CBSE Class 12 Chemistry Question Paper 2016 with Solution PDF-Set 56/1/1 - Compartment

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper contains 26 questions. All questions are compulsory.

(ii) There is no overall choice. An internal choice is provided in 5 questions (Q10, Q20, Q24, Q25, Q26); attempt only one of the alternatives in such questions.

(iii) Marks for each question are indicated against it.

1. Define rate of reaction. [1 mark]

Solution:

Concept:

- Reaction rate measures how rapidly reactants are consumed or products are formed.
- Concentration is the amount per unit volume; its change per unit time has units such as mol L^{-1} s^{-1}.

Step 1: Identify the concentration change During a reaction, the concentration of a reactant decreases while that of a product increases. Thus either change can be used to measure the progress of the reaction.

Step 2: Express the change per unit time For a reaction $R \longrightarrow P$, the average rate over a time interval Δt is

$$r = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}.$$

The minus sign for the reactant makes its rate of disappearance positive.

Step 3: Conclusion The rate of a reaction is the change in concentration of a reactant or a product per unit time.

Quick Tip to Solve: Write a minus sign for a reactant's concentration change and a plus sign for a product's concentration change.

2. Why is adsorption always exothermic? [1 mark]

Solution:

Concept:

- Adsorption concentrates particles on the surface of an adsorbent, restricting their freedom of motion.
- For a spontaneous process, the Gibbs energy change is negative: $\Delta G = \Delta H - T\Delta S < 0$, where T is the absolute temperature.

Step 1: Determine the entropy change On adsorption, particles that were free to move become attached to the surface. Their randomness decreases, so the entropy change is negative, $\Delta S < 0$.

Step 2: Apply the condition for spontaneity Since $\Delta S < 0$, the term $-T\Delta S$ is positive. Therefore, for adsorption to occur spontaneously with $\Delta G < 0$, the enthalpy change must be negative and sufficiently large in magnitude to outweigh this term. The attractive interactions formed between the surface and adsorbed particles release energy.

Step 3: Conclusion Adsorption is exothermic because the decrease in entropy must be accompanied by a sufficiently negative enthalpy change for adsorption to be spontaneous: $\Delta H < 0$.

Quick Tip to Solve: First establish that surface attachment reduces randomness; then use $\Delta G = \Delta H - T\Delta S$ to determine the sign of ΔH.

3. Write the IUPAC name of the following complex : $[Co(NH_3)_6]^{3+}$ [1 mark]

Solution:

Concept:

- In coordination nomenclature, ligand names precede the central metal name, and the metal oxidation state is written in Roman numerals.
- The neutral ligand NH_3 is named ammine; six identical ligands take the prefix hexa.

Step 1: Find the oxidation state of cobalt All six ammonia ligands are neutral. If x is the oxidation state of cobalt in $[Co(NH_3)_6]^{3+}$, charge balance gives

$$x + 6(0) = +3.$$

Thus the oxidation state to be included in the name is III.

Step 2: Combine the ligand and metal names Six ammine ligands give the ligand name hexaammine. Since the complex is cationic, the metal retains the name cobalt; the ending cobaltate is used for an anionic cobalt complex. Add the oxidation state in parentheses after the metal name.

Step 3: Conclusion The IUPAC name is **hexaamminecobalt(III) ion**.

Quick Tip to Solve: Spell the ammonia ligand ammine with two m's; neutral ammonia means cobalt's oxidation state equals the complex charge here.

4. Write equation of the nitration of anisole. [1 mark]

Solution:

Concept:

- Anisole, $C_6H_5OCH_3$, undergoes electrophilic aromatic substitution on nitration.
- The methoxy group donates electron density to the ring by resonance and directs substitution mainly to its ortho and para positions.

Step 1: Identify the nitrating mixture Concentrated nitric acid in the presence of concentrated sulphuric acid supplies the nitronium ion, NO_2^+, which attacks the activated aromatic ring of anisole.

Step 2: Write the two substitution pathways One ring hydrogen is replaced by a nitro group. The alternative product equations are

$$C_6H_5OCH_3 + HNO_3 \xrightarrow{\text{conc} \cdot H_2SO_4} o\text{-}NO_2C_6H_4OCH_3 + H_2O,$$
$$C_6H_5OCH_3 + HNO_3 \xrightarrow{\text{conc} \cdot H_2SO_4} p\text{-}NO_2C_6H_4OCH_3 + H_2O.$$

Both products occur in the reaction mixture. Para substitution is favoured because it experiences less steric crowding near the methoxy group.

Step 3: Conclusion Nitration of anisole gives **2-nitroanisole (ortho, minor)** and **4-nitroanisole (para, major)** with concentrated HNO_3 and H_2SO_4.

Quick Tip to Solve: Place the nitro group ortho or para to methoxy and identify the less crowded para product as the major product.

5. Draw the structure of 2-methylbutanal. [1 mark]

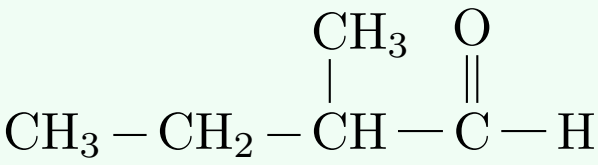
Solution:

Concept:

- The suffix -al denotes an aldehyde group, $-\mathrm{CHO}$, whose carbon belongs to the parent chain and is numbered 1.
- Butanal has a four-carbon parent chain; the prefix 2-methyl places an additional $-\mathrm{CH_3}$ group on carbon 2.

Step 1: Construct the parent chain Begin with a four-carbon chain ending in an aldehyde group. Number from the aldehyde end, so the carbon adjacent to $-\mathrm{CHO}$ is carbon 2. The aldehyde carbon is already included in the four carbons of butanal.

Step 2: Attach the methyl branch Replace one hydrogen on carbon 2 by a methyl group. Carbon 2 then has bonds to the aldehyde carbon, the ethyl group, the methyl branch and one hydrogen. The structure contains five carbon atoms altogether while its longest chain containing the aldehyde group still has four.



2-Methylbutanal: the methyl branch is on carbon 2.

Step 3: Conclusion The structure of 2-methylbutanal is $\mathrm{CH_3CH_2CH(CH_3)CHO}$, as drawn above.

Quick Tip to Solve: Count the aldehyde carbon as carbon 1 before placing the methyl branch on the adjacent carbon.

6. Define the following terms :

(i) n-type semiconductor

(ii) Ferrimagnetism [2 marks]

Solution:

Concept:

- Doping changes the electrical conductivity of an intrinsic semiconductor by introducing impurity atoms and additional charge carriers.
- Magnetic behaviour depends on how atomic or ionic magnetic moments align and whether their vector sum cancels.

Step 1: Define an n-type semiconductor An n-type semiconductor is obtained by doping a group 14 semiconductor, such as silicon or germanium, with a small amount of a group 15 element, such as phosphorus or arsenic. Four of the dopant's five valence electrons form covalent bonds with neighbouring atoms; the fifth is available for conduction. Thus electrons are the majority charge carriers and holes are the minority carriers. The crystal remains electrically neutral; n-type refers to

Quick Tip to Solve: Link n-type to extra electrons; for ferrimagnetism check that opposite moments are unequal, rather than merely opposite.

the negative charge of the majority carriers.

Step 2: Define ferrimagnetism Ferrimagnetism is the magnetic behaviour in which magnetic moments are aligned in opposite directions but have unequal magnitudes, so they do not completely cancel. The solid therefore has a nonzero resultant magnetic moment. Magnetite, Fe_3O_4, is an example. This differs from antiferromagnetism, where equal opposing moments cancel completely.

Step 3: Conclusion (i) An n-type semiconductor has electrons as its majority carriers because of donor doping. (ii) A ferrimagnetic solid has unequal, oppositely aligned moments and hence a net magnetisation.

Quick Tip to Solve: Link n-type to extra electrons; for ferrimagnetism check that opposite moments are unequal, rather than merely opposite.

7. What is osmotic pressure? Why it is a colligative property? [2 marks]

Solution:

Concept:

- Osmosis is the spontaneous movement of solvent through a semipermeable membrane from pure solvent, or a more dilute solution, towards the more concentrated solution.
- For a dilute ideal solution, the osmotic pressure obeys $\pi V = nRT$, where n is the amount of solute particles, V is the solution volume, R is the gas constant and T is the absolute temperature.

Step 1: Define osmotic pressure Osmotic pressure, π, is the minimum excess pressure that must be applied to the solution side to stop the net flow of solvent into it through a semipermeable membrane. The membrane allows solvent molecules to pass but does not allow the solute particles to pass. At this applied pressure, the tendency of solvent to enter the solution is just balanced.

Step 2: Explain its colligative nature Rearranging the dilute-solution relation gives

$$\pi = \frac{n}{V}RT = CRT,$$

where $C = n/V$ is the molar concentration of solute particles. At a fixed temperature, osmotic pressure depends on the number of solute particles per unit volume of solution and not on their chemical identity. Solutions with equal particle concentrations therefore have equal osmotic pressures under these conditions. If a solute dissociates or associates, the resulting number of particles must be used.

Step 3: Conclusion Osmotic pressure is the excess pressure needed to prevent osmosis into a solution. It is a colligative property because, at a given temperature, it depends only on the concentration of solute particles.

Quick Tip to Solve: Use $\pi = CRT$ to justify the definition: keep temperature fixed and compare the concentration of particles, not the mass of solute.

8. Draw the structures of the following compounds :

(i) BrF_3

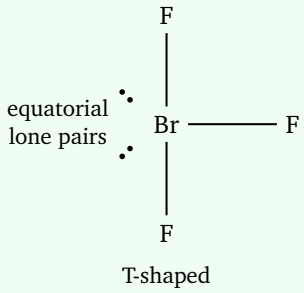
(ii) XeF_4 [2 marks]

Solution:

Concept:

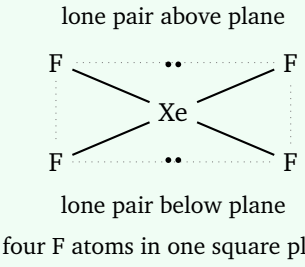
- According to VSEPR theory, electron pairs around a central atom arrange themselves to minimise repulsion. Lone pairs occupy space but are excluded when naming the molecular shape.
- Five electron domains give a trigonal-bipyramidal arrangement; six give an octahedral arrangement.

Step 1: Determine and draw the structure of bromine trifluoride In BrF_3, bromine has seven valence electrons. Three single bonds leave two lone pairs on bromine. The five electron domains correspond to sp^3d hybridisation in the usual school model. The two lone pairs occupy equatorial positions of a trigonal bipyramid because these positions have fewer $90°$ interactions. The fluorine atoms occupy two axial and one equatorial position, giving a T-shaped molecule with angles close to $90°$ and $180°$.



T-shaped BrF_3; dots show the two equatorial lone pairs on Br.

Step 2: Determine and draw the structure of xenon tetrafluoride In XeF_4, xenon has eight valence electrons. Four single bonds leave two lone pairs. The six electron domains correspond to sp^3d^2 hybridisation in the school model and an octahedral electron-pair arrangement. The lone pairs occupy opposite positions to minimise their mutual repulsion. The four fluorine atoms lie in one square plane, giving a square-planar molecule with $90°$ and $180°$ bond angles.



Square-planar XeF_4, shown in perspective; the two lone pairs are above and below the bond plane.

Step 3: Conclusion (i) BrF_3 is T-shaped, with two equatorial lone pairs on bromine. (ii) XeF_4 is square planar, with two opposite lone pairs perpendicular to the plane of its four bonds.

Quick Tip to Solve: Count central-atom lone pairs first: BrF_3 has five electron domains, while XeF_4 has six; neither molecular shape includes the lone pairs.

9. Give reasons :

(i) Transition metals show variable oxidation states.

(ii) Actinoids show wide range of oxidation states. [2 marks]

Solution:

Concept:

- An element can exhibit different oxidation states when different numbers of its valence electrons can participate in bonding or be removed.
- The smaller the energy separation between occupied valence subshells, the more readily electrons from more than one subshell become available for chemical bonding.

Step 1: Explain variable oxidation states of transition metals In transition metals, the energies of the outer ns and inner $(n-1)d$ orbitals are close. Therefore, in addition to the ns electrons, a variable number of $(n-1)d$ electrons can participate in bond formation or be removed. Different numbers of participating electrons produce different oxidation states. For example, iron commonly forms Fe^{2+} and Fe^{3+}: removal of its two $4s$ electrons gives the former, while removal of one additional $3d$ electron gives the latter.

Step 2: Explain the wider range in actinoids In actinoids, the $5f$, $6d$ and $7s$ subshells have comparable energies, especially among the early members. Electrons from all three can therefore participate in bonding, allowing different numbers of electrons to be involved and hence a wide range of oxidation states. For example, uranium exhibits $+3$, $+4$, $+5$ and $+6$. The range is particularly broad among the early actinoids; it need not be equally wide for every member of the series.

Step 3: Conclusion (i) Transition metals show variable oxidation states because both ns and $(n-1)d$ electrons can participate. (ii) Actinoids show a wide range because the $5f$, $6d$ and $7s$ subshells have comparable energies.

Quick Tip to Solve: Name the close-energy subshells explicitly: $ns, (n-1)d$ for transition metals and $5f, 6d, 7s$ for actinoids.

10(a). Write the definitions of the following :

(i) Racemic mixture

(ii) Chiral compound [2 marks]

Solution:

Concept:

- Enantiomers are a pair of stereoisomers whose molecules are non-superimposable mirror images of one another.
- Optical rotation is the rotation of plane-polarised light; equal amounts of two enantiomers produce equal and opposite rotations under identical conditions.

Step 1: Define a racemic mixture A racemic mixture is an equimolar mixture of the two enantiomers of a chiral compound: the dextrorotatory $(+)$ form and the laevorotatory $(-)$ form. Its observed optical rotation is zero because the rotations of the two forms cancel. This is called external compensation;

Quick Tip to Solve: Distinguish molecular chirality from the net rotation of a sample: a racemic sample contains chiral molecules but has zero optical rotation.

individual molecules of the enantiomers are still chiral.

Step 2: Define a chiral compound A chiral compound is one whose molecule cannot be superimposed on its mirror image. Such a molecule and its mirror image constitute an enantiomeric pair. For example, butan-2-ol is chiral because its second carbon bears four different groups: H, OH, CH_3 and C_2H_5.

Step 3: Conclusion (i) A racemic mixture contains equal amounts of two enantiomers and is optically inactive by external compensation. (ii) A chiral compound has molecules non-superimposable on their mirror images.

Quick Tip to Solve: Distinguish molecular chirality from the net rotation of a sample: a racemic sample contains chiral molecules but has zero optical rotation.

OR

10(b). Write the ambident nucleophiles? Give an example. [2 marks]

Solution:

Concept:

- A nucleophile is an electron-pair donor that forms a bond with an electron-deficient centre.
- An ambident nucleophile has two different potential donor atoms, either of which can form the new bond in a substitution reaction.

Step 1: Define an ambident nucleophile Ambident nucleophiles are nucleophiles which possess two alternative nucleophilic centres and can attack an electrophile through either centre. In a particular substitution product the bond is formed through one of these centres. Thus, the same nucleophile can give products with different atom connectivities, depending on the attacking atom and reaction conditions.

Step 2: Give the cyanide-ion example The cyanide ion, CN^-, is an ambident nucleophile because it can bond through its carbon atom or its nitrogen atom. Carbon-end attack gives an alkyl cyanide, $R-C\equiv N$, whereas nitrogen-end attachment gives an alkyl isocyanide, $R-N\equiv C$. For example, alkyl halides with ionic KCN predominantly form cyanides, while $AgCN$ favours isocyanides.

Step 3: Conclusion An ambident nucleophile can attack through either of two donor atoms; CN^-, with carbon and nitrogen as alternative donor centres, is an example.

Quick Tip to Solve: For cyanide, track the atom bonded directly to the alkyl group: carbon gives a cyanide, while nitrogen gives an isocyanide.

11. If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancies? [3 marks]

Solution:

Concept:

- Impurity doping must preserve the electrical neutrality of an ionic crystal. A divalent cation replacing a monovalent cation introduces one extra positive charge.
- One vacant monovalent-cation site compensates that extra positive charge. The number of cation vacancies therefore equals the number of incorporated divalent impurity ions.
- A molar percentage is the number of moles per 100 moles of the host; Avogadro's constant is $N_A = 6.022 \times 10^{23}\,\text{mol}^{-1}$.

Step 1: Determine the charge-compensating defect In doped sodium chloride, Sr^{2+} occupies a site normally occupied by Na^+. Its charge exceeds that of the replaced sodium ion by one unit. Hence one other sodium-ion site remains vacant for every strontium ion introduced. The two affected cation sites contain one Sr^{2+} and one vacancy instead of two Na^+ ions, retaining their total charge of $+2$.

Step 2: Convert molar percentage into moles of vacancies The dopant level is 10^{-3} mol %, so the amount of $SrCl_2$ per mole of NaCl is

$$n(SrCl_2) = \frac{10^{-3}}{100} = 10^{-5}\,\text{mol}.$$

Each formula unit supplies one Sr^{2+} ion. Since each such ion creates one cation vacancy, there are 10^{-5} moles of vacancies per mole of sodium chloride.

Step 3: Calculate the number of vacant sites Multiplying the vacancy amount by Avogadro's constant gives

$$N_{vac} = 10^{-5} \times 6.022 \times 10^{23} = 6.022 \times 10^{18}.$$

This is a number per mole of host, rather than a number per unit volume; a volume concentration would additionally require the crystal density.

Step 4: Conclusion The cation-vacancy concentration is $\boxed{6.022 \times 10^{18}\text{ vacancies per mole of NaCl}}$, corresponding to a vacancy fraction of 10^{-5}.

Quick Tip to Solve: First divide mol percent by 100, then use one sodium vacancy per strontium ion; do not create two vacancies for a divalent dopant.

12. Calculate the mass of a non-volatile solute (molecular mass 40) which should be dissolved in 114 g octane to reduce the vapour pressure to 80%. [3 marks]

Solution:

Concept:

- For an ideal solution containing a non-volatile solute, Raoult's law gives $p = x_1 p^0$, where p^0 is the pure solvent's vapour pressure and x_1 is its mole fraction.
- The solvent mole fraction is $x_1 = n_1/(n_1 + n_2)$, and the relative lowering of vapour pressure is $(p^0 - p)/p^0 = x_2$, where n_1, n_2 are the solvent and solute amounts.

Quick Tip to Solve: Interpret 'to 80 percent' as a pressure ratio of 0.80; use the full mole-fraction denominator when the pressure lowering is 20 percent.

Step 1: Calculate the amount of octane Octane has the formula C_8H_{18}. Using the atomic masses $C = 12$ and $H = 1$, its molar mass is

$$M_1 = 8(12) + 18(1) = 114\,\text{g mol}^{-1}.$$

Thus the given $114\,\text{g}$ of octane contains $n_1 = 114/114 = 1\,\text{mol}$. Let the required solute mass be w grams; its molar mass is $40\,\text{g mol}^{-1}$, so $n_2 = w/40$.

Step 2: Apply the required vapour-pressure ratio Reducing the vapour pressure to 80% means $p/p^0 = 0.80$, so the solvent mole fraction must equal 0.80. Apply Raoult's law at the same temperature:

$$\frac{p}{p^0} = \frac{n_1}{n_1 + n_2}, \qquad 0.80 = \frac{1}{1 + w/40}.$$

The total amount in the denominator includes both solvent and solute. Here the solute mole fraction is 0.20, so the dilute approximation that replaces the total amount by the solvent amount should not be used.

Step 3: Solve for the solute mass Rearranging the exact mole-fraction equation,

$$1 + \frac{w}{40} = \frac{1}{0.80} = 1.25, \qquad \frac{w}{40} = 0.25, \qquad w = 10\,\text{g}.$$

As a check, $10\,\text{g}$ of solute supplies $0.25\,\text{mol}$; hence the octane mole fraction is $1/(1 + 0.25) = 0.80$, exactly the required pressure ratio.

Step 4: Conclusion The required mass of the non-volatile solute is $\boxed{10\,\text{g}}$.

Quick Tip to Solve: Interpret 'to 80 percent' as a pressure ratio of 0.80; use the full mole-fraction denominator when the pressure lowering is 20 percent.

13. If the half-life period of a first order reaction in A is 2 minutes, how long will it take [A] to reach 25% of its initial concentration? [3 marks]

Solution:

Concept:

- For a first order reaction, the half-life $t_{1/2}$ is independent of the initial concentration. Each half-life reduces the remaining concentration to half its previous value.
- The integrated rate equation is $kt = \ln([A]_0/[A]_t)$, where $[A]_0$ and $[A]_t$ are the initial concentration and concentration at time t, respectively, and k is the rate constant. Also, $k = \ln 2/t_{1/2}$.

Step 1: Express the required concentration as a fraction The question asks for the time when the concentration remaining is 25% of its initial value, so

$$[A]_t = \frac{25}{100}[A]_0 = \frac{[A]_0}{4}.$$

Thus the concentration ratio to use in the rate equation is $[A]_0/[A]_t = 4$. This corresponds to 75%

Quick Tip to Solve: For a first order reaction, write the fraction remaining as $(1/2)^n$. Here $1/4 = (1/2)^2$, so multiply the half-life by two.

reaction completion; it does not mean that only 25% has reacted.

Step 2: Substitute the half-life into the rate equation Since $t_{1/2} = 2\,\text{min}$, the rate constant expressed in inverse minutes is

$$k = \frac{\ln 2}{2}\,\text{min}^{-1}.$$

Substitute the concentration ratio and this rate constant:

$$t = \frac{\ln 4}{k} = \frac{2\ln 4}{\ln 2}\,\text{min}.$$

Using $\ln 4 = 2\ln 2$, this is twice the given half-life. As a check, the first half-life leaves 50%, and the second halves that amount to 25%. No initial numerical concentration is needed because it cancels in the ratio.

Step 3: Conclusion The time required is $t = 2t_{1/2} = 2 \times 2 = \boxed{4\,\text{min}}$.

Quick Tip to Solve: For a first order reaction, write the fraction remaining as $(1/2)^n$. Here $1/4 = (1/2)^2$, so multiply the half-life by two.

14. What are emulsions? What are their different types? Give an example of each type. [3 marks]

Solution:

Concept:

- An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids. One immiscible liquid is distributed as fine droplets in the other.
- Emulsions are classified by the liquid forming the continuous dispersion medium: oil-in-water (O/W) and water-in-oil (W/O). Here oil denotes the water-immiscible liquid phase.

Step 1: Identify the dispersed and continuous phases In an emulsion, the small droplets constitute the dispersed phase, while the surrounding liquid constitutes the dispersion medium. The two liquids do not form a homogeneous molecular solution. Thus, the nature of the surrounding continuous liquid determines which of the two types of emulsion is present. An emulsifying agent can help stabilise the droplets by preventing their coalescence into larger drops.

Step 2: Describe the oil-in-water type In an oil-in-water emulsion, oil is the dispersed phase and water is the dispersion medium: fine oil droplets are surrounded by a continuous aqueous phase. Milk is a familiar example, with liquid fat droplets dispersed in water. The name oil-in-water refers to the fat droplets being inside the aqueous continuous medium.

Step 3: Describe the water-in-oil type In a water-in-oil emulsion, water is the dispersed phase and oil is the dispersion medium: water droplets are distributed throughout the continuous oil phase. Butter is a standard example, with small water droplets dispersed in the continuous fat phase. This reverses the roles of the two phases compared with milk.

Step 4: Conclusion Emulsions are liquid-in-liquid colloids. Their two types are oil-in-water, exemplified by milk, and water-in-oil, exemplified by butter.

Quick Tip to Solve: Read the name from left to right: the first liquid forms the droplets and the liquid after "in" is the continuous medium. Thus milk is O/W and butter is W/O.

15. Describe the following :

(i) Role of depressant in froth floatation process

(ii) Role of silica in the metallurgy of copper

(iii) Role of cryolite in the metallurgy of aluminium [3 marks]

Solution:

Concept:

- Froth flotation concentrates sulphide ores using preferential wetting. A depressant selectively prevents one sulphide from entering the froth, allowing separation of a mixture.
- A flux combines with an impurity to form a removable slag. In electrolytic extraction, additives can make the molten electrolyte easier to maintain and improve its electrical conductivity.

Step 1: Explain the role of a depressant (i) A depressant prevents a selected sulphide mineral from being wetted by the collector and carried into the froth. For a mixture of ZnS and PbS, sodium cyanide, $NaCN$, depresses ZnS, so it remains in the aqueous slurry while PbS is collected with the froth. The depressant therefore makes flotation selective and permits separation of the two sulphide ores.

Step 2: Explain silica as a flux in copper extraction (ii) During the extraction of copper from sulphide ores, iron sulphide impurity is oxidised to iron(II) oxide. Silica, SiO_2, acts as an acidic flux and combines with the basic oxide, FeO, to form fusible iron silicate slag:

$$FeO + SiO_2 \longrightarrow FeSiO_3.$$

This slag separates from the copper-containing material and can be removed. Thus silica removes iron oxide impurity; it is not the reducing agent for copper.

Step 3: Explain cryolite in aluminium extraction (iii) Cryolite, Na_3AlF_6, is added to alumina, Al_2O_3, in the Hall–Heroult process. It serves as a solvent for alumina, lowers the fusion temperature of the electrolytic mixture compared with pure alumina, and increases the electrical conductivity of the melt. This permits electrolysis at a more practical temperature with easier current flow. Cryolite facilitates electrolysis rather than chemically reducing alumina.

Step 4: Conclusion A depressant enables selective flotation of sulphide ores; silica removes FeO as $FeSiO_3$ slag; and cryolite lowers the fusion temperature and increases the conductivity of the alumina electrolyte.

Quick Tip to Solve: Link each additive to its stage: depressant selects the ore in flotation, silica removes iron oxide as slag, and cryolite improves the molten electrolyte.

16. In the 3d series (Sc = 21 to Zn = 30) :

(i) Which element shows maximum number of oxidation states?

(ii) Which element shows only +3 oxidation state?

(iii) Which element has the lowest enthalpy of atomization? [3 marks]

Solution:

Concept:

- Variable oxidation states in the first transition series arise because the energies of the $3d$ and $4s$ orbitals are close enough for electrons from both to participate in bonding.
- Enthalpy of atomization is the energy needed to form gaseous atoms from the element in its standard state. Stronger metallic bonding generally gives a larger value.

Step 1: (i) Identify the element with the widest oxidation-state range Manganese has the configuration $[\mathrm{Ar}]\,3d^5 4s^2$. Its five $3d$ electrons and two $4s$ electrons allow the widest range of oxidation states in the $3d$ series. The commonly considered positive states are $+2, +3, +4, +5, +6$ and $+7$; for example, manganese is $+2$ in $MnCl_2$ and $+7$ in $KMnO_4$. Thus the required element is manganese, Mn.

Step 2: (ii) Identify the element showing only the +3 state Scandium has configuration $[\mathrm{Ar}]\,3d^1 4s^2$. Loss of its two $4s$ electrons and one $3d$ electron gives Sc^{3+}, with the stable noble-gas configuration $[\mathrm{Ar}]$. Hence scandium, Sc, exhibits only the $+3$ oxidation state in its ordinary compounds.

Step 3: (iii) Compare the metallic bonding Zinc has configuration $[\mathrm{Ar}]\,3d^{10} 4s^2$. Its filled $3d$ subshell has no unpaired electrons and contributes little to metallic bonding. Zinc consequently has comparatively weak metallic bonding and the lowest enthalpy of atomization among the elements from scandium to zinc. This property concerns separation into neutral gaseous atoms, rather than removal of an electron to form an ion.

Step 4: Conclusion (i) Manganese, Mn; (ii) scandium, Sc; (iii) zinc, Zn.

Quick Tip to Solve: Recall the three configurations: $3d^5 4s^2$ gives manganese's wide range, $3d^1 4s^2$ gives scandium's $+3$ state, and filled $3d^{10}$ identifies zinc's weak metallic bonding.

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17. Write down the hybridization and magnetic character of the following complexes :

(i) $[Ni(CO)_4]$

(ii) $[CoF_6]^{3-}$

(Atomic number : Ni = 28, Co = 27) [3 marks]

Solution:

Concept:

- First find the metal's oxidation state from the ligand charges and the overall complex charge, then obtain its d-electron count. Electrons are removed from $4s$ before $3d$ when forming a transition-metal cation.
- In valence-bond theory, ligand strength determines electron pairing and the orbitals available for hybridization. A complex with unpaired electrons is paramagnetic; one with all electrons paired is

Quick Tip to Solve: Count the metal's electrons before choosing hybridization: neutral CO gives Ni(0), whereas six F^- ligands in a $3-$ complex give Co^{3+}.

diamagnetic.

Step 1: (i) Determine the electronic arrangement in nickel carbonyl Carbon monoxide, CO, is a neutral ligand. Since $[Ni(CO)_4]$ is neutral, nickel has oxidation state zero. The free nickel atom has configuration $[Ar]\,3d^8 4s^2$. Under the influence of the strong-field CO ligands, the valence electrons pair in the $3d$ orbitals, giving the $3d^{10}$ arrangement used in the valence-bond description of this complex. The vacant $4s$ orbital and three vacant $4p$ orbitals form four sp^3 hybrid orbitals. Four ligand lone pairs occupy these orbitals, giving tetrahedral geometry. All electrons are paired, so the complex is diamagnetic.

Step 2: (ii) Determine the electronic arrangement in the cobalt complex Each fluoride ligand carries charge -1. If cobalt has oxidation state x, then

$$x + 6(-1) = -3 \quad \Rightarrow \quad x = +3.$$

Cobalt is $[Ar]\,3d^7 4s^2$, so Co^{3+} is $[Ar]\,3d^6$. Fluoride is a weak-field ligand and does not cause additional pairing of the $3d$ electrons. The high-spin d^6 arrangement contains one paired orbital and four singly occupied orbitals, hence four unpaired electrons. The complex uses the outer $4s$, three $4p$, and two $4d$ orbitals to form six sp^3d^2 hybrids. It is an outer-orbital octahedral complex and is paramagnetic.

Step 3: Conclusion (i) $[Ni(CO)_4]$: sp^3 hybridization, diamagnetic (zero unpaired electrons). (ii) $[CoF_6]^{3-}$: sp^3d^2 hybridization, paramagnetic (four unpaired electrons).

Quick Tip to Solve: Count the metal's electrons before choosing hybridization: neutral CO gives Ni(0), whereas six F^- ligands in a $3-$ complex give Co^{3+}.

18. In the following pairs of the halogen compounds which compound undergoes faster S_N1 reaction.

(i) $CH_3-CH_2-CH_2-CH_2-Cl$ and $(CH_3)_3C-Cl$

(ii) CH_3CH_2-Br and CH_3CH_2-I [3 marks]

Solution:

Concept:

- In an S_N1 reaction, the slow, rate-determining step is ionization of the carbon–halogen bond to form a carbocation and a halide ion: $R-X \longrightarrow R^+ + X^-$. The rate law is $v = k[R-X]$.
- For comparable substrates and reaction conditions, greater carbocation stability and better leaving-group ability favour faster ionization. Alkyl carbocation stability generally follows tertiary $>$ secondary $>$ primary.

Step 1: (i) Compare carbocation stability for the two chlorides Both compounds have chloride as the leaving group, so compare the carbocations formed after carbon–chlorine bond cleavage. $CH_3CH_2CH_2CH_2Cl$ would form a primary butyl carbocation, whereas $(CH_3)_3CCl$ forms a tertiary tert-butyl carbocation:

$$(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-.$$

The three methyl groups stabilize the tertiary carbocation by their electron-releasing inductive effect and hyperconjugation. Formation of this more stable carbocation is favoured over formation of

Quick Tip to Solve: With the same halogen, compare the carbocations; with the same alkyl group, compare leaving groups. Here these tests select tertiary chloride and ethyl iodide, respectively.

the primary carbocation. Consequently, tert-butyl chloride undergoes S_N1 substitution faster than 1-chlorobutane.

Step 2: (ii) Compare leaving-group ability for the ethyl halides CH_3CH_2Br and CH_3CH_2I have the same ethyl group, so the carbocation-stability factor is the same. The carbon–iodine bond is weaker than the carbon–bromine bond, and I^- is a better leaving group than Br^-. Thus ethyl iodide ionizes more readily and is the faster member of this pair in the stated S_N1 comparison. Both compounds are primary halides and are intrinsically poor S_N1 substrates; the relative comparison does not imply that a primary ethyl carbocation forms readily under ordinary conditions.

Step 3: Conclusion The faster compounds are (i) $(CH_3)_3CCl$ and (ii) CH_3CH_2I, on comparing each pair under the same reaction conditions.

Quick Tip to Solve: With the same halogen, compare the carbocations; with the same alkyl group, compare leaving groups. Here these tests select tertiary chloride and ethyl iodide, respectively.

19. How are the following conversions carried out?

(i) Propene → Propan-2-ol

(ii) Benzyl chloride → Benzyl alcohol

(iii) Ethyl magnesium chloride → Propan-1-ol [3 marks]

Solution:

Concept:

- Acid-catalysed hydration adds water across an alkene double bond according to Markovnikov's rule: the hydroxyl group goes to the more substituted carbon.
- Aqueous alkali hydrolyses benzyl chloride by replacing chlorine with a hydroxyl group.
- A Grignard reagent reacts with methanal in dry ether; subsequent acidic hydrolysis gives a primary alcohol with one more carbon than the alkyl group of the reagent.

Step 1: (i) Hydrate propene Treat propene with water in the presence of dilute sulphuric acid. Protonation favours the more stable secondary carbocation, so water attacks the middle carbon and loss of a proton gives the alcohol:

$$CH_3CH{=}CH_2 + H_2O \xrightarrow{\text{dilute } H_2SO_4} CH_3CH(OH)CH_3.$$

This is Markovnikov addition; the hydroxyl group is attached to carbon 2.

Step 2: (ii) Hydrolyse benzyl chloride Warm benzyl chloride with aqueous potassium hydroxide. The hydroxide ion substitutes for chloride at the benzylic carbon:

$$C_6H_5CH_2Cl + KOH(aq) \xrightarrow{\text{warm}} C_6H_5CH_2OH + KCl.$$

The aqueous medium supplies hydroxide for substitution, and the benzene ring remains unchanged.

Step 3: (iii) Extend the ethyl group by one carbon React ethyl magnesium chloride with methanal in

Quick Tip to Solve: Count the carbons first: a two-carbon Grignard reagent needs one-carbon methanal to produce the three-carbon primary alcohol.

dry ether, then hydrolyse the magnesium alkoxide with dilute acid:

$$C_2H_5MgCl + HCHO \xrightarrow{\text{dry ether}} C_2H_5CH_2OMgCl,$$
$$C_2H_5CH_2OMgCl + H_2O \longrightarrow C_2H_5CH_2OH + Mg(OH)Cl.$$

The second equation represents hydrolytic work-up. Keep water away until the carbonyl addition is complete, because it would otherwise destroy the Grignard reagent. Methanal contributes the third carbon.

Step 4: Conclusion Use (i) acid-catalysed hydration to obtain propan-2-ol, (ii) warm aqueous KOH to obtain benzyl alcohol, and (iii) methanal in dry ether followed by acidic hydrolysis to obtain propan-1-ol.

Quick Tip to Solve: Count the carbons first: a two-carbon Grignard reagent needs one-carbon methanal to produce the three-carbon primary alcohol.

20(a). Write major product(s) in the following reactions :

(i) $C_6H_5-NO_2 \xrightarrow{Sn/HCl}$ **?**

(ii) $C_6H_5-N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl}$ **?**

(iii) $CH_3CONH_2 \xrightarrow{Br_2/KOH(aq)}$ **?** [3 marks]

Solution:

Concept:

- Tin and hydrochloric acid reduce an aromatic nitro group to an amino group without reducing the benzene ring.
- In the Sandmeyer reaction, cuprous chloride replaces the diazonium group by chlorine with liberation of nitrogen gas.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into a primary amine, RNH_2, containing one carbon fewer.

Step 1: (i) Reduce nitrobenzene Tin and hydrochloric acid provide the reducing conditions that convert $-NO_2$ into $-NH_2$. The conventional organic transformation is

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

Here $[H]$ denotes a reducing hydrogen equivalent. In the acidic reaction mixture the amine is protonated and occurs as anilinium chloride, $C_6H_5NH_3^+Cl^-$. Alkaline work-up liberates free aniline:

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

Step 2: (ii) Replace the diazonium group Benzenediazonium chloride reacts with cuprous chloride in hydrochloric acid. The whole diazonium group leaves as nitrogen, and chlorine becomes bonded

Quick Tip to Solve: Track the carbon count: nitro reduction and Sandmeyer substitution retain all six ring carbons, whereas Hofmann degradation removes the amide carbonyl carbon.

directly to the ring:

$$C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl + N_2 \uparrow .$$

This is the Sandmeyer reaction; the organic product is chlorobenzene, not benzyl chloride.

Step 3: (iii) Degrade ethanamide Bromine and aqueous potassium hydroxide cause Hofmann bromamide degradation. The carbonyl carbon is removed as carbonate, leaving the original methyl group attached to nitrogen:

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

Thus a two-carbon amide gives a one-carbon amine; this reagent does not convert the carbonyl group into a methylene group.

Step 4: Conclusion The major organic products are (i) aniline, $C_6H_5NH_2$, after alkaline work-up (anilinium chloride in the acidic mixture); (ii) chlorobenzene, C_6H_5Cl, with nitrogen gas; and (iii) methylamine, CH_3NH_2.

Quick Tip to Solve: Track the carbon count: nitro reduction and Sandmeyer substitution retain all six ring carbons, whereas Hofmann degradation removes the amide carbonyl carbon.

OR

20(b). Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reaction involved. [3 marks]

Solution:

Concept:

- Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. Its reaction with amines in aqueous alkali distinguishes primary, secondary and tertiary amines.
- A primary-amine sulphonamide retains an acidic N-H bond and dissolves in alkali as a salt; a secondary-amine sulphonamide has no N-H bond and is insoluble in alkali.
- Tertiary amines do not form sulphonamides under these conditions but form soluble ammonium salts with dilute acid. Here R denotes an alkyl group.

Step 1: Carry out the Hinsberg test Shake each amine with benzenesulphonyl chloride and excess aqueous NaOH. Observe reaction and solubility, then add dilute HCl.

Step 2: Identify a primary amine A primary amine forms an N-substituted benzenesulphonamide:

$$C_6H_5SO_2Cl + RNH_2 + NaOH \longrightarrow C_6H_5SO_2NHR + NaCl + H_2O.$$

Its remaining N-H hydrogen is acidic because of the electron-withdrawing sulphonyl group. It therefore dissolves in excess alkali:

$$C_6H_5SO_2NHR + NaOH \longrightarrow C_6H_5SO_2NR^-Na^+ + H_2O.$$

Quick Tip to Solve: Count N-H bonds in the sulphonamide product: one permits alkali dissolution, zero prevents it; then use dilute acid to identify unreacted tertiary amine.

Acidification regenerates the insoluble sulphonamide as a precipitate:

$$C_6H_5SO_2NR^-Na^+ + HCl \longrightarrow C_6H_5SO_2NHR \downarrow + NaCl.$$

Step 3: Identify a secondary amine A secondary amine forms an N,N-disubstituted sulphonamide:

$$C_6H_5SO_2Cl + R_2NH + NaOH \longrightarrow C_6H_5SO_2NR_2 + NaCl + H_2O.$$

The product has no N-H hydrogen to lose, so it is insoluble in aqueous alkali. It also remains insoluble on adding dilute acid under the test conditions.

Step 4: Identify a tertiary amine A tertiary amine, R_3N, has no N-H bond and does not form a sulphonamide with Hinsberg's reagent. On adding dilute hydrochloric acid, it forms a water-soluble trialkylammonium salt:

$$R_3N + HCl \longrightarrow R_3NH^+Cl^-.$$

Acid dissolution distinguishes the tertiary amine from a secondary-amine sulphonamide.

Step 5: Conclusion In the Hinsberg test, a primary amine gives an alkali-soluble sulphonamide that precipitates on acidification; a secondary amine gives an alkali-insoluble sulphonamide that remains insoluble in dilute acid; a tertiary amine forms no sulphonamide and dissolves in dilute acid as an ammonium salt.

Quick Tip to Solve: Count N-H bonds in the sulphonamide product: one permits alkali dissolution, zero prevents it; then use dilute acid to identify unreacted tertiary amine.

21. Write two uses of each of the following polymers.

(i) Polypropylene

(ii) PVC

(iii) Nylon-66 [3 marks]

Solution:

Concept:

- A polymer's use depends on properties such as strength, flexibility, resistance to chemicals and electrical insulation. Polypropylene and PVC are thermoplastics, which can be softened and moulded into useful articles.
- Nylon-66 is a polyamide with strong intermolecular hydrogen bonding between its chains. Its strength and resistance to abrasion make it suitable for fibres and ropes.

Step 1: (i) Uses of polypropylene Polypropylene is used for making (1) ropes and (2) packaging films. It is light, tough and resistant to many chemicals. The polymer can be drawn into fibres for ropes or formed into thin films for wrapping and packaging goods.

Step 2: (ii) Uses of PVC Polyvinyl chloride (PVC) is used for making (1) water pipes and (2) insulation around electrical wires and cables. Its resistance to water and chemicals is useful in pipes, while its poor electrical conductivity makes it suitable as an insulating covering. Plasticisers can make PVC

Quick Tip to Solve: Associate PVC with pipes and wire insulation, and nylon-66 with strong fibres; give two distinct finished uses for each polymer.

flexible for cable coverings.

Step 3: (iii) Uses of nylon-66 Nylon-66 is used for making (1) textile fibres for fabrics and (2) ropes. Its fibres have high tensile strength and withstand repeated rubbing, so they are useful in clothing as well as articles subjected to pulling forces.

Step 4: Conclusion Two uses of each are: polypropylene—ropes and packaging films; PVC—water pipes and electrical-wire insulation; nylon-66—textile fibres and ropes.

Quick Tip to Solve: Associate PVC with pipes and wire insulation, and nylon-66 with strong fibres; give two distinct finished uses for each polymer.

22. Define the following as related to proteins :

(i) Peptide linkage

(ii) Primary structure

(iii) Denaturation [3 marks]

Solution:

Concept:

- Proteins are polymers of α-amino acids joined by peptide bonds. The order of their amino-acid residues determines their primary structure.
- Biological activity depends on the protein's specific three-dimensional arrangement. Forces stabilising this arrangement can be disturbed without breaking the covalent peptide backbone.

Step 1: (i) Peptide linkage A peptide linkage is the amide linkage $-\mathrm{CO}-\mathrm{NH}-$ formed between the carboxyl group of one amino acid and the amino group of another, with elimination of a water molecule. For two α-amino acids, the formation of a dipeptide is represented by

$$\begin{aligned}&\mathrm{H_2N}-\mathrm{CH}(\mathrm{R}^1)-\mathrm{COOH}+\mathrm{H_2N}-\mathrm{CH}(\mathrm{R}^2)-\mathrm{COOH}\\&\longrightarrow \mathrm{H_2N}-\mathrm{CH}(\mathrm{R}^1)-\mathrm{CO}-\mathrm{NH}-\mathrm{CH}(\mathrm{R}^2)-\mathrm{COOH}+\mathrm{H_2O}.\end{aligned}$$

Here R^1 and R^2 denote the side chains of the two amino acids; the newly formed $\mathrm{CO}-\mathrm{NH}$ group joins their residues.

Step 2: (ii) Primary structure The primary structure of a protein is the specific sequence of amino-acid residues in its polypeptide chain. The sequence is conventionally stated from the amino-terminal (N-terminal) end to the carboxyl-terminal (C-terminal) end. It specifies the order of residues, rather than the folded shape of the chain.

Step 3: (iii) Denaturation Denaturation is the loss of a protein's native conformation and biological activity due to a physical or chemical change, such as heating or a change in pH. It disrupts the secondary and tertiary structures, while the primary structure and peptide linkages remain intact. Coagulation of egg white on heating is a familiar example; denaturation is distinct from hydrolysis of the peptide bonds.

Step 4: Conclusion Peptide linkage means the $-\mathrm{CO}-\mathrm{NH}-$ bond between amino-acid residues; primary structure means their definite sequence; denaturation means loss of native folding and

Quick Tip to Solve: Keep sequence and shape separate: denaturation changes protein folding, whereas peptide-bond hydrolysis breaks its primary structure.

biological activity without changing that sequence.

Quick Tip to Solve: Keep sequence and shape separate: denaturation changes protein folding, whereas peptide-bond hydrolysis breaks its primary structure.

23. Ms. Kirti was pursuing her studies in medicine at Bangalore. When she visited her family during holidays, she noticed that their maid was always complaining of stomach ache and some burning sensation. Kirti took her maid to the doctor where she was diagnosed for early stage of ulcers due to excessive use of Antacids.

Answer the following:

(i) What are the values displayed by Kirti?

(ii) What are antacids? Give two examples.

(iii) Why prolong use of antacids is harmful? [4 marks]

Solution:

Concept:

- Antacids are basic substances that neutralise excess hydrochloric acid in the stomach and relieve acidity and the associated burning sensation.
- Acid–base neutralisation consumes hydrogen ions: $H^+ + OH^- \longrightarrow H_2O$. Excessive neutralisation can disturb the normal acidic conditions needed in the stomach.

Step 1: (i) Values displayed by Kirti Kirti shows compassion, empathy, social responsibility and concern for the health of others. She takes the maid's repeated complaints seriously and acts promptly by taking her to a doctor. Her willingness to help a person working in her home also shows respect for human dignity and a scientific attitude towards illness: she seeks proper diagnosis and treatment.

Step 2: (ii) Meaning and examples of antacids Antacids are mild bases used to neutralise excess acid in the stomach. Two examples are magnesium hydroxide, $Mg(OH)_2$, commonly called milk of magnesia, and aluminium hydroxide, $Al(OH)_3$. Their neutralisation reactions are

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O,$$
$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O.$$

These substances relieve acidity by consuming excess acid; they do not themselves stop its production.

Step 3: (iii) Harm from prolonged excessive use Excessive use of antacids can make the stomach too alkaline. This can stimulate the stomach to produce more acid, so the acidity returns and the burning sensation or an existing ulcer may worsen. Repeated self-medication therefore gives temporary relief without controlling the underlying excessive acid secretion. The poorly soluble hydroxides used above are generally preferable to soluble sodium hydrogencarbonate because they are less likely to raise the stomach pH excessively. Persistent symptoms require the doctor's treatment rather than continually increasing the amount of antacid.

Step 4: Conclusion Kirti displays empathy, care and social responsibility. Antacids neutralise excess stomach acid; examples are $Mg(OH)_2$ and $Al(OH)_3$. Excessive prolonged use may cause over-

Quick Tip to Solve: Distinguish acid neutralisation by an antacid from suppression of acid secretion: this difference explains why repeated doses may give only temporary relief.

neutralisation and renewed acid secretion, aggravating acidity and ulcer symptoms.

Quick Tip to Solve: Distinguish acid neutralisation by an antacid from suppression of acid secretion: this difference explains why repeated doses may give only temporary relief.

24(a). Define the following :

(a) (i) Molar conductivity

(ii) Fuel cell

(b) The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of the solution. [5 marks]

Solution:

Concept:

- Molar conductivity $\Lambda_m = \kappa V$, where κ is conductivity and V is the volume of solution containing one mole of electrolyte.
- For concentration c in mol L^{-1}, $\Lambda_m = 1000\kappa/c$, with Λ_m in S cm^2 mol^{-1} and κ in S cm^{-1}.
- A fuel cell uses a spontaneous redox reaction to convert the chemical energy of continuously supplied reactants directly into electrical energy.

Step 1: Define molar conductivity, part (a)(i) Molar conductivity is the conductance of the volume of solution containing one mole of an electrolyte, placed between parallel electrodes of unit separation and sufficiently large area to contain that volume. It includes the contribution of all the ions formed from that mole at the stated concentration. Its common unit is S cm^2 mol^{-1}; the SI unit is S m^2 mol^{-1}.

Step 2: Define a fuel cell, part (a)(ii) A fuel cell is a galvanic cell in which a fuel and an oxidant are continuously supplied to the electrodes, and their chemical energy is converted directly into electrical energy. It operates while reactants are supplied and products removed. For example, the hydrogen–oxygen fuel cell has the overall reaction

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O\,(l).$$

Oxidation and reduction at separate electrodes drive electrons through the external circuit.

Step 3: Convert concentration and calculate conductivity, part (b) The concentration is $c = 1.5\,\text{mol L}^{-1}$. Since $1\,\text{L} = 1000\,\text{cm}^3$, the volume containing one mole is $V = (1000/1.5)\,\text{cm}^3\ \text{mol}^{-1}$. Rearranging $\Lambda_m = 1000\kappa/c$ and substituting $\Lambda_m = 138.9\,\text{S cm}^2\ \text{mol}^{-1}$,

$$\begin{aligned}\kappa &= \frac{\Lambda_m c}{1000} \\ &= \frac{138.9 \times 1.5}{1000}\,\text{S cm}^{-1} \\ &= \frac{208.35}{1000}\,\text{S cm}^{-1}.\end{aligned}$$

Multiplying molar conductivity by concentration in mol cm^{-3} leaves S cm^{-1}, confirming the unit and the factor of 1000.

Quick Tip to Solve: With molarity in mol L^{-1} and molar conductivity in S cm^2 mol^{-1}, multiply the two values and divide by 1000 for conductivity in S cm^{-1}.

Step 4: Conclusion Molar conductivity measures the conductance of a one-mole solution volume between electrodes of unit separation; a fuel cell converts continuously supplied fuel and oxidant into electrical energy. The solution conductivity is $\boxed{0.20835\,\text{S cm}^{-1}}$, or approximately $0.21\,\text{S cm}^{-1}$ to two significant figures.

Quick Tip to Solve: With molarity in mol L^{-1} and molar conductivity in S cm^2 mol^{-1}, multiply the two values and divide by 1000 for conductivity in S cm^{-1}.

OR

24(b). (a) Define the following terms :

(i) Primary batteries

(ii) Corrosion

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? [5 marks]

Solution:

Concept:

- A primary battery supplies electrical energy through a spontaneous chemical reaction that is not practically reversible by passing an external current.
- Corrosion is the gradual deterioration of a metal through chemical or electrochemical reaction with its surroundings; the metal is oxidised.
- For a conductivity cell, $R = \rho l/A$ and $\kappa = 1/\rho$, so the cell constant is $l/A = \kappa R$. Here R is resistance, ρ resistivity, κ conductivity, l electrode separation and A effective electrode area.

Step 1: (a)(i) Define primary batteries Primary batteries are electrochemical cells in which the electrode reactions occur during discharge and cannot be reversed effectively by applying an external current. They are therefore not rechargeable and must be replaced when their active reactants are exhausted. The common dry cell is an example.

Step 2: (a)(ii) Define corrosion Corrosion is the slow destruction or deterioration of a metal by reaction with its environment, such as air, moisture or other chemicals. Rusting of iron in moist air is a familiar example: iron is oxidised and ultimately forms hydrated iron(III) oxide, $\text{Fe}_2\text{O}_3 \cdot \text{xH}_2\text{O}$.

Step 3: (b) Relate cell constant to the measured resistance The cell constant depends on the geometry of the conductivity cell. Using the known conductivity of the standard KCl solution at the same temperature gives

$$\kappa = G\frac{l}{A} = \frac{1}{R}\frac{l}{A} \quad \Rightarrow \quad \frac{l}{A} = \kappa R.$$

The concentration identifies the standard solution; no separate concentration conversion is needed.

Step 4: Substitute the data and check the units At 298 K, the resistance is $1500\,\Omega$ and the conductivity

Quick Tip to Solve: Use cell constant $= \kappa R$. With conductivity in S cm^{-1} and resistance in Ω, the answer is directly in cm^{-1}.

is 0.146×10^{-3} S cm^{-1}. Therefore,

$$\frac{l}{A} = (0.146 \times 10^{-3})(1500)\ \text{cm}^{-1}$$
$$= 0.219\ \text{cm}^{-1}.$$

Since S $= \Omega^{-1}$, the resistance unit cancels the siemens in conductivity, leaving cm^{-1}, as required for l/A.

Step 5: Conclusion Primary batteries are non-rechargeable cells with practically irreversible discharge reactions. Corrosion is the gradual deterioration of a metal through reaction with its surroundings. The cell constant is $\boxed{0.219\ \text{cm}^{-1}}$.

Quick Tip to Solve: Use cell constant $= \kappa R$. With conductivity in S cm^{-1} and resistance in Ω, the answer is directly in cm^{-1}.

25(a). What happens when :

(i) HCl reacts with finely powdered iron.

(ii) Cl_2 reacts with hot concentrated solution of NaOH.

(b) Give appropriate reason for each of the following :

(i) Sulphur vapour exhibits some paramagnetic character.

(ii) NH_3 is more basic than PH_3

(iii) Dioxygen is a gas but sulphur a solid. [5 marks]

Solution:

Concept:

- A metal above hydrogen in the activity series displaces hydrogen from a non-oxidising acid. Hydrochloric acid gives iron in its +2 oxidation state.
- Disproportionation is a redox reaction in which the same element is both oxidised and reduced. The products of chlorine with alkali depend on temperature and concentration.
- Unpaired electrons cause paramagnetism. A Lewis base donates a lone pair; greater availability of that pair generally increases basic strength.
- Molecular size and intermolecular attractions help determine physical state at ordinary temperature. Bonding within a molecule must be distinguished from attractions between molecules.

Step 1: (a)(i) React iron with hydrochloric acid Finely powdered iron dissolves in hydrochloric acid with the evolution of hydrogen gas, producing a pale-green solution of iron(II) chloride (ferrous chloride):

$$\text{Fe} + 2\,\text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2\uparrow.$$

Iron loses two electrons and the hydrogen ions gain them. Hydrochloric acid is non-oxidising, so the salt formed is $FeCl_2$, rather than $FeCl_3$. Powdering increases the exposed surface and therefore speeds up the reaction.

Step 2: (a)(ii) React chlorine with hot concentrated alkali Chlorine reacts with hot concentrated

Quick Tip to Solve: For chlorine with alkali, write chlorate for hot concentrated conditions and hypochlorite for cold dilute conditions. For sulphur, distinguish vapour-phase S_2 from solid-state S_8.

sodium hydroxide to form sodium chloride, sodium chlorate and water:

$$3\,Cl_2 + 6\,NaOH \xrightarrow{\text{hot, conc}\cdot} 5\,NaCl + NaClO_3 + 3\,H_2O.$$

Chlorine changes from oxidation state 0 to -1 in chloride and +5 in chlorate. Thus it undergoes disproportionation. The hot concentrated condition is essential: cold dilute alkali instead gives hypochlorite, NaClO.

Step 3: (b)(i) Explain the magnetism of sulphur vapour At high temperature, sulphur vapour contains some diatomic S_2 molecules. Like O_2, an S_2 molecule has two unpaired electrons in antibonding molecular orbitals. These unpaired electrons are attracted by a magnetic field, so sulphur vapour exhibits some paramagnetic character. This explanation concerns the diatomic species in the vapour, rather than the closed-shell S_8 rings characteristic of ordinary solid sulphur.

Step 4: (b)(ii) Compare the basicity of ammonia and phosphine Both NH_3 and PH_3 have a lone pair on the central atom and can act as electron-pair donors. Nitrogen is much smaller than phosphorus, so its lone-pair electron density is concentrated in a smaller region and is more readily donated to a proton. The lone pair on the larger phosphorus atom is less available for donation. Consequently, ammonia accepts a proton more readily:

$$NH_3 + H^+ \longrightarrow NH_4{}^+.$$

Thus NH_3 is more basic than PH_3.

Step 5: (b)(iii) Relate molecular structure to physical state The small oxygen atom forms effective $p\pi$-$p\pi$ multiple bonds, so oxygen exists as small diatomic O_2 molecules. Their intermolecular dispersion forces are weak and the boiling point is low, making dioxygen a gas at ordinary temperature. Sulphur forms much less effective multiple bonds and predominantly exists as puckered S_8 rings. These larger, more polarisable molecules experience stronger dispersion attractions and form a solid under the same conditions.

Step 6: Conclusion Iron and hydrochloric acid give $FeCl_2$ and H_2; chlorine and hot concentrated NaOH give NaCl, $NaClO_3$ and water. Unpaired electrons in S_2 explain the paramagnetism of sulphur vapour. Greater lone-pair availability makes NH_3 more basic than PH_3, while stronger attractions between large S_8 rings explain why sulphur is solid and O_2 is gaseous.

Quick Tip to Solve: For chlorine with alkali, write chlorate for hot concentrated conditions and hypochlorite for cold dilute conditions. For sulphur, distinguish vapour-phase S_2 from solid-state S_8.

OR

25(b). (a) Complete the following equations :

(i) $PCl_5 \xrightarrow{heat}$?

(ii) C + Conc. $H_2SO_4 \rightarrow$?

(b) Explain giving reason in each case :

(i) Halogens are strong oxidising agents

(ii) Fluorine forms only one oxoacid, HOF

(iii) Helium is used in diving apparatus [5 marks]

Solution:

Concept:

- Heating can dissociate phosphorus pentachloride, while hot concentrated sulphuric acid acts as an oxidising agent and is reduced to sulphur dioxide.
- An oxidising agent accepts electrons. Halogen atoms have the outer configuration ns^2np^5 and need one electron to complete their octet.
- Fluorine's small size, very high electronegativity and absence of vacant d orbitals distinguish its chemistry from that of the other halogens.
- A gas used in a breathing mixture for deep diving should be chemically inert and have low solubility in blood.

Step 1: (a)(i) Thermal dissociation of phosphorus pentachloride On heating, phosphorus pentachloride dissociates into phosphorus trichloride and chlorine:

$$\mathrm{PCl_5} \overset{\Delta}{\rightleftharpoons} \mathrm{PCl_3 + Cl_2}.$$

The equation is balanced: one phosphorus atom and five chlorine atoms occur on each side. The dissociation is reversible; heating favours the dissociated products.

Step 2: (a)(ii) Oxidation of carbon by concentrated sulphuric acid Carbon is oxidised to carbon dioxide, while hot concentrated sulphuric acid is reduced to sulphur dioxide:

$$\mathrm{C + 2\,H_2SO_4\ (conc.)} \xrightarrow{\Delta} \mathrm{CO_2 + 2\,SO_2 + 2\,H_2O}.$$

Carbon changes from oxidation state 0 to $+4$, losing four electrons. Two sulphur atoms each change from $+6$ to $+4$, accepting those four electrons in total. This accounts for the coefficient 2 before the acid and sulphur dioxide.

Step 3: (b)(i) Oxidising action of halogens Halogens readily accept electrons to form halide ions and attain a stable noble-gas configuration:

$$\mathrm{X_2 + 2\,e^- \longrightarrow 2\,X^-}.$$

Their strong tendency to gain electrons makes them strong oxidising agents: the substance supplying those electrons is oxidised while the halogen is reduced. Their oxidising strength generally decreases

Quick Tip to Solve: Balance the carbon-acid reaction by electron transfer: carbon loses four electrons, so two sulphur atoms must each gain two. For diving, connect helium's low blood solubility with reduced gas-bubble formation.

down the group from fluorine to iodine.

Step 4: (b)(ii) Why fluorine forms only HOF Fluorine is extremely small and is the most electronegative element. It has no vacant d orbitals in its valence shell and cannot expand its octet. Unlike the heavier halogens, it cannot act as a central atom with higher covalency in a series of oxoacids. It therefore forms only the oxoacid HOF, hypofluorous acid, with the connectivity $\mathrm{H-O-F}$.

Step 5: (b)(iii) Suitability of helium for diving apparatus Helium is chemically inert and has very low solubility in blood. It is mixed with oxygen for deep-sea divers, replacing nitrogen in the breathing mixture. This reduces nitrogen narcosis at high pressure and reduces the risk of decompression sickness associated with dissolved nitrogen coming out as bubbles during ascent. Oxygen supplies the respiratory requirement; helium is the inert diluent.

Step 6: Conclusion Heating gives $\mathrm{PCl_3 + Cl_2}$ from $\mathrm{PCl_5}$; carbon with hot concentrated $\mathrm{H_2SO_4}$ gives $\mathrm{CO_2}$, $\mathrm{SO_2}$ and water as balanced above. Halogens readily accept electrons; fluorine's size, electronegativity and restricted valence shell limit it to HOF; helium is used with oxygen because it is inert and sparingly soluble in blood.

Quick Tip to Solve: Balance the carbon-acid reaction by electron transfer: carbon loses four electrons, so two sulphur atoms must each gain two. For diving, connect helium's low blood solubility with reduced gas-bubble formation.

26(a). Write the product(s) in the following :

(i) $\mathbf{2CH_3CHO \xrightarrow{dil\ NaOH} ?}$

(ii) $\mathbf{C_6H_5COCH_3 \xrightarrow{Zn-Hg/Conc.HCl} ?}$

(b) Give simple tests to distinguish the following pairs of compounds :

(i) Ethanal and Propanal

(ii) Benzaldehyde and Acetophenone

(iii) Benzoic acid and Ethyl benzoate [5 marks]

Solution:

Concept:

- Aldehydes containing an alpha hydrogen undergo aldol addition with dilute alkali, forming a beta-hydroxy aldehyde. Dehydration requires heating.
- Clemmensen reduction, using zinc amalgam and concentrated hydrochloric acid, converts the carbonyl group of an aldehyde or ketone into a methylene group.
- The iodoform test detects the $\mathrm{CH_3CO}$ group; ethanal also gives this test. Tollens' reagent oxidises aldehydes and deposits metallic silver.
- Carboxylic acids react with aqueous sodium hydrogen carbonate to release carbon dioxide; esters do not give this immediate effervescence.

Step 1: (a)(i) Form the aldol addition product Ethanal has alpha hydrogen atoms. Dilute sodium hydroxide removes an alpha hydrogen from one molecule, generating a nucleophile that attacks the carbonyl carbon of a second molecule. Protonation gives the four-carbon beta-hydroxy aldehyde,

Quick Tip to Solve: Both ethanal and propanal reduce Tollens' reagent, so use iodoform for that pair. For an acid versus an ester, look for immediate carbon dioxide evolution with sodium hydrogen carbonate.

3-hydroxybutanal (aldol):

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

The aldehyde group remains at carbon 1 and the hydroxyl group lies at carbon 3. Since heating is not specified, the required product is the aldol addition product; dehydration to but-2-enal is a subsequent reaction on heating.

Step 2: (a)(ii) Apply Clemmensen reduction Zinc amalgam and concentrated hydrochloric acid reduce the carbonyl group of acetophenone to $-CH_2-$, while preserving its carbon skeleton and the benzene ring:

$$C_6H_5COCH_3 + 4\,[H] \xrightarrow{Zn-Hg/\text{conc}\cdot\ HCl} C_6H_5CH_2CH_3 + H_2O.$$

Thus acetophenone gives ethylbenzene. The product is a hydrocarbon, rather than the secondary alcohol obtained by reducing only the carbonyl double bond with a hydride reagent.

Step 3: (b)(i) Distinguish ethanal from propanal Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3, whereas propanal gives no yellow precipitate:

$$CH_3CHO + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3\downarrow + HCOONa + 3\,NaI + 3\,H_2O.$$

Ethanal contains the required CH_3CO unit, with hydrogen as the other substituent on the carbonyl carbon. Propanal, CH_3CH_2CHO, lacks this unit. Tollens' reagent would not distinguish this pair because both are aldehydes and give a silver mirror.

Step 4: (b)(ii) Distinguish benzaldehyde from acetophenone Warm separate samples gently with freshly prepared Tollens' reagent. Benzaldehyde gives a silver mirror (or deposit of metallic silver) as its aldehyde group is oxidised to benzoate:

$$C_6H_5CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^-$$

$$\longrightarrow C_6H_5COO^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O.$$

Acetophenone is a ketone and does not reduce Tollens' reagent, so no silver mirror forms. This is a clear positive-versus-negative observation for the two compounds.

Step 5: (b)(iii) Distinguish benzoic acid from ethyl benzoate Add aqueous sodium hydrogen carbonate to each sample. Benzoic acid gives brisk effervescence of carbon dioxide:

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

The evolved gas turns limewater milky. Ethyl benzoate, $C_6H_5COOC_2H_5$, has no free carboxylic acid group and gives no such effervescence with this reagent. Use the immediate observation, without heating or attempting ester hydrolysis.

Step 6: Conclusion (a) The products are (i) 3-hydroxybutanal, $CH_3CH(OH)CH_2CHO$, and (ii) ethylbenzene, $C_6H_5CH_2CH_3$. (b) Use (i) the iodoform test: ethanal gives yellow CHI_3, propanal does not; (ii) Tollens' test: benzaldehyde gives silver, acetophenone does not; and (iii) aqueous $NaHCO_3$:

Quick Tip to Solve: Both ethanal and propanal reduce Tollens' reagent, so use iodoform for that pair. For an acid versus an ester, look for immediate carbon dioxide evolution with sodium hydrogen carbonate.

benzoic acid effervesces, ethyl benzoate does not.

Quick Tip to Solve: Both ethanal and propanal reduce Tollens' reagent, so use iodoform for that pair. For an acid versus an ester, look for immediate carbon dioxide evolution with sodium hydrogen carbonate.

OR

26(b). (a) Give reasons :

(i) CH_3-CHO is more reactive than CH_3COCH_3 towards HCN.

(ii) 4-nitrobenzoic acid is more acidic than benzoic acid.

(b) Describe the following :

(i) Acetylation

(ii) Cannizzaro reaction

(iii) Cross aldol condensation [5 marks]

Solution:

Concept:

- Cyanide ion is a nucleophile: it attacks the electrophilic carbonyl carbon. Both electron donation by alkyl groups and steric crowding reduce the ease of this addition.
- An acid is stronger when its conjugate base is more stable. Electron-withdrawing substituents stabilise a carboxylate ion and favour loss of H^+.
- Acetylation introduces an acetyl group, CH_3CO-. Cannizzaro reaction involves aldehydes without an α-hydrogen, whereas an aldol reaction requires an enolate-forming carbonyl compound with an α-hydrogen.

Step 1: (a)(i) Compare the carbonyl groups towards HCN The addition of HCN begins with attack of CN^- on the carbonyl carbon, followed by protonation of the oxygen to form a cyanohydrin. Ethanal, CH_3CHO, has one methyl group and one hydrogen attached to its carbonyl carbon; propanone, CH_3COCH_3, has two methyl groups. The two methyl groups in propanone exert a greater electron-releasing inductive effect, decreasing the positive character of its carbonyl carbon. They also cause greater steric hindrance to the approaching nucleophile. Ethanal therefore undergoes nucleophilic addition more readily, for both electronic and steric reasons.

Step 2: (a)(ii) Compare the stability of the conjugate bases Dissociation of the acids forms benzoate and 4-nitrobenzoate ions, respectively. The NO_2 group at the para position withdraws electrons through its negative inductive effect and its negative resonance effect. It consequently stabilises the negative charge of the carboxylate conjugate base relative to unsubstituted benzoate. Formation of this more stable conjugate base is more favourable, so 4-nitrobenzoic acid releases H^+ more readily and is more acidic than benzoic acid.

Step 3: (b)(i) Acetylation Acetylation is the introduction of an acetyl group, CH_3CO-, into a compound, commonly by replacing an active hydrogen of an alcohol, phenol or amine. Acetyl chloride or acetic anhydride is used as the acetylating reagent. For example, ethanol reacts with acetic

Quick Tip to Solve: Check for an α-hydrogen first: its absence favours Cannizzaro reaction in concentrated alkali; its presence allows enolate formation for aldol reactions in dilute base.

anhydride to give ethyl ethanoate:

$$C_2H_5OH + (CH_3CO)_2O \longrightarrow CH_3COOC_2H_5 + CH_3COOH.$$

Here the hydrogen of the hydroxyl group is replaced by the acetyl group, forming an ester.

Step 4: (b)(ii) Cannizzaro reaction An aldehyde having no α-hydrogen undergoes disproportionation on treatment with concentrated aqueous alkali. One aldehyde molecule is oxidised to the salt of a carboxylic acid, while another molecule is reduced to the corresponding primary alcohol. For example:

$$2HCHO + NaOH \xrightarrow{\text{concentrated}} HCOONa + CH_3OH.$$

Methanal has no α-carbon and hence no α-hydrogen. Its products are sodium methanoate and methanol; the carboxylic acid itself is obtained from the salt only after acidification.

Step 5: (b)(iii) Cross aldol condensation An aldol condensation involving two different aldehydes and/or ketones is called a cross aldol condensation. At least one reactant must contain an α-hydrogen so that it can form an enolate ion in dilute base. The enolate attacks the other carbonyl compound, giving a β-hydroxy carbonyl intermediate, which loses water on heating to form an α,β-unsaturated carbonyl compound. For example, benzaldehyde and ethanal give cinnamaldehyde:

$$C_6H_5CHO + CH_3CHO \xrightarrow[\Delta]{\text{dilute NaOH}} C_6H_5CH{=}CHCHO + H_2O.$$

Ethanal supplies the enolate because it has α-hydrogens; benzaldehyde acts as the carbonyl acceptor because it has none. If both starting carbonyl compounds have α-hydrogens, self- and cross-condensation can produce a mixture of products.

Step 6: Conclusion Ethanal reacts faster with HCN because its carbonyl carbon is more electrophilic and less hindered. The para-nitro group stabilises 4-nitrobenzoate, increasing acidity. Acetylation introduces CH_3CO-; Cannizzaro reaction gives an alcohol and a carboxylate salt; cross aldol condensation couples two different carbonyl compounds and, after dehydration, gives an unsaturated carbonyl product.

Quick Tip to Solve: Check for an α-hydrogen first: its absence favours Cannizzaro reaction in concentrated alkali; its presence allows enolate formation for aldol reactions in dilute base.