii) What type of ionic substances show such defect? [2 marks]

A^+	B^-	A^+	B^-	A^+
B^-	0	B^-	A^+	B^-
A^+	B^-	A^+	0	A^+
B^-	A^+	B^-	A^+	B^-

Solution:

Concept:

- A stoichiometric defect preserves the ratio of cations to anions and electrical neutrality of the ionic solid.
- In a Schottky defect, equal numbers of cations and anions are missing from their normal lattice sites; the resulting vacancies reduce the mass per unit volume.

Step 1: (i) Identify the vacancies In the regular alternating arrangement, the vacant site marked 0 in the second row should contain A^+, while the vacant site in the third row should contain B^-. Thus one cation and one anion are absent. Equal loss of positive and negative ions preserves electrical neutrality and the $1:1$ composition. This is a Schottky defect.

Step 2: (ii) Explain the density change Ions are missing from the lattice, so its mass decreases while its volume remains essentially unchanged. Hence $\rho =$ mass/volume decreases. This differs from a Frenkel defect, in which a displaced ion remains in an interstitial position and the crystal's mass is unchanged.

Step 3: (iii) State the substances that show this defect Schottky defects are characteristic of ionic solids whose cations and anions have nearly similar sizes and whose coordination numbers are high. Examples include NaCl, KCl and CsCl. Their paired vacancies maintain the required stoichiometric ratio.

Step 4: Conclusion (i) Schottky defect; (ii) density decreases; (iii) ionic solids with similarly sized ions and high coordination numbers, such as NaCl and KCl.

Quick Tip to Solve: Count which ions the empty sites should contain: a missing cation-anion pair identifies Schottky vacancies and reduced density.

14. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (K_f = 5.12 K kg mol^{-1}). [2 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile non-electrolyte, the freezing-point depression is $\Delta T_f = K_f m$, where K_f is the cryoscopic constant and m is molality.
- Molality is moles of solute per kilogram of solvent: $m = (w/M)/W$, with solute mass w in grams, molar mass M in g mol^{-1}, and solvent mass W in kilograms.

Step 1: Find the required molality The freezing point must fall by $\Delta T_f = 0.48\,\text{K}$. No association or dissociation is specified, so the usual non-electrolyte relation applies:

$$m = \frac{\Delta T_f}{K_f} = \frac{0.48}{5.12} = 0.09375\,\text{mol kg}^{-1}.$$

Step 2: Convert the solvent mass and calculate solute mass The mass of benzene is $75\,\text{g} = 0.075\,\text{kg}$. Therefore

$$\begin{aligned} n_{\text{solute}} &= mW = 0.09375 \times 0.075 \\ &= 0.00703125\,\text{mol}, \\ w &= nM = 0.00703125 \times 256 \\ &= 1.80\,\text{g}. \end{aligned}$$

Molality uses the mass of benzene alone, rather than the combined mass of benzene and dissolved compound.

Step 3: Conclusion Dissolve $\boxed{1.80\,\text{g}}$ of the compound in $75\,\text{g}$ of benzene.

Quick Tip to Solve: Use solvent mass in kilograms with the given cryoscopic constant; the direct formula is $w = \Delta T_f MW/K_f$.

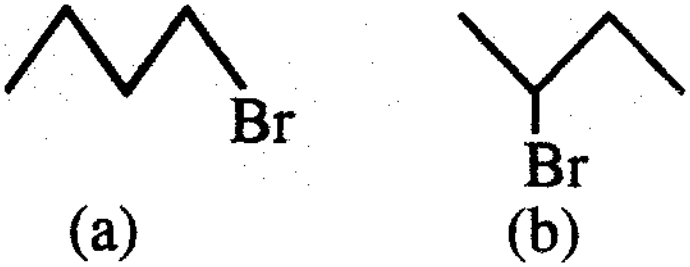
15. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a) 1-bromobutane (b) 2-bromobutane

(ii) Out of S_N1 and S_N2, which reaction occurs with

(a) Inversion of configuration

(b) Racemisation [2 marks]



Solution:

Concept:

- A carbon bearing four different groups is a stereogenic centre. Chirality and the rate of nucleophilic substitution must be assessed separately.
- An S_N2 reaction proceeds by concerted backside attack and is favoured by low steric hindrance; S_N1 proceeds through a planar carbocation intermediate.

Step 1: (i) Identify the chiral alkyl halide Structure (b) is 2-bromobutane, $CH_3CH(Br)CH_2CH_3$. Its second carbon is attached to four different groups: H, Br, CH_3 and C_2H_5. Hence (b) is chiral. Structure (a), 1-bromobutane, has a terminal CH_2Br group and no stereogenic carbon, so it is achiral.

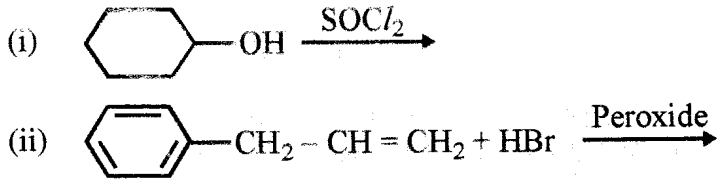
Step 2: (i) Compare the substitution rates Structure (a) is a primary alkyl halide whereas (b) is secondary. Under the same S_N2 conditions, the nucleophile approaches the carbon bearing bromine more easily in (a), which has less steric crowding. Therefore (a) reacts faster. The two requested properties belong to different members of the pair: (b) is chiral and (a) undergoes faster S_N2 reaction.

Step 3: (ii) Relate mechanism to stereochemical outcome (a) S_N2 gives inversion of configuration: backside attack reverses the arrangement around the reacting stereogenic carbon (Walden inversion). (b) S_N1 gives racemisation: the intermediate carbocation is planar, permitting nucleophilic attack from either face and producing both configurations. Racemisation may be partial in practice because the departing group or ion pair can shield one face.

Step 4: Conclusion (i) (b), 2-bromobutane, is chiral; (a), 1-bromobutane, reacts faster by S_N2. (ii) Inversion: S_N2; racemisation: S_N1.

Quick Tip to Solve: First check four different groups for chirality, then compare steric hindrance independently to predict the faster S_N2 substrate.

16. Draw the structure of major monohalo product in each of the following reactions: [2 marks]



Solution:

Concept:

- Thionyl chloride, $SOCl_2$, converts an alcohol into an alkyl chloride by replacing its $-OH$ group with $-Cl$. The carbon skeleton remains unchanged.
- In the presence of peroxide, HBr adds to an unsymmetrical alkene by a free-radical mechanism with anti-Markovnikov orientation: bromine attaches to the less substituted carbon of the double bond.

Step 1: (i) Replace the hydroxyl group of cyclohexanol Cyclohexanol gives chlorocyclohexane (cyclohexyl chloride). Its six-membered saturated ring is retained, with chlorine attached to the carbon that originally carried the hydroxyl group. The balanced conversion is

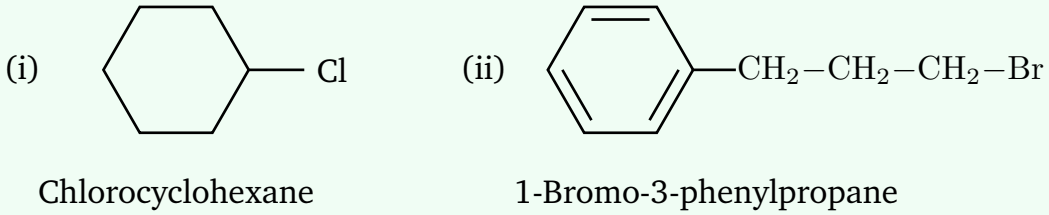
$$C_6H_{11}OH + SOCl_2 \longrightarrow C_6H_{11}Cl + SO_2 + HCl.$$

The gaseous by-products are sulphur dioxide and hydrogen chloride; only the organic chloride is the requested monohalo product.

Step 2: (ii) Add HBr to the side-chain double bond The substrate is $C_6H_5CH_2CH{=}CH_2$. A bromine radical adds to its terminal CH_2 carbon, producing the more stable secondary radical on the neighbouring carbon. That radical abstracts hydrogen from HBr, giving

$$C_6H_5CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} C_6H_5CH_2CH_2CH_2Br.$$

Thus the product is 1-bromo-3-phenylpropane. The benzene ring is unaffected by this addition.



Structures of the two major monohalo products

Step 3: Conclusion The major products are (i) chlorocyclohexane and (ii) $C_6H_5CH_2CH_2CH_2Br$, 1-bromo-3-phenylpropane, with the structures shown above.

Quick Tip to Solve: Circle the peroxide condition first: it puts Br on the terminal carbon of the side-chain double bond.

17(a). Complete the following chemical equations:

(i) Ca_3P_2 + H_2O $\rightarrow$

(ii) Cu + H_2SO_4(conc.) $\rightarrow$ [2 marks]

Solution:

Concept:

- Metal phosphides react with water to liberate phosphine, PH_3, and form the corresponding metal hydroxide.
- Concentrated sulphuric acid is an oxidising acid: it oxidises copper to Cu^{2+}, while sulphur in the acid is reduced from oxidation state $+6$ to $+4$ in SO_2.

Step 1: (i) Hydrolysis of calcium phosphide Calcium phosphide gives calcium hydroxide and phosphine. Three calcium atoms require three formula units of $Ca(OH)_2$, and two phosphorus atoms require two molecules of PH_3. Balancing oxygen and hydrogen then requires six water molecules:

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

Both sides contain three calcium, two phosphorus, six oxygen and twelve hydrogen atoms.

Step 2: (ii) Copper with concentrated sulphuric acid On heating, copper reacts with concentrated sulphuric acid to give copper(II) sulphate, sulphur dioxide and water:

$$\boxed{Cu + 2H_2SO_4\,(conc.) \xrightarrow{\Delta} CuSO_4 + SO_2\uparrow + 2H_2O}.$$

One acid molecule supplies the sulphate ion of the salt, while the other is reduced to sulphur dioxide. Copper loses two electrons as its oxidation state increases from 0 to $+2$; sulphur gains two electrons as its oxidation state decreases from $+6$ to $+4$. Hydrogen gas is therefore not the gaseous product.

Step 3: Conclusion (i) $Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$.

(ii) $Cu + 2H_2SO_4\,(conc.) \xrightarrow{\Delta} CuSO_4 + SO_2 + 2H_2O$.

Quick Tip to Solve: Use six waters for calcium phosphide; with Cu and concentrated sulphuric acid, write sulphur dioxide instead of hydrogen.

OR

17(b). Arrange the following in the order of property indicated against each set:

(i) HF, HCl, HBr, HI – increasing bond dissociation enthalpy.

(ii) H_2O, H_2S, H_2Se, H_2Te – increasing acidic character. [2 marks]

Solution:

Concept:

- Down a group, increasing atomic size lengthens the bond to hydrogen and generally lowers its bond dissociation enthalpy, the energy needed to break one mole of gaseous bonds.
- For group 16 hydrides, acidic character increases down the group because the progressively weaker

Quick Tip to Solve: For these hydrides, track the weakening H-element bond down the group; reverse the direction only for increasing bond enthalpy.

hydrogen-element bond makes release of a proton easier; the larger conjugate-base ion also accommodates negative charge more readily.

Step 1: (i) Compare the hydrogen-halogen bonds Fluorine is the smallest halogen, so the $H-F$ bond is the shortest and strongest. As the halogen size increases from chlorine to bromine to iodine, the $H-X$ bond becomes longer and easier to break. Thus the bond dissociation enthalpy decreases down the group. Reversing this trend to meet the requested increasing order gives

$$\boxed{HI < HBr < HCl < HF}.$$

This is a comparison of bond strength, not the acidic strength of the hydrogen halides.

Step 2: (ii) Compare the acidic character of group 16 hydrides The size of the central atom increases from oxygen to sulphur, selenium and tellurium. The corresponding bond to hydrogen becomes weaker down this sequence, allowing the hydride to donate a proton more readily. Consequently, despite oxygen being the most electronegative element in the set, water is the weakest acid here. The requested increasing order of acidic character is

$$\boxed{H_2O < H_2S < H_2Se < H_2Te}.$$

The dominant trend in this group is decreasing bond strength down the group.

Step 3: Conclusion (i) Increasing bond dissociation enthalpy: $HI < HBr < HCl < HF$. (ii) Increasing acidic character: $H_2O < H_2S < H_2Se < H_2Te$.

Quick Tip to Solve: For these hydrides, track the weakening H-element bond down the group; reverse the direction only for increasing bond enthalpy.

18. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit?

[2 marks]

Solution:

Concept:

- An ammine ligand, NH_3, is neutral, whereas each chlorido ligand, Cl^-, has charge -1. The oxidation state of the metal follows from the overall charge of the complex.
- An octahedral complex of the form $[MA_4B_2]$ can have the two identical B ligands adjacent (cis) or opposite (trans), giving geometrical isomerism.

Step 1: Determine the oxidation state and name Let the oxidation state of chromium be x. Charge balance gives

$$x + 4(0) + 2(-1) = +1, \qquad x = +3.$$

Name the ligands alphabetically: ammine comes before chlorido, and four ammine ligands require the prefix tetra. Since the coordination entity is cationic, the metal retains the name chromium. Thus its name is tetraamminedichloridochromium(III) ion.

Step 2: Identify the isomerism There are six donor atoms around chromium, so the coordination

Quick Tip to Solve: For an octahedral MA_4B_2 complex, compare whether the two B ligands are adjacent or opposite to identify cis and trans forms.

arrangement is octahedral. The two chlorido ligands may occupy adjacent positions, with a 90° Cl–Cr–Cl angle, or opposite positions, with a 180° angle. These are the cis and trans forms, respectively, and they exhibit geometrical isomerism.

Step 3: Conclusion The IUPAC name is $\boxed{\text{tetraamminedichloridochromium(III) ion}}$. It exhibits $\boxed{\text{geometrical (cis–trans) isomerism}}$.

Quick Tip to Solve: For an octahedral MA_4B_2 complex, compare whether the two B ligands are adjacent or opposite to identify cis and trans forms.

19. (a) Write the mechanism of the following reaction:

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(b) Write the equation involved in Reimer-Tiemann reaction. [3 marks]

Solution:

Concept:

- In an alcohol, $-OH$ is a poor leaving group. Protonation converts it into $-OH_2^+$, which can leave as neutral water.
- Ethanol is a primary alcohol; bromide displaces water from protonated ethanol by a concerted S_N2 step.
- The Reimer–Tiemann reaction introduces a formyl group, $-CHO$, mainly ortho to the phenolic $-OH$, using chloroform and aqueous alkali followed by acidification.

Step 1: (a) Protonate ethanol The oxygen atom of ethanol uses a lone pair to accept a proton from HBr. The H–Br bond of HBr breaks towards bromine, furnishing bromide ion. The first equilibrium is

$$CH_3CH_2OH + HBr \rightleftharpoons CH_3CH_2OH_2^+ + Br^-.$$

This activation is needed because expelling hydroxide directly would be unfavourable, whereas water is a good leaving group.

Step 2: (a) Displace water with bromide Bromide attacks the primary carbon bonded to oxygen from the side opposite the C–O bond. Formation of the C–Br bond and cleavage of the C–O bond occur in the same step:

$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

Thus no free primary ethyl carbocation is required. Adding the two steps gives the printed overall conversion of ethanol into bromoethane and water.

Step 3: (b) Write the Reimer–Tiemann equation Phenol is heated with chloroform and aqueous sodium hydroxide, then the mixture is acidified. The principal product is salicylaldehyde (2-hydroxybenzaldehyde). A balanced overall equation, showing the neutral organic product after acid work-up, is

$$C_6H_5OH + CHCl_3 + 3NaOH \longrightarrow o-HOC_6H_4CHO + 3NaCl + 2H_2O.$$

Quick Tip to Solve: For ethanol plus HBr, protonate oxygen before showing bromide attack; for Reimer–Tiemann, place CHO ortho to the retained phenolic OH.

The reaction is carried out with heating and followed by H^+ work-up; a small amount of the para isomer can also form.

Step 4: Conclusion (a) Ethanol first forms $CH_3CH_2OH_2^+$; Br^- then displaces water by S_N2, yielding bromoethane. (b) Phenol with $CHCl_3/NaOH$, heat and acidification gives mainly $o-HOC_6H_4CHO$ (salicylaldehyde).

Quick Tip to Solve: For ethanol plus HBr, protonate oxygen before showing bromide attack; for Reimer–Tiemann, place CHO ortho to the retained phenolic OH.

20. (a) Draw the structures of the following compounds:

(i) XeF_4

(ii) N_2O_5

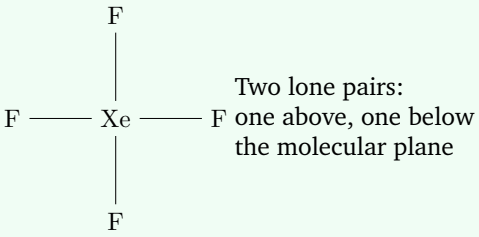
(b) Write the structural difference between white phosphorus and red phosphorus. [3 marks]

Solution:

Concept:

- VSEPR theory uses bonding and lone pairs to predict molecular shape: XeF_4 has four bond pairs and two lone pairs on xenon.
- N_2O_5 has a bridging oxygen; white phosphorus contains discrete P_4 molecules, whereas red phosphorus has a polymeric structure.

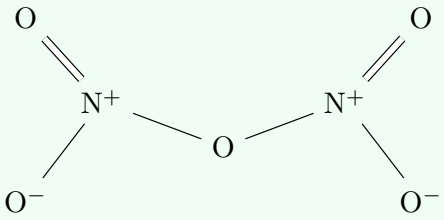
Step 1: (a)(i) Structure of xenon tetrafluoride The six electron-pair regions around xenon have an octahedral arrangement. The two lone pairs occupy opposite positions. The four fluorine atoms lie in one plane at the corners of a square, with xenon at its centre; adjacent F–Xe–F angles are $90°$. The two lone pairs lie above and below this plane.



Square planar XeF4; opposite lone pairs lie normal to the F4 plane.

Step 2: (a)(ii) Structure of dinitrogen pentoxide Molecular N_2O_5 has the skeleton $O_2N-O-NO_2$, with a bridging oxygen. In this resonance contributor, each nitrogen has an octet and formal charge $+1$; each singly bonded terminal oxygen has charge -1. On each nitro group, the double bond and negative charge can exchange between the terminal oxygen atoms. Nitrogen is approximately trigonal planar. Solid N_2O_5 is ionic: $[NO_2]^+[NO_3]^-$.

Quick Tip to Solve: Count six electron-pair regions but only four bonded atoms in XeF4; in N2O5, retain the bridging oxygen and keep an octet on each nitrogen.



One resonance contributor of molecular N2O5.

Step 3: (b) Compare the phosphorus structures White phosphorus has discrete tetrahedral P_4 molecules: each phosphorus bonds to the other three atoms, giving strained $60°$ P–P–P angles. Red phosphorus is polymeric, with phosphorus units joined by covalent P–P bonds into extended chains or networks rather than isolated tetrahedra. Its extended, less strained structure is more stable.

Step 4: Conclusion XeF_4: square planar; molecular N_2O_5: $O_2N - O - NO_2$. White phosphorus is tetrahedral P_4; red phosphorus is polymeric.

Quick Tip to Solve: Count six electron-pair regions but only four bonded atoms in XeF4; in N2O5, retain the bridging oxygen and keep an octet on each nitrogen.

21(a). Give the structures of A, B and C in the following reactions:

(i) $\mathbf{CH_3Br} \xrightarrow{KCN} \mathbf{A} \xrightarrow{LiAlH_4} \mathbf{B} \xrightarrow[273\,K]{HNO_2} \mathbf{C}$

(ii) $\mathbf{CH_3COOH} \xrightarrow[\Delta]{NH_3} \mathbf{A} \xrightarrow{Br_2+KOH} \mathbf{B} \xrightarrow{CHCl_3+NaOH} \mathbf{C}$ [3 marks]

Solution:

Concept:

- With ionic potassium cyanide, the carbon end of CN^- substitutes the halogen of an alkyl halide to form a nitrile; its carbon chain gains one carbon atom.
- Lithium aluminium hydride reduces $-C \equiv N$ to $-CH_2NH_2$. A primary aliphatic amine reacts with nitrous acid to give the corresponding alcohol with evolution of nitrogen.
- Heating an ammonium carboxylate gives an amide. Hofmann bromamide degradation converts $RCONH_2$ to RNH_2, removing the carbonyl carbon; a primary amine gives an isocyanide in the carbylamine reaction.

Step 1: (i) Form the nitrile and reduce it Methyl bromide undergoes substitution with KCN to form ethanenitrile. Reduction of the nitrile retains both carbon atoms and produces ethanamine:

$$CH_3Br + KCN \longrightarrow CH_3C \equiv N + KBr$$

$$CH_3CN + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2NH_2.$$

Therefore $A = CH_3C \equiv N$ and $B = CH_3CH_2NH_2$.

Step 2: (i) Treat ethanamine with nitrous acid At 273 K, the unstable aliphatic diazonium intermediate

Quick Tip to Solve: Track carbon atoms: KCN adds one, nitrile reduction retains it, and Hofmann degradation removes the amide carbonyl carbon.

loses nitrogen, giving ethanol:

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.$$

Thus $C = CH_3CH_2OH$.

Step 3: (ii) Prepare ethanamide, then remove its carbonyl carbon Ethanoic acid first forms ammonium ethanoate with ammonia; heating dehydrates this salt to ethanamide:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Hence $A = CH_3CONH_2$. Hofmann degradation then gives methanamine:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Thus $B = CH_3NH_2$.

Step 4: (ii) Carry out the carbylamine reaction Methanamine is a primary amine and reacts with chloroform and alkali on heating to form methyl isocyanide:

$$CH_3NH_2 + CHCl_3 + 3NaOH \longrightarrow CH_3N \equiv C + 3NaCl + 3H_2O.$$

Thus $C = CH_3N \equiv C$. The amine's nitrogen bonds to the terminal isocyanide carbon, unlike the carbon-linked nitrile in sequence (i).

Step 5: Conclusion (i) $A = CH_3CN$, $B = CH_3CH_2NH_2$, $C = CH_3CH_2OH$.
(ii) $A = CH_3CONH_2$, $B = CH_3NH_2$, $C = CH_3NC$.

Quick Tip to Solve: Track carbon atoms: KCN adds one, nitrile reduction retains it, and Hofmann degradation removes the amide carbonyl carbon.

OR

21(b). How will you convert the following:

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

(iii) Aniline into N-phenylethanamide (Write the chemical equations involved.) [3 marks]

Solution:

Concept:

- Reduction of an aromatic nitro group converts $-NO_2$ to $-NH_2$ without changing the benzene ring.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into a primary amine, RNH_2, with one fewer carbon atom.

Quick Tip to Solve: For ethanoic acid to methanamine, choose Hofmann degradation because the required amine contains one carbon fewer than the acid.

- Acetylation replaces one hydrogen of an amine by CH_3CO-. Aniline therefore gives $CH_3CONHC_6H_5$, N-phenylethanamide, also called acetanilide.

Step 1: (i) Reduce nitrobenzene to aniline Reduce nitrobenzene with tin and hydrochloric acid. In the acidic medium the amine is present as its anilinium salt; adding sodium hydroxide liberates free aniline. The reduction and liberation can be represented by:

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O,$$

$$C_6H_5NH_2 + HCl \longrightarrow C_6H_5NH_3Cl,$$

$$C_6H_5NH_3Cl + NaOH \longrightarrow C_6H_5NH_2 + NaCl + H_2O.$$

The first equation expresses the net change of the nitro group; the following equations show why an alkaline work-up is needed.

Step 2: (ii) Convert ethanoic acid into methanamine React ethanoic acid with ammonia and heat the resulting ammonium ethanoate to prepare ethanamide:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4,$$

$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Treat ethanamide with bromine and aqueous potassium hydroxide. Hofmann degradation removes its carbonyl carbon:

$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

The two-carbon acid has thereby been converted into the one-carbon amine, methanamine.

Step 3: (iii) Acetylate aniline Treat aniline with ethanoic anhydride. The amino nitrogen attacks the acyl group and forms the amide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow CH_3CONHC_6H_5 + CH_3COOH.$$

The phenyl group is attached to nitrogen, so the product is N-phenylethanamide. The acetyl group enters the amino group rather than replacing a ring hydrogen.

Step 4: Conclusion (i) $C_6H_5NO_2$ gives $C_6H_5NH_2$ by reduction followed by alkaline work-up. (ii) CH_3COOH gives CH_3CONH_2, then CH_3NH_2 by Hofmann degradation. (iii) Acetylation of aniline gives $CH_3CONHC_6H_5$.

Quick Tip to Solve: For ethanoic acid to methanamine, choose Hofmann degradation because the required amine contains one carbon fewer than the acid.

22. Account for the following:

(i) Sulphur in vapour form exhibits paramagnetic behaviour.

(ii) $SnCl_4$ is more covalent than $SnCl_2$.

(iii) H_3PO_2 is a stronger reducing agent than H_3PO_3. [3 marks]

Solution:

Concept:

- Paramagnetism arises from unpaired electrons. A molecule with unpaired electrons is attracted by an external magnetic field.
- By Fajans' rules, a cation with higher charge and smaller size has greater polarising power. It distorts the electron cloud of an anion more strongly, increasing covalent character.
- The reducing behaviour of phosphorus oxyacids is associated with their $P-H$ bonds. During oxidation these bonds can be replaced by $P-OH$ bonds; $P-OH$ hydrogens instead account for ionisable acidity.

Step 1: (i) Explain the magnetic behaviour of sulphur vapour At high temperature, sulphur vapour contains diatomic S_2 molecules. Like O_2, an S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons give a net magnetic moment, so the vapour exhibits paramagnetic behaviour. The explanation concerns the high-temperature diatomic species rather than the usual cyclic S_8 form of solid sulphur.

Step 2: (ii) Compare the covalent character of the tin chlorides Tin has oxidation state $+4$ in $SnCl_4$ and $+2$ in $SnCl_2$. For the same element, Sn^{4+} has a higher charge and a smaller radius than Sn^{2+}. Its charge density and polarising power are therefore greater. It distorts the electron cloud of the same Cl^- anion more strongly, drawing electron density into the region between the bonded atoms. According to Fajans' rules, this greater polarisation makes $SnCl_4$ more covalent than $SnCl_2$.

Step 3: (iii) Compare the reducing behaviour of the phosphorus oxyacids Their condensed structures are

$$H_3PO_2:\ H_2P(=O)(OH), \qquad H_3PO_3:\ HP(=O)(OH)_2.$$

Hypophosphorous acid, H_3PO_2, contains two $P-H$ bonds, whereas phosphorous acid, H_3PO_3, contains only one. Consequently H_3PO_2 has greater reducing action and is the stronger reducing agent. The relevant comparison is the number of hydrogens bonded directly to phosphorus, not the total number of hydrogens in the formula or the number of ionisable $O-H$ hydrogens.

Step 4: Conclusion (i) S_2 in sulphur vapour has two unpaired electrons. (ii) The greater polarising power of Sn^{4+} makes $SnCl_4$ more covalent. (iii) H_3PO_2 has two $P-H$ bonds, compared with one in H_3PO_3, giving stronger reducing behaviour.

Quick Tip to Solve: Write the oxyacid structures before counting P-H bonds: H3PO2 has two P-H bonds, while H3PO3 has one; O-H bonds govern acidity.

23. (i) What are disinfectants? Give an example.

(ii) Give two examples of macromolecules that are chosen as drug targets.

(iii) What are anionic detergents? Give an example. [3 marks]

Solution:

Concept:

- Disinfectants are antimicrobial chemicals used on non-living objects to destroy or inhibit microorganisms; their concentration and site of use matter.
- Drugs interact with biological macromolecules. In an anionic detergent the long-chain organic ion carrying the cleansing action has a negative charge.

Step 1: (i) Define disinfectants and give an example Disinfectants are chemicals that kill or prevent the growth of microorganisms on inanimate objects such as floors, drains and instruments. They are generally too harmful for direct application to living tissues at disinfecting concentrations. For example, a 1% aqueous phenol solution acts as a disinfectant. The distinction from an antiseptic is the intended application: antiseptics are suitable for living tissue at the concentration used.

Step 2: (ii) Identify two macromolecular drug targets Two examples are **proteins** and **nucleic acids**. Proteins include enzymes, whose catalytic activity may be inhibited by drugs, and receptors, through which chemical signals are received. Nucleic acids, such as DNA, may also be targeted to interfere with cellular processes. Thus proteins and nucleic acids are two classes of target macromolecules, rather than names of drug molecules.

Step 3: (iii) Define anionic detergents and give an example Anionic detergents are synthetic cleansing agents in which the anionic part of the molecule is responsible for the cleansing action. They commonly include sodium salts of sulfates of long-chain alcohols or sodium salts of long-chain alkylbenzenesulfonic acids. An example is **sodium lauryl sulfate**, $CH_3(CH_2)_{11}OSO_3^-Na^+$. Its long hydrocarbon chain associates with grease, while its negatively charged sulfate head interacts with water, helping disperse oily dirt.

Step 4: Conclusion (i) Disinfectant: an antimicrobial chemical for non-living objects; example: 1% phenol. (ii) Drug targets: proteins and nucleic acids. (iii) Anionic detergent: a detergent with an anionic cleansing part; example: sodium lauryl sulfate.

Quick Tip to Solve: Classify the detergent by the charge on its organic cleansing ion, not by the sodium counterion.

24. (i) Deficiency of which vitamin leads to scurvy?

(ii) What type of linkage is responsible for the formation of proteins?

(iii) Write the product formed when glucose is treated with HI. [3 marks]

Solution:

Concept:

- Vitamins are required in small quantities for normal physiological functions; specific deficiencies produce characteristic diseases.

Quick Tip to Solve: For glucose, distinguish exhaustive reduction by hot HI to hexane from mild reduction to sorbitol.

- Proteins are amino-acid polymers linked by peptide bonds. Exhaustive reduction of glucose with HI reveals its six-carbon chain.

Step 1: (i) Identify the deficient vitamin Scurvy is caused by deficiency of **vitamin C**, also called **ascorbic acid**. Vitamin C is a water-soluble vitamin. It is needed for normal collagen formation, so a deficiency weakens connective tissue and commonly produces bleeding gums and delayed wound healing. These characteristic symptoms connect scurvy specifically with vitamin C deficiency.

Step 2: (ii) State the linkage forming proteins The linkage is a **peptide linkage**, $-\mathrm{CO}-\mathrm{NH}-$. It forms by condensation between the carboxyl group of one amino acid and the amino group of another, with loss of a water molecule:

$$\mathrm{H_2N}-\mathrm{CH(R)}-\mathrm{COOH}+\mathrm{H_2N}-\mathrm{CH(R')}-\mathrm{COOH}$$

$$\longrightarrow \mathrm{H_2N}-\mathrm{CH(R)}-\mathrm{CO}-\mathrm{NH}-\mathrm{CH(R')}-\mathrm{COOH}+\mathrm{H_2O}.$$

Repeated formation of peptide bonds joins many amino-acid residues into a polypeptide chain.

Step 3: (iii) Give the product of reduction with HI On prolonged heating with excess HI, glucose undergoes exhaustive reduction and gives **normal hexane**, or n-hexane:

$$\mathrm{C_6H_{12}O_6}+14\mathrm{HI}\longrightarrow \mathrm{C_6H_{14}}+6\mathrm{H_2O}+7\mathrm{I_2}.$$

The organic product has the straight-chain structure $\mathrm{CH_3(CH_2)_4CH_3}$. This reaction removes the oxygen-containing groups and supports the presence of an unbranched chain of six carbon atoms in glucose. It should not be confused with the milder reduction of its aldehyde group to give sorbitol.

Step 4: Conclusion (i) Vitamin C (ascorbic acid). (ii) Peptide linkage, $-\mathrm{CO}-\mathrm{NH}-$. (iii) n-Hexane, $\mathrm{CH_3(CH_2)_4CH_3}$.

Quick Tip to Solve: For glucose, distinguish exhaustive reduction by hot HI to hexane from mild reduction to sorbitol.

25. (a) In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid. [3 marks]

Solution:

Concept:

- Adsorption is accumulation at a surface. The Freundlich isotherm relates the amount of gas adsorbed per unit mass of adsorbent to pressure at fixed temperature.
- Lyophilic colloids have strong affinity for the dispersion medium. Associated colloids form micelles, whereas multimolecular colloids contain aggregates of many small molecules or atoms.

Step 1: (a) Write the Freundlich adsorption equation For adsorption of a gas on a solid at a fixed

Quick Tip to Solve: In Freundlich́s equation use gas pressure at fixed temperature; remember soap forms micelles and gold atoms form aggregates.

temperature, the Freundlich adsorption isotherm is

$$\frac{x}{m} = kp^{1/n}, \qquad 0 < \frac{1}{n} < 1.$$

Here x is the mass of gas adsorbed, m is the mass of solid adsorbent, p is the equilibrium gas pressure, and k and n are constants for the given adsorbent, gas and temperature. Its logarithmic form is

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p.$$

The empirical power law describes a limited pressure range; it does not represent saturation at very high pressure.

Step 2: (b) State a characteristic of lyophilic sols An important characteristic is that **lyophilic sols are reversible**. Their dispersed particles have strong affinity for the dispersion medium and are strongly solvated. After separating the dispersed phase by removing the medium, the sol can generally be regenerated by adding the dispersion medium again. This strong particle-medium interaction also accounts for their high stability.

Step 3: (c) Give examples of the two colloid classes **Associated colloid:** a soap solution, such as sodium stearate in water, above its critical micelle concentration and at a suitable temperature. Individual surfactant ions associate to form micelles of colloidal size. **Multimolecular colloid:** a gold sol. Many gold atoms aggregate to form each dispersed particle of colloidal dimensions. Thus micelle formation by surface-active molecules distinguishes the associated example from an aggregate of metal atoms in the multimolecular example.

Step 4: Conclusion (a) $x/m = kp^{1/n}$ at fixed temperature. (b) Lyophilic sols are reversible. (c) Associated colloid: soap solution above its critical micelle concentration; multimolecular colloid: gold sol.

Quick Tip to Solve: In Freundlichś equation use gas pressure at fixed temperature; remember soap forms micelles and gold atoms form aggregates.

26. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) [3 marks]

Solution:

Concept:

- At constant temperature and volume, the partial pressure of a gas is proportional to its amount. For the decomposition $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$, every mole consumed forms two moles of products.
- For a first order reaction, $k = \dfrac{2.303}{t} \log \dfrac{p_0}{p_A}$, where p_0 is the initial reactant pressure and p_A its remaining partial pressure at time t.

Step 1: Express the total pressure using the reaction stoichiometry Initially only sulphuryl chloride is present, so $p_0 = 0.4$ atm. Let x atm be the fall in its partial pressure after 100 s. The partial pressures are then

$$p_{SO_2Cl_2} = 0.4 - x, \qquad p_{SO_2} = x, \qquad p_{Cl_2} = x.$$

Thus the measured total pressure is $P_t = 0.4 + x = 0.7$ atm, giving $x = 0.3$ atm.

Step 2: Find the unreacted sulphuryl chloride pressure The pressure needed in the integrated rate law is the reactant's partial pressure, not the total pressure:

$$p_A = p_0 - x = 0.4 - 0.3 = 0.1 \text{ atm}.$$

Equivalently, $p_A = 2p_0 - P_t = 0.8 - 0.7 = 0.1$ atm. Hence one quarter of the original reactant remains.

Step 3: Substitute in the first order rate equation Using the elapsed time $t = 100$ s and the supplied logarithm,

$$\begin{aligned} k &= \frac{2.303}{100} \log\left(\frac{0.4}{0.1}\right) \\ &= \frac{2.303}{100} \log 4 \\ &= \frac{2.303 \times 0.6021}{100} = 1.3866 \times 10^{-2}\, s^{-1}. \end{aligned}$$

The pressure ratio is dimensionless, and a first order rate constant has units of inverse time.

Step 4: Conclusion The rate constant for the decomposition is $\boxed{k \simeq 1.39 \times 10^{-2}\, s^{-1}}$.

Quick Tip to Solve: For a pure gas decomposing as one mole into two, use the remaining reactant pressure $2P_0 - P_t$ in the first order equation.

27. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions:

(i) What values are shown by the students?

(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a condensation or an addition polymer? [3 marks]

Solution:

Concept:

- Responsible environmental action includes recognising pollution, informing the community and adopting alternatives that reduce persistent plastic waste.
- Biodegradable polymers can be broken down by microorganisms, through enzymatic action, into simpler substances. Addition polymers form by repeated addition of unsaturated monomers without elimination of small molecules.

Step 1: (i) Identify the values shown by the students The students show environmental awareness and concern for the conservation of the Yamuna River. Their rally and distribution of paper bags demonstrate social responsibility, initiative and commitment to protecting their surroundings. By joining hands with other schools, they also show cooperation and teamwork. Their pledge to avoid polythene bags connects their public message with responsible personal behaviour.

Step 2: (ii) Define biodegradable polymers and give an example Biodegradable polymers are polymers that are decomposed by microorganisms such as bacteria, through enzymatic action, into simpler substances. Their polymer chains contain linkages that can undergo biological breakdown under suitable conditions. An example is PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate). It is a biodegradable copolymer containing ester linkages. Ordinary polythene is not an example of such a biodegradable polymer.

Step 3: (iii) Classify polythene by its formation reaction Polythene is an addition polymer of ethene. The carbon–carbon double bonds of ethene monomers open, allowing the monomers to join into a long chain:

$$n\,\mathrm{CH_2{=}CH_2} \longrightarrow [-\mathrm{CH_2} - \mathrm{CH_2}-]_n\,.$$

No small molecule such as water or hydrogen chloride is eliminated during this polymerisation. Therefore the process is addition polymerisation, whereas condensation polymerisation typically involves the elimination of a small molecule.

Step 4: Conclusion (i) Environmental concern, social responsibility, cooperation and initiative. (ii) Biodegradable polymers undergo microbial decomposition; an example is PHBV. (iii) Polythene is an addition polymer.

Quick Tip to Solve: To classify polythene, write ethene forming the repeating unit and check that no small molecule is lost.

28(a). How do you prepare:

(i) K_2MnO_4 from MnO_2?

(ii) $Na_2Cr_2O_7$ from Na_2CrO_4? [2 marks]

Solution:

Concept:

- Manganese dioxide gives manganate when oxidised by air in a strongly alkaline melt; manganese changes from oxidation state $+4$ to $+6$.
- Chromate and dichromate ions are interconverted by changing the acidity of the solution. Acidification favours dichromate formation, with chromium remaining in oxidation state $+6$.

Step 1: (i) Prepare potassium manganate from manganese dioxide Fuse MnO_2 with potassium hydroxide in the presence of atmospheric oxygen. The oxygen oxidises manganese dioxide in the alkaline melt, forming green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{heat}} 2K_2MnO_4 + 2H_2O.$$

Thus the required conditions are fusion with KOH and an oxidising agent such as air or oxygen.

Step 2: (ii) Prepare sodium dichromate from sodium chromate Acidify an aqueous solution of sodium chromate with sulphuric acid. Yellow chromate ions are converted into orange dichromate ions:

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

The underlying ionic equilibrium is

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

Adding acid shifts this equilibrium towards dichromate; this conversion does not change chromium's oxidation state.

Step 3: Conclusion (i) Fuse MnO_2 with KOH in air or oxygen to form K_2MnO_4. (ii) Acidify Na_2CrO_4 solution with H_2SO_4 to form $Na_2Cr_2O_7$.

Quick Tip to Solve: Remember alkaline oxidation for manganate preparation, but acidification for converting chromate into dichromate.

28(b). Account for the following:

(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(ii) The enthalpy of atomization is lowest for Zn in 3d series of the transition elements.

(iii) Actinoid elements show wide range of oxidation states. [3 marks]

Solution:

Concept:

- Half-filled and completely filled subshells have additional stability. Oxidation removes an electron, so compare the electronic configurations before and after removal.
- Enthalpy of atomization measures the energy required to separate a metal into gaseous atoms; stronger metallic bonding gives a larger value.
- Orbitals with comparable energies can all participate in bonding, allowing an element to exhibit several oxidation states.

Step 1: (i) Compare the divalent and trivalent configurations The relevant configurations are

$$\mathrm{Mn}^{2+} : [\mathrm{Ar}]\, 3d^5, \quad \mathrm{Mn}^{3+} : [\mathrm{Ar}]\, 3d^4,$$
$$\mathrm{Fe}^{2+} : [\mathrm{Ar}]\, 3d^6, \quad \mathrm{Fe}^{3+} : [\mathrm{Ar}]\, 3d^5.$$

Oxidation of Mn^{2+} removes an electron from its stable half-filled $3d^5$ subshell and destroys that arrangement. Oxidation of Fe^{2+}, on the other hand, produces the stable half-filled $3d^5$ configuration of Fe^{3+}. Hence the divalent manganese ion resists oxidation to the trivalent state more strongly than the divalent iron ion.

Step 2: (ii) Relate zinc's configuration to metallic bonding The zinc atom has configuration $[\mathrm{Ar}]\, 3d^{10}4s^2$, with a completely filled $3d$ subshell and no unpaired electrons. The filled $3d$ electrons contribute little to the metallic bonding compared with the partially filled $3d$ subshells of the other metals in the series. Consequently, zinc has comparatively weak metallic bonding. Less energy is required to separate its atoms, so it has the lowest enthalpy of atomization in the $3d$ series.

Step 3: (iii) Identify the orbitals available to actinoids In actinoids, the $5f$, $6d$ and $7s$ orbitals have comparable energies, especially among the earlier members. Different numbers of electrons from these orbitals can therefore participate in bonding. This availability of several electrons of similar energy accounts for the wide range of oxidation states shown by actinoid elements.

Step 4: Conclusion Mn^{2+} retains a stable half-filled $3d^5$ subshell; zinc has weak metallic bonding associated with its filled $3d^{10}$ subshell; actinoids have accessible $5f$, $6d$ and $7s$ electrons of comparable energies.

Quick Tip to Solve: For the manganese–iron comparison, write both configurations after oxidation: manganese loses a half-filled subshell, whereas iron gains one.

OR

28. (i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?

(ii) Which transition metal of 3d series has positive $E^\circ(M^{2+}/M)$ value and why?

(iii) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why?

(iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

(v) Complete the following equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow$ [5 marks]

Solution:

Concept:

- The similar energies of $3d$ and $4s$ electrons permit variable oxidation states; stable half-filled subshells influence the relative stability of ions.
- The standard electrode potential $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$ depends on atomization, ionization and hydration energies. A positive reduction potential means oxidation of the metal by standard hydrogen ions is unfavourable.
- An oxidizing agent accepts electrons. A redox half-equation must conserve both atoms and total charge.

Step 1: (i) Count manganese's available valence electrons Manganese, Mn, shows the maximum number of oxidation states in the $3d$ transition series. Its electronic configuration is $[\mathrm{Ar}]\,3d^5 4s^2$. Since the energies of the $3d$ and $4s$ orbitals are close, different numbers of these electrons can participate in bonding. Its five $3d$ and two $4s$ electrons allow oxidation states ranging from $+2$ to $+7$.

Step 2: (ii) Explain copper's positive reduction potential Copper, Cu, has a positive standard electrode potential:

$$E^\circ(\mathrm{Cu}^{2+}/\mathrm{Cu}) \simeq +0.34\,\mathrm{V}.$$

Converting solid copper to $\mathrm{Cu}^{2+}(\mathrm{aq})$ requires atomization and removal of two electrons. Copper has high atomization and ionization enthalpies; its second ionization also disrupts the stable $3d^{10}$ configuration of Cu^+. The energy released on hydration of Cu^{2+} is insufficient to compensate for these energy requirements. Oxidation is therefore unfavourable relative to the standard hydrogen electrode, giving a positive reduction potential.

Step 3: (iii) Compare the electron-accepting tendencies Mn^{3+} is the stronger oxidizing agent. It readily accepts an electron according to

$$\mathrm{Mn}^{3+} + \mathrm{e}^- \longrightarrow \mathrm{Mn}^{2+},$$

changing from $3d^4$ to the particularly stable half-filled $3d^5$ configuration. In contrast, Cr^{3+} already has the stable $3d^3$ configuration, corresponding to a half-filled t_{2g} set in an octahedral environment. Its reduction to Cr^{2+}, with $3d^4$, is less favourable.

Step 4: (iv) Give a lanthanoid with the divalent state Europium, Eu, is well known to exhibit the $+2$ oxidation state. The Eu^{2+} ion has the stable half-filled $4f^7$ configuration, which helps stabilize this state.

Step 5: (v) Balance the acidic permanganate half-reaction The oxidation state of manganese in

Quick Tip to Solve: For acidic permanganate, remember the linked changes: manganese falls from $+7$ to $+2$, so five electrons are needed, and its four oxygens become four water molecules.

MnO_4^- is $+7$. Acceptance of five electrons lowers it to $+2$. Four water molecules balance the four oxygen atoms, using the eight hydrogen ions given:

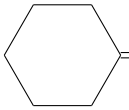
$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O.$$

Both sides contain one manganese, four oxygen and eight hydrogen atoms. The charge on the left is $-1 + 8 - 5 = +2$, matching the charge of Mn^{2+} on the right.

Step 6: Conclusion (i) Manganese; (ii) copper; (iii) Mn^{3+}; (iv) europium; (v) the products are $Mn^{2+} + 4\,H_2O$.

Quick Tip to Solve: For acidic permanganate, remember the linked changes: manganese falls from $+7$ to $+2$, so five electrons are needed, and its four oxygens become four water molecules.

29(a). Write the products of the following reactions:

(i)  **+ H_2N-OH** $\xrightarrow{H^+}$

(ii) $2\,C_6H_5CHO$ + conc. NaOH $\rightarrow$

(iii) CH_3COOH $\xrightarrow{Cl_2/P}$ [3 marks]

Solution:

Concept:

- Hydroxylamine, NH_2OH, condenses with the carbonyl group of an aldehyde or ketone to form an oxime, containing $C{=}N{-}OH$, with loss of water.
- Aldehydes without an alpha-hydrogen undergo the Cannizzaro reaction in concentrated alkali: one aldehyde molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.
- The Hell–Volhard–Zelinsky reaction replaces an alpha-hydrogen of a carboxylic acid by a halogen in the presence of red phosphorus.

Step 1: Form the oxime of cyclohexanone In acid-catalysed condensation, the oxygen of the carbonyl group is replaced by $=N-OH$. The six-membered carbon ring remains intact:

$$\text{Cyclohexanone} + NH_2OH \xrightarrow{H^+} \text{cyclohexanone oxime} + H_2O.$$

The product is the cyclic ketoxime, with the carbon of the $C{=}N{-}OH$ group forming one vertex of the ring.

Step 2: Disproportionate benzaldehyde Benzaldehyde has no alpha-hydrogen, so concentrated sodium hydroxide causes the Cannizzaro reaction:

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

The organic products are benzyl alcohol and sodium benzoate. Since the medium is alkaline and no acidification is specified, the oxidised product is the sodium salt, not free benzoic acid.

Quick Tip to Solve: For these reagents, use the sequence: hydroxylamine gives an oxime; concentrated alkali disproportionates benzaldehyde; chlorine/red phosphorus halogenates the alpha-carbon.

Step 3: Chlorinate the alpha-position of ethanoic acid In the presence of red phosphorus, chlorine substitutes one hydrogen on the carbon adjacent to the carboxyl group:

$$CH_3COOH + Cl_2 \xrightarrow{\text{red P}} ClCH_2COOH + HCl.$$

The organic product is chloroethanoic acid (chloroacetic acid). The carboxyl group is retained; chlorination occurs at the alpha-carbon.

Step 4: Conclusion The products are (i) cyclohexanone oxime, (ii) benzyl alcohol and sodium benzoate, and (iii) chloroethanoic acid.

Quick Tip to Solve: For these reagents, use the sequence: hydroxylamine gives an oxime; concentrated alkali disproportionates benzaldehyde; chlorine/red phosphorus halogenates the alpha-carbon.

29(b). Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and Propanone [2 marks]

Solution:

Concept:

- A carboxylic acid releases carbon dioxide from aqueous sodium hydrogen carbonate. An aldehyde does not give this acid–carbonate reaction.
- Tollens' reagent is ammoniacal silver(I) solution. An aliphatic aldehyde reduces it to metallic silver, whereas a simple ketone such as propanone does not.

Step 1: Distinguish benzaldehyde from benzoic acid Add aqueous sodium hydrogen carbonate, $NaHCO_3$, separately to the two samples. Benzoic acid gives brisk effervescence of carbon dioxide:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 \uparrow + H_2O.$$

Benzaldehyde gives no effervescence. The evolved carbon dioxide may be confirmed by passing it into limewater, which turns milky.

Step 2: Distinguish propanal from propanone Warm each sample gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the inner wall of the test tube because its aldehyde group is oxidised to propanoate:

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

Propanone gives no silver mirror under these conditions, since its ketone group is not oxidised by this mild reagent.

Step 3: Conclusion Use aqueous sodium hydrogen carbonate: benzoic acid effervesces, benzaldehyde does not. Use Tollens' reagent: propanal gives a silver mirror, propanone does not.

Quick Tip to Solve: Write both observations for each pair: gas versus no gas for bicarbonate, and silver mirror versus no mirror for Tollens' reagent.

OR

29(a). Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol. [2 marks]

Solution:

Concept:

- Addition of HCN to a carbonyl compound begins with nucleophilic attack of CN^- on the electrophilic carbonyl carbon. Electron donation and crowding both reduce its susceptibility to attack.
- Acid strength depends on the stability of the conjugate base: a more stable conjugate base corresponds to easier loss of H^+.

Step 1: Compare ethanal and propanone towards HCN In CH_3CHO, the carbonyl carbon is attached to one methyl group and one hydrogen. In CH_3COCH_3, it is attached to two methyl groups. Methyl groups donate electron density by the positive inductive effect, reducing the partial positive charge on the carbonyl carbon. The extra methyl group therefore makes propanone less electrophilic.

The two methyl groups of propanone also hinder approach of CN^- more than the methyl group and small hydrogen atom of ethanal. Thus both the electronic effect and the steric effect favour faster nucleophilic addition to ethanal.

Step 2: Compare carboxylic acid and phenol acidity Loss of a proton gives carboxylate and phenoxide ions, respectively:

$$RCOOH \rightleftharpoons RCOO^- + H^+, \qquad C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+.$$

In a carboxylate ion, the negative charge is delocalised equally over two electronegative oxygen atoms through two equivalent resonance structures. In phenoxide, the resonance structures are not equivalent: contributors place negative charge on the less electronegative ring carbon atoms as well as oxygen. Carboxylate is therefore more effectively stabilised than phenoxide, so a carboxylic acid loses its proton more readily than phenol.

Step 3: Conclusion (i) Ethanal reacts faster with HCN because it has less electron donation and less steric hindrance at the carbonyl carbon. (ii) Carboxylic acids are stronger acids because carboxylate ions are more resonance-stabilised than phenoxide ions.

Quick Tip to Solve: For carbonyl addition compare electrophilicity and crowding; for acidity compare the stability of the conjugate bases, especially where the negative charge resides.

29(b). Write the chemical equations to illustrate the following name reactions:

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and strong base on heating.
- Aldehydes or ketones having an alpha hydrogen undergo aldol addition in dilute alkali; heating the aldol eliminates water to give an alpha,beta-unsaturated carbonyl compound.
- Aldehydes without an alpha hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: (i) Illustrate Wolff-Kishner reduction Acetone first forms a hydrazone with hydrazine. Heating with potassium hydroxide in ethylene glycol reduces the carbonyl group to a methylene group, liberating nitrogen:

$$\mathrm{CH_3COCH_3 + H_2NNH_2 \xrightarrow{KOH,\,heat} CH_3CH_2CH_3 + N_2 + H_2O.}$$

Thus propanone is converted to propane; the carbon skeleton remains unchanged. Ethylene glycol provides the high-boiling reaction medium.

Step 2: (ii) Illustrate aldol condensation Ethanal has alpha hydrogen atoms and gives 3-hydroxybutanal (aldol) in dilute sodium hydroxide:

$$\mathrm{2\,CH_3CHO \xrightarrow{dil\cdot NaOH} CH_3CH(OH)CH_2CHO.}$$

On heating, the beta-hydroxy aldehyde loses water to form but-2-enal:

$$\mathrm{CH_3CH(OH)CH_2CHO \xrightarrow{heat} CH_3CH{=}CHCHO + H_2O.}$$

The addition followed by dehydration constitutes aldol condensation.

Step 3: (iii) Illustrate the Cannizzaro reaction Benzaldehyde has no alpha hydrogen and disproportionates on treatment with concentrated sodium hydroxide:

$$\mathrm{2\,C_6H_5CHO + NaOH \xrightarrow{conc\cdot} C_6H_5COONa + C_6H_5CH_2OH.}$$

One molecule gives sodium benzoate by oxidation; the other gives benzyl alcohol by reduction. The acid remains as its salt in the alkaline reaction mixture.

Step 4: Conclusion The examples are propanone to propane (Wolff-Kishner), ethanal to but-2-enal via aldol (aldol condensation), and benzaldehyde to sodium benzoate plus benzyl alcohol (Cannizzaro).

Quick Tip to Solve: Check for alpha hydrogen before choosing aldol or Cannizzaro, and include the dehydration step when illustrating aldol condensation.

30(a). Define the following terms:

(i) Limiting molar conductivity

(ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 $\times$ 10^{-2} Ω^{-1} cm^{-1}. [5 marks]

Solution:

Concept:

- In a galvanic cell, a spontaneous redox reaction produces electrical energy.
- Conductivity is $\kappa = K_{\text{cell}}/R$, where R is resistance and $K_{\text{cell}} = l/A$ is the cell constant. For concentration c in mol L^{-1} and κ in $\Omega^{-1}\,\text{cm}^{-1}$, $\Lambda_m = 1000\kappa/c$.

Step 1: (a)(i) Define limiting molar conductivity Limiting molar conductivity, Λ_m°, is the molar conductivity of an electrolyte at infinite dilution, that is, in the limit of concentration tending to zero:

$$\Lambda_m^\circ = \lim_{c \to 0} \Lambda_m.$$

At this limit, interionic interactions become negligible.

Step 2: (a)(ii) Define a fuel cell A fuel cell is an electrochemical cell that converts the chemical energy released by the reaction of a fuel with an oxidant directly into electrical energy. Reactants are supplied continuously to the electrodes. For example, hydrogen and oxygen form water in a hydrogen-oxygen fuel cell.

Step 3: (b) Determine the cell constant For the reference $0.1\,\text{mol L}^{-1}$ solution of KCl, the resistance is $R_1 = 100\,\Omega$ and conductivity is $\kappa_1 = 1.29 \times 10^{-2}\,\Omega^{-1}\,\text{cm}^{-1}$. Therefore,

$$K_{\text{cell}} = \kappa_1 R_1 = (1.29 \times 10^{-2})(100) = 1.29\,\text{cm}^{-1}.$$

The cell geometry, and hence its cell constant, remains unchanged.

Step 4: Calculate the conductivity of the dilute solution With $R_2 = 520\,\Omega$, substitute the cell constant into $\kappa_2 = K_{\text{cell}}/R_2$:

$$\kappa_2 = \frac{1.29}{520} = 2.4808 \times 10^{-3}\,\Omega^{-1}\,\text{cm}^{-1}.$$

Step 5: Calculate the molar conductivity Use $c_2 = 0.02\,\text{mol L}^{-1}$. The factor 1000 converts litres to cubic centimetres:

$$\Lambda_{m,2} = \frac{1000\kappa_2}{c_2} = \frac{1000(2.4808 \times 10^{-3})}{0.02} = 124.04\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}.$$

Step 6: Conclusion For the $0.02\,\text{mol L}^{-1}$ solution, $\kappa \approx 2.48 \times 10^{-3}\,\Omega^{-1}\,\text{cm}^{-1}$ and $\Lambda_m \approx 124\,\Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$.

Quick Tip to Solve: First find $\kappa_1 R_1$, which stays fixed for the cell; then divide by the new resistance and use $1000\kappa/c$ with concentration in mol per litre.

OR

30(b). (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu?

(b) Calculate emf of the following cell at 298 K:

$$Mg(s)\,|\,Mg^{2+}(0.1\,M)\,\|\,Cu^{2+}(0.01)\,|\,Cu(s)$$

[Given $E^\circ_{cell} = +2.71\,V$, $1\,F = 96500\,C\,mol^{-1}$] [5 marks]

Solution:

Concept:

- Faraday's first law states that the mass m deposited or liberated at an electrode is directly proportional to the electric charge q passed through the electrolyte: $m = Zq = ZIt$, where Z is the electrochemical equivalent, I is current and t is time.
- One mole of electrons carries one Faraday of charge. The electron count in a balanced electrode reaction determines the charge required per mole of product.
- At $298\,K$, the Nernst equation is $E_{cell} = E^\circ_{cell} - (0.0591/n)\log_{10} Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: (a) State the law and identify the electron requirement Faraday's first law of electrolysis: the mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus, at fixed electrolyte and electrode reaction,

$$m \propto q, \qquad m = Zq = ZIt.$$

The reduction half-reaction for copper is

$$Cu^{2+} + 2e^- \longrightarrow Cu.$$

Consequently, each mole of Cu^{2+} needs two moles of electrons to form one mole of copper.

Step 2: (a) Calculate the charge Since one mole of electrons corresponds to one Faraday, the required charge is

$$q = 2\,F = 2(96500) = 193000\,C.$$

This is the charge for the complete reduction of the specified one mole of copper(II) ions; the factor two comes from the ionic charge, independently of the duration or current chosen for electrolysis.

Step 3: (b) Write the cell reaction and its reaction quotient Magnesium is oxidised at the left-hand electrode and copper(II) ions are reduced at the right-hand electrode:

$$\text{Anode: } Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-,$$
$$\text{Cathode: } Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s).$$

Adding these half-reactions gives

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s).$$

Quick Tip to Solve: Balance the two half-reactions first: the electron count is two, and the Nernst quotient is magnesium-ion concentration divided by copper-ion concentration, with both solid metals omitted.

Thus $n = 2$. Omitting pure solid magnesium and copper from the quotient and using the given ionic concentrations,

$$Q = \frac{[\mathrm{Mg}^{2+}]}{[\mathrm{Cu}^{2+}]} = \frac{0.1}{0.01} = 10.$$

Step 4: (b) Apply the Nernst equation at 298 K Substitute $E^{\circ}_{\text{cell}} = +2.71\,\text{V}$, $n = 2$ and $Q = 10$:

$$\begin{aligned} E_{\text{cell}} &= 2.71 - \frac{0.0591}{2}\log_{10}(10) \\ &= 2.71 - 0.02955 \\ &= 2.68045\,\text{V}. \end{aligned}$$

Since the reaction quotient exceeds unity, the concentration correction lowers the emf relative to its standard value. The calculated positive emf is consistent with the spontaneous oxidation of magnesium and reduction of copper(II) ions in the cell as written.

Step 5: Conclusion (a) Faraday's first law is $m \propto q$, or $m = ZIt$. Reduction of $1\,\text{mol}$ of Cu^{2+} requires $\boxed{2\,\text{F} = 1.93 \times 10^{5}\,\text{C}}$.

(b) The cell emf at $298\,\text{K}$ is $\boxed{E_{\text{cell}} \simeq +2.68\,\text{V}}$.

Quick Tip to Solve: Balance the two half-reactions first: the electron count is two, and the Nernst quotient is magnesium-ion concentration divided by copper-ion concentration, with both solid metals omitted.