

CBSE Class 12 Chemistry Question Paper 2004 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) Marks for each question are indicated against it.
- (iii) Question numbers 1 to 5 are very short-answer, carrying 1 mark each. Answer these in one word or about one-sentence each.
- (iv) Question numbers 6 to 12 are short-answer, carrying 2 marks each. Answer these in about 30 words each.
- (v) Question numbers 13 to 24 are short-answer questions of 3 marks each. Answer these in about 40 words each.
- (vi) Question numbers 25 and 27 are long-answer questions of 5 marks each. Answer these in about 70 words each.
- (vii) Use Log Tables, if necessary. Use of calculators is not permitted.

1. What makes alkali metal halides sometimes coloured, which are otherwise colourless? [1 mark]

Solution:

Concept:

- Anion vacancies containing trapped electrons are called F-centres; they cause colour in otherwise colourless alkali metal halides.

Step 1: Identify the defect When an alkali metal halide has an anion vacancy, an electron can become trapped at the vacant anion site. Such an electron-containing vacancy is called an F-centre, or colour centre. The crystal retains overall electrical neutrality.

Step 2: Explain the colour The trapped electron absorbs energy from visible light and becomes excited to a higher energy level. Selective absorption removes certain wavelengths from white light, so the crystal appears coloured in the complementary transmitted or reflected light.

Step 3: Conclusion The colour is due to F-centres: electrons trapped in anion vacancies absorb visible light.

Quick Tip to Solve: For an alkali halide with excess metal, connect colour directly to electrons in anion vacancies.

2. State Henry's law about the solubility of a gas in a liquid. [1 mark]

Solution:

Concept:

- Henry's law relates gas solubility to its partial pressure above the liquid at a fixed temperature.

Step 1: State the proportionality At constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas in contact with the liquid. Thus increasing the gas partial pressure increases the amount of dissolved gas at equilibrium.

Step 2: Write its mathematical form In mole-fraction form, Henry's law is $p = K_H x$, where p is the gas partial pressure, x is its mole fraction in the liquid and K_H is the Henry's law constant for that gas-solvent pair at the specified temperature.

Step 3: Conclusion At constant temperature, gas solubility in a liquid is directly proportional to its partial pressure above the liquid: $p = K_H x$.

Quick Tip to Solve: Always specify constant temperature and use the gas partial pressure, especially for a mixture.

3. Define the order of a reaction.

[1 mark]

Solution:

Concept:

- The experimentally determined rate law gives the dependence of reaction rate on reactant concentrations.

Step 1: Write a general rate law For a reaction with rate law $r = k[A]^m[B]^n$, r denotes the reaction rate, k is the rate constant, and m and n are the experimentally determined powers of the concentrations of reactants A and B.

Step 2: Add the concentration powers The order of the reaction is the sum of these powers, namely $m + n$. These powers are taken from the experimentally determined rate equation; they need not equal the stoichiometric coefficients in the balanced chemical equation.

Step 3: Conclusion The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.

Quick Tip to Solve: Read the powers from the rate law, then add them; do not add balanced-equation coefficients.

4. Mention two properties of acetonitrile because of which it acts as a good solvent.

[1 mark]

Solution:

Concept:

- Acetonitrile, CH_3CN , is a polar solvent with a large dielectric constant and can solvate many substances.

Step 1: Identify its polarity Acetonitrile has a highly polar carbon-nitrogen triple bond and a large molecular dipole moment. Its high dielectric constant reduces the electrostatic attraction between oppositely charged ions, helping ionic or polar solutes to dissolve.

Step 2: Identify its solvent compatibility Acetonitrile is miscible with water and with many organic solvents. Consequently it can provide a common liquid medium for a broad range of polar and organic substances, which makes it useful as a solvent.

Step 3: Conclusion Acetonitrile is a good solvent because it has high polarity (a high dielectric constant) and is miscible with water and many organic solvents.

Quick Tip to Solve: For acetonitrile, recall its polar nitrile group and its compatibility with aqueous and organic media.

5. Write the IUPAC name of the following: $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$

[1 mark]

Solution:

Concept:

- Choose the longest chain containing the ketone carbonyl and number it to give the carbonyl carbon the lowest locant.

Step 1: Choose and number the parent chain Rewrite the structure as $\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)_2$. The longest chain containing both the carbonyl group and the double bond has five carbons. Numbering from the carbonyl end places the ketone group at carbon 2 rather than carbon 4.

Step 2: Locate the double bond and substituent The carbon-carbon double bond joins carbons 3 and 4, and the remaining methyl substituent is on carbon 4. The parent name is therefore pent-3-en-2-one, with the prefix 4-methyl. The ketone suffix determines the numbering priority over the double bond.

Step 3: Conclusion The IUPAC name is 4-methylpent-3-en-2-one.

Quick Tip to Solve: Number from the end nearer the ketone group before assigning the alkene and methyl locants.

6. What is meant by an entropy-driven reaction? How can a reaction with positive changes of enthalpy and entropy be made entropy-driven?

[2 marks]

Solution:

Concept:

- At constant temperature and pressure, a reaction is spontaneous when its Gibbs energy change is negative: $\Delta G = \Delta H - T\Delta S < 0$, where T is the absolute temperature.
- ΔH is the enthalpy change and ΔS is the entropy change of the reaction. The term $-T\Delta S$ favours spontaneity when $\Delta S > 0$.

Step 1: Meaning of an entropy-driven reaction An entropy-driven reaction is one in which the favourable entropy contribution makes ΔG negative, overcoming an unfavourable positive enthalpy change. Thus, the increase in entropy provides the driving force even though the reaction absorbs heat.

Step 2: Condition for positive enthalpy and entropy changes For $\Delta H > 0$ and $\Delta S > 0$, raise the temperature until the entropy term exceeds the enthalpy term:

$$T\Delta S > \Delta H \implies T > \frac{\Delta H}{\Delta S}.$$

Then $\Delta G = \Delta H - T\Delta S < 0$. Use consistent energy units for ΔH and ΔS ; the ratio has units of kelvin. At equality, $\Delta G = 0$, so it is the equilibrium boundary rather than a condition of forward spontaneity.

Step 3: Conclusion An entropy-driven reaction is made spontaneous by the favourable entropy term. With both changes positive, it becomes entropy-driven at sufficiently high temperature, $T > \Delta H/\Delta S$, assuming the signs and values remain applicable over that range.

Quick Tip to Solve: For positive enthalpy and entropy changes, compare T with the ratio of enthalpy change to entropy change in consistent units.

7. Give chemical evidence for each of the following:

(i) Fluorine is a stronger oxidising agent than chlorine.

(ii) The +1 oxidation state is more stable for thallium than for gallium.

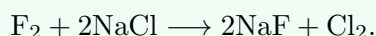
[2 marks]

Solution:

Concept:

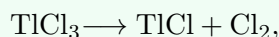
- A stronger oxidising agent oxidises the anion of a weaker halogen to the free halogen.
- The inert-pair effect stabilises the lower oxidation state down Group 13: retention of the ns^2 pair becomes more favourable.

Step 1: Fluorine compared with chlorine Fluorine liberates chlorine from a chloride, for example:



Here chloride loses electrons, $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$, while fluorine gains them, $\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$. Thus fluorine oxidises chloride to chlorine, demonstrating its stronger oxidising power. Chlorine cannot displace fluorine from fluoride under comparable conditions.

Step 2: Thallium compared with gallium Thallium(III) compounds readily undergo reduction to thallium(I), whereas gallium(I) compounds tend to form gallium(III). Chemical evidence is the instability of the higher thallium chloride on heating and the disproportionation of gallium(I) chloride:



The first reaction produces stable Tl(I); the second shows that Ga(I) is unstable relative to Ga(III) and the metal. This agrees with the stronger inert-pair effect in thallium.

Step 3: Conclusion Fluorine displaces chlorine from chlorides. Thallium(III) chloride tends to yield thallium(I) chloride, while gallium(I) chloride disproportionates; these reactions provide the required chemical evidence.

Quick Tip to Solve: Give an actual displacement equation for oxidising power and a decomposition or disproportionation equation for oxidation-state stability.

8. Draw a diagram showing the formation of bonding and antibonding molecular orbitals by the LCAO in homonuclear hydrogen molecule.

[2 marks]

Solution:

Concept:

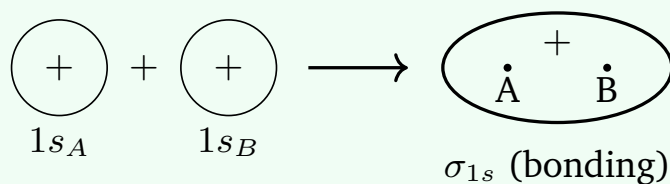
- The linear combination of the two hydrogen $1s$ atomic orbitals, ϕ_A and ϕ_B , gives two molecular orbitals.
- In-phase addition gives the bonding orbital $\psi_+ = N_+(\phi_A + \phi_B)$; opposite-phase subtraction gives the antibonding orbital $\psi_- = N_-(\phi_A - \phi_B)$. The constants N_+ and N_- normalise the

wavefunctions.

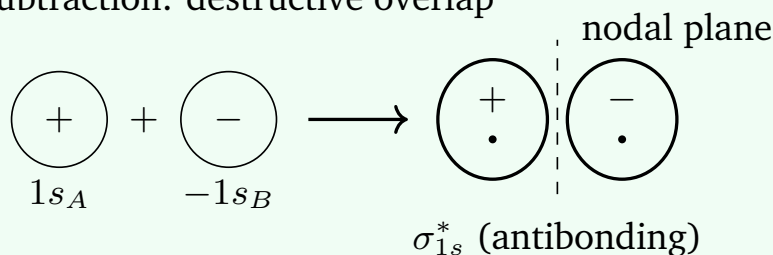
Step 1: Constructive overlap: bonding orbital When the two $1s$ wavefunctions have the same phase, their amplitudes reinforce in the internuclear region. Electron density between the nuclei increases, attracting both nuclei and lowering the energy. The resulting orbital is σ_{1s} . In the diagram, $+$ and $-$ denote wavefunction phase, not electric charge.

Step 2: Destructive overlap: antibonding orbital When the overlapping wavefunctions have opposite phases, they cancel at the plane midway between the nuclei. This nodal plane has zero electron density. The resulting σ_{1s}^* orbital has higher energy than the original $1s$ atomic orbitals. In ground-state H_2 , the two electrons occupy σ_{1s} with opposite spins, leaving σ_{1s}^* empty.

Addition: constructive overlap



Subtraction: destructive overlap



In-phase and opposite-phase combinations of hydrogen $1s$ orbitals

Step 3: Conclusion The two hydrogen $1s$ orbitals form a lower-energy bonding σ_{1s} orbital by addition and a higher-energy antibonding σ_{1s}^* orbital by subtraction. Ground-state H_2 has configuration $(\sigma_{1s})^2$.

Quick Tip to Solve: Always label the internuclear node in the antibonding combination and use phase signs rather than treating the signs as charges.

9. Write the cell reactions which occur in lead storage battery (i) when the battery is in use (ii) when the battery is on charging. [2 marks]

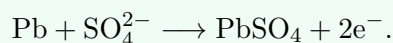
Solution:

Concept:

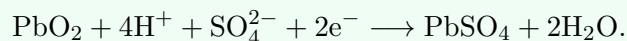
- A lead storage battery is a secondary cell: discharge converts both electrode materials into lead sulphate, while an external source reverses this change during charging.
- The negative electrode is lead, the positive electrode is lead dioxide, and the electrolyte is aqueous

sulphuric acid. Electrons lost by oxidation equal electrons gained by reduction.

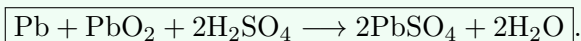
Step 1: Reactions when the battery is in use During discharge, lead is oxidised at the negative electrode (anode):



At the positive electrode (cathode), lead dioxide is reduced:

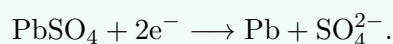


Adding the half-reactions gives the overall discharge reaction:

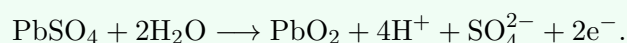


Sulphuric acid is consumed, so its concentration decreases.

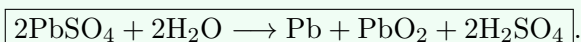
Step 2: Reactions when the battery is on charging An external direct-current source forces the reverse reaction. Lead sulphate at the negative electrode is reduced back to lead:



At the positive electrode, lead sulphate is oxidised back to lead dioxide:



Hence the overall charging reaction is



The acid concentration increases during charging.

Step 3: Conclusion Discharge forms PbSO_4 at both electrodes; charging regenerates Pb , PbO_2 , and sulphuric acid.

Quick Tip to Solve: Write the discharge equation first, then reverse it for charging; check that both sulphur atoms and all oxygen atoms balance.

10(a). Write the modes of free radical polymerization of an alkene.

[2 marks]

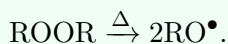
Solution:

Concept:

- Free-radical polymerisation is chain-growth addition polymerisation: successive alkene double bonds open to form a carbon backbone without elimination of small molecules.
- The mechanism has three stages: chain initiation, chain propagation and chain termination. A peroxide supplies the initiating radicals.

Step 1: Chain initiation For ethene as a representative alkene, a peroxide undergoes homolytic

cleavage on heating:



An alkoxy radical attacks the double bond to generate the first chain radical:



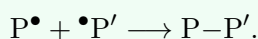
The unpaired electron now lies at the growing end of the carbon chain.

Step 2: Chain propagation The chain radical adds more ethene molecules successively:



Each addition consumes a double bond but produces another radical at the new chain end. Repetition builds a long polyethylene chain.

Step 3: Chain termination Growth stops when two radical chain ends combine:



Here $\text{P}\cdot$ and $\cdot\text{P}'$ denote growing polymer chains. Their unpaired electrons form a covalent bond, leaving no radical end for further propagation. Termination may also occur by disproportionation, involving hydrogen transfer between chain radicals.

Step 4: Conclusion The modes (stages) are initiation, propagation and termination, illustrated above by the free-radical polymerisation of ethene.

Quick Tip to Solve: Track the radical dot: it is created in initiation, survives each propagation step, and disappears on termination.

OR

10(b). Differentiate between addition and condensation polymers based on mode of polymerization. Give one example of each type. [2 marks]

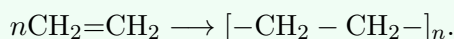
Solution:

Concept:

- Polymers are classified by how their monomer molecules join. Addition joins unsaturated molecules directly, whereas condensation joins suitable functional groups with elimination of small molecules.
- An example must match the mode of formation: polyethylene is an addition polymer, and nylon-6,6 is a condensation polymer.

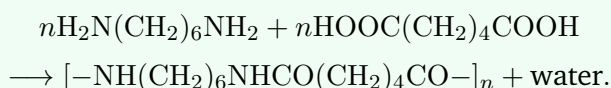
Step 1: Addition polymers: mode and example Addition polymers form by repeated addition of unsaturated monomers, usually containing a carbon-carbon double bond. The double bond opens and the molecules link into a chain without loss of a small molecule; the repeating unit has the same

elemental composition as the monomer. For example, ethene forms polyethylene (polythene):



Thus all the atoms of the ethene molecules are retained in the polymer.

Step 2: Condensation polymers: mode and example Condensation polymers form by repeated reactions between monomers bearing two or more reactive functional groups, with elimination of small molecules such as water. Polymer growth occurs through reactions of these functional groups. For example, hexamethylenediamine and adipic acid form nylon-6,6:



The amide links arise by reaction of amino and carboxyl groups with loss of water; the displayed equation represents the repeating-unit formation, with chain-end groups omitted.

Step 3: Conclusion Addition: unsaturated monomers add without elimination, as in polyethylene. Condensation: functional groups react with elimination of small molecules, as in nylon-6,6.

Quick Tip to Solve: Compare the repeating unit with the monomers: atom retention suggests addition; loss of water during link formation identifies condensation.

11. Write the names of the reagents and equations in the conversion of

(i) phenol to salicyl aldehyde

(ii) anisole to p-methoxyacetophenone

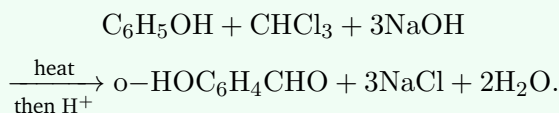
[2 marks]

Solution:

Concept:

- The Reimer–Tiemann reaction introduces a formyl group mainly ortho to the hydroxyl group of phenol using chloroform and aqueous alkali, followed by acidification.
- Friedel–Crafts acylation introduces an acyl group into an aromatic ring using an acyl chloride and anhydrous aluminium chloride. The methoxy group directs substitution to ortho and para positions.

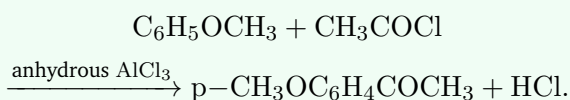
Step 1: Phenol to salicylaldehyde Reagents: chloroform (CHCl_3) and aqueous sodium hydroxide on heating, followed by acidification with dilute acid. This is the Reimer–Tiemann reaction.



The reaction is carried out in alkaline medium and acid work-up liberates the phenolic product. The formyl group enters mainly adjacent to the hydroxyl group, giving salicylaldehyde (2-hydroxybenzaldehyde).

Step 2: Anisole to para-methoxyacetophenone Reagents: acetyl chloride (ethanoyl chloride,

CH_3COCl) and anhydrous aluminium chloride (AlCl_3), followed by aqueous work-up. This is Friedel–Crafts acetylation.



The methoxy group activates the ring and directs the incoming acetyl group to ortho and para positions. The para product is the major product because substitution there is less sterically hindered; an ortho product is also formed. The desired para isomer is 4-methoxyacetophenone.

Step 3: Conclusion Phenol gives salicylaldehyde by the Reimer–Tiemann reaction. Anisole gives the required para product by Friedel–Crafts acetylation.

Quick Tip to Solve: Distinguish the introduced groups: salicylaldehyde needs ortho-CHO, while para-methoxyacetophenone needs para-COCH₃.

12. Explain the following terms:

(i) Asymmetric molecule

(ii) R and S notations

[2 marks]

Solution:

Concept:

- Chirality means that a molecule and its mirror image cannot be superimposed by rotation or translation.
- The Cahn–Ingold–Prelog priority rules specify absolute configuration; *R* and *S* do not indicate the sign of optical rotation.

Step 1: (i) Asymmetric molecule An asymmetric molecule has a mirror image that cannot be superimposed on it. A common example is a tetrahedral carbon bonded to four different groups, as in $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. Its mirror-image arrangements are enantiomers. An asymmetric molecule lacks a plane of symmetry; the spatial arrangement, rather than merely the molecular formula, determines this property.

Step 2: (ii) R and S notations These notations describe the absolute configuration around a chiral centre. Rank its four groups from 1 (highest priority) to 4 (lowest priority), first using the atomic numbers of the directly attached atoms and resolving ties by comparison at the next point of difference. View the centre with group 4 pointing away. A clockwise sequence $1 \rightarrow 2 \rightarrow 3$ denotes *R* (rectus), and an anticlockwise sequence denotes *S* (sinister). Reverse the apparent result if group 4 points towards you.

Step 3: Conclusion (i) An asymmetric molecule has a non-superimposable mirror image. (ii) With the lowest-priority group away, clockwise priority order gives *R*, while anticlockwise order gives *S*.

Quick Tip to Solve: Place the lowest-priority group away before reading the direction; *R* does not automatically mean dextrorotatory.

13. Write the IUPAC name of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ and draw the structures of all the isomers with this formula of the complex. [3 marks]

Solution:

Concept:

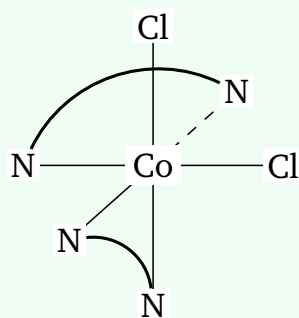
- Ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand; each en contributes two nitrogen donor atoms.
- An octahedral $[\text{M}(\text{en})_2\text{Cl}_2]^+$ ion has cis and trans geometrical forms. The cis form has two non-superimposable mirror images.

Step 1: Determine the oxidation state and name The chloride outside the brackets is the counter-ion, so the complex ion has charge +1. If the oxidation state of cobalt is x , neutrality of en gives

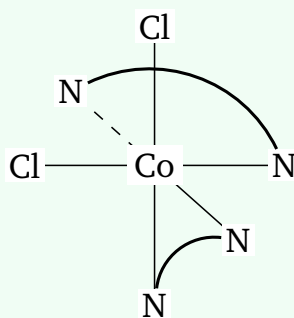
$$x + 2(0) + 2(-1) = +1, \quad x = +3.$$

Two en ligands provide four donor atoms and two coordinated chlorido ligands provide two more, giving coordination number six and octahedral geometry. The name is dichloridobis(ethane-1,2-diamine)cobalt(III) chloride. The traditional ligand spelling dichloro is also used in older nomenclature.

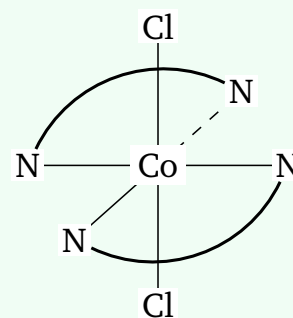
Step 2: Draw and count the stereoisomers In the cis arrangement, the two coordinated chlorido ligands occupy adjacent vertices and make a 90° angle at cobalt. The two chelate rings can have either of two opposite handed arrangements, conventionally called Δ and Λ ; these are optical isomers. In the trans arrangement, the chlorido ligands occupy opposite vertices and make a 180° angle. This form is optically inactive and does not give an additional enantiomeric pair. The drawings show all three stereoisomers; each curved N–N connection represents one complete en ligand, $\text{N}-\text{CH}_2\text{CH}_2-\text{N}$. The external chloride is the same in each salt and is omitted from the coordination sketches.



cis: one enantiomer



cis: mirror image



trans

Octahedral coordination sketches: the cis mirror pair and the trans form. Curved links join the donor atoms of each en ligand.

Step 3: Conclusion The name is dichloridobis(ethane-1,2-diamine)cobalt(III) chloride. There are three stereoisomers: a pair of cis optical isomers and one trans isomer.

Quick Tip to Solve: Count both cis mirror images separately, but count the optically inactive trans form only once.

14. Describe the following in brief:

(i) Carbon dating

(ii) Thermonuclear reactions

(iii) Group displacement law

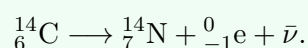
[3 marks]

Solution:

Concept:

- Radioactive nuclei decay at a characteristic rate; half-life is the time for half the radioactive nuclei in a sample to decay.
- Fusion combines light nuclei. Displacement laws describe changes in atomic number Z and mass number A during radioactive decay.

Step 1: (i) Carbon dating Carbon dating determines the age of once-living material by measuring its residual carbon-14 content or activity. Living organisms exchange carbon with their environment, maintaining approximately the same carbon-14 to carbon-12 ratio as the atmosphere. After death this exchange stops, and carbon-14 continues to decay:



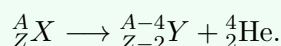
Comparing the remaining activity with that of living material, using the carbon-14 half-life of about 5730 years, gives the time since death.

Step 2: (ii) Thermonuclear reactions These are fusion reactions in which light nuclei combine to form a heavier nucleus and release a large amount of energy. Extremely high temperatures give the positively charged nuclei sufficient kinetic energy to overcome their electrostatic repulsion. For example,

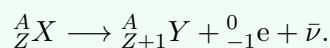


The decrease in mass supplies the released energy according to $E = \Delta mc^2$. Fusion reactions supply the Sun's energy.

Step 3: (iii) Group displacement law The Soddy–Fajans group displacement law states that alpha emission decreases atomic number by two and mass number by four:



Thus the daughter moves two places to the left in the periodic table. Beta-minus emission increases atomic number by one without changing mass number:



The daughter moves one place to the right. Gamma emission changes neither number and causes no displacement.

Step 4: Conclusion Carbon dating uses carbon-14 decay to estimate age; thermonuclear reactions are high-temperature fusion reactions; the group displacement law predicts the daughter element from the emitted radiation.

Quick Tip to Solve: Track atomic number separately: alpha gives $Z - 2$, beta-minus gives $Z + 1$, and gamma leaves Z unchanged.

15. How are antiseptics distinguished from disinfectants? Give two examples of each.

[3 marks]

Solution:

Concept:

- Antiseptics and disinfectants control microorganisms. Their main distinction is whether their concentration and toxicity permit application to living tissue.
- The same substance can have different uses at different concentrations; therefore suitability for living tissue must be considered along with antimicrobial action.

Step 1: Distinguish their uses Antiseptics are chemical substances that kill microorganisms or inhibit their growth and can be applied to living tissues, such as skin, wounds, cuts and ulcers, without harming those tissues at the prescribed concentration. They help prevent infection at the site of application. Disinfectants also kill microorganisms, but are used on inanimate objects and surfaces, such as floors, drains, toilets and instruments. They are generally too toxic or damaging for direct application to living tissue at their disinfecting concentration. Thus the distinction concerns the site of use and tissue safety, rather than simply whether microbes are killed.

Step 2: Give two examples of each Two antiseptics are tincture of iodine, a dilute solution of iodine in an alcohol-water mixture used on skin, and Dettol, whose antiseptic formulation contains chloroxylenol and terpineol. These are used at suitable concentrations for external application. Two disinfectants are phenol at about 1% concentration and chlorine, used for disinfection of water. Their application is to non-living materials or media. Concentration matters: dilute phenol, about 0.2%, can act as an antiseptic, whereas the stronger 1% solution is used as a disinfectant.

Step 3: Conclusion Antiseptics are suitable for living tissues: examples are tincture of iodine and Dettol. Disinfectants are used on non-living materials: examples are 1% phenol and chlorine.

Quick Tip to Solve: State the site of application first, then give two examples for each category; include concentration when using phenol as an example.

16. What information is given by (i) Radial probability density, R^2 and (ii) Radial probability function, $4\pi r^2 R^2$ in hydrogen atom? How do they vary with r for 1s orbital of hydrogen atom? Show diagrammatically.

[3 marks]

Solution:

Concept:

- Probability density gives probability per unit volume, whereas radial probability gives probability per unit radial distance in a complete spherical shell.
- For the hydrogen 1s orbital, the wave amplitude depends only on distance r from the nucleus and decreases exponentially; a_0 denotes the Bohr radius.

Step 1: Interpret radial probability density In the convention of the question, R^2 is the probability density at a point a distance r from the nucleus. Thus $R^2 dV$ is the probability of finding the electron

in a small volume dV there. For the spherically symmetric $1s$ orbital,

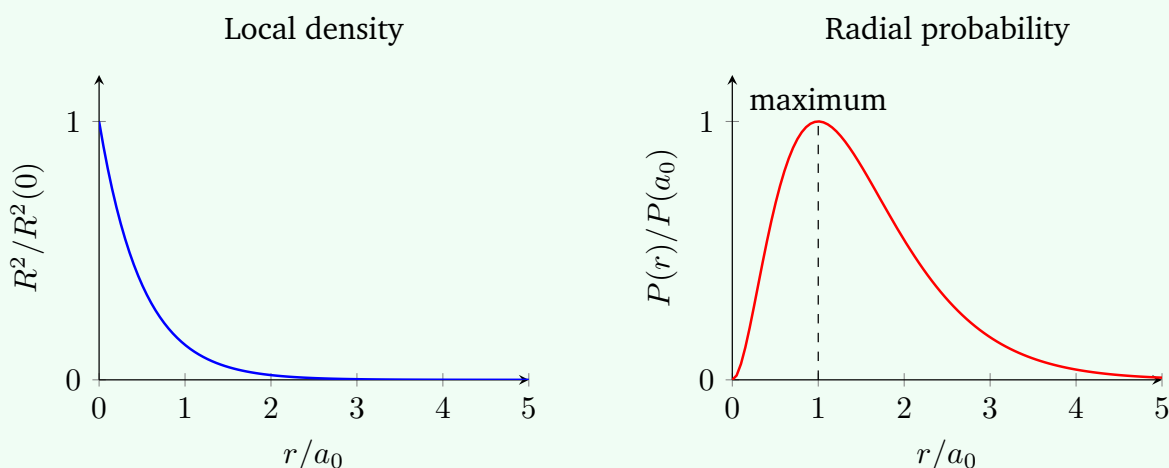
$$R^2 = \frac{1}{\pi a_0^3} e^{-2r/a_0}.$$

It has its greatest value at $r = 0$, decreases continuously as r increases, and approaches zero at large distance. A large density at the nucleus does not mean that a shell of zero radius has a finite probability.

Step 2: Interpret the radial probability function A thin spherical shell of radius r and thickness dr has volume $4\pi r^2 dr$. Consequently $P(r) = 4\pi r^2 R^2$ is the probability per unit radial distance, and $P(r)dr$ is the probability of finding the electron anywhere in that shell. For $1s$,

$$P(r) = \frac{4r^2}{a_0^3} e^{-2r/a_0}.$$

It is zero at the nucleus because the shell volume is zero. It rises to a maximum at $r = a_0$, the most probable radial distance, and then falls towards zero. Indeed, for $r > 0$, dP/dr has the sign of $1 - r/a_0$; hence it changes from positive to negative at a_0 . There are no radial nodes at finite positive r for $1s$.



Hydrogen 1s: local density falls from its maximum at the nucleus, while radial probability peaks at the Bohr radius. Vertical scales are normalized separately.

Step 3: Conclusion R^2 describes local probability density and is greatest at the nucleus; $4\pi r^2 R^2$ describes probability per unit shell thickness and is greatest at $r = a_0$ for hydrogen $1s$.

Quick Tip to Solve: Multiply the local density by the spherical-shell factor $4\pi r^2$ before locating the most probable distance.

17. Calculate the density of silver which crystallizes in the face-centred cubic structure. The distance between the nearest silver atoms in this structure is 287 pm.

(Molar mass of Ag = 107.87 g mol⁻¹, N_A = 6.02 × 10²³ mol⁻¹)

[3 marks]

Solution:

Concept:

- In a face-centred cubic (fcc) unit cell, atoms touch along a face diagonal, so the nearest-neighbour distance is $d = a/\sqrt{2}$, where a is the edge length.
- The density is $\rho = ZM/(N_A a^3)$, where Z is the number of atoms per unit cell, M is molar mass and N_A is Avogadro's constant.

Step 1: Obtain the edge length from the nearest-neighbour distance A face diagonal joins a corner atom, a face-centred atom and the opposite corner atom. The distance from the first corner centre to the face-centred atom is half the face diagonal. Therefore the given distance is $a/\sqrt{2}$, rather than the cube edge. Using 1 pm = 10⁻¹⁰ cm,

$$a = \sqrt{2} d = \sqrt{2}(287) \text{ pm} = 405.88 \text{ pm} = 4.0588 \times 10^{-8} \text{ cm}.$$

The unit-cell volume is consequently $a^3 = 6.6864 \times 10^{-23} \text{ cm}^3$.

Step 2: Calculate mass per cell and divide by cell volume Each of the eight corner atoms contributes 1/8, while each of the six face-centred atoms contributes 1/2. Thus

$$Z = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4.$$

The mass of one unit cell is $4M/N_A$. Substituting the given molar mass and Avogadro constant gives

$$\begin{aligned} \rho &= \frac{4(107.87)}{(6.02 \times 10^{23})(4.0588 \times 10^{-8})^3} \text{ g cm}^{-3} \\ &= 10.719 \text{ g cm}^{-3}. \end{aligned}$$

Here molar units cancel in the cell mass, leaving grams, and the cubed edge supplies cubic centimetres in the denominator.

Step 3: Conclusion The density of silver is 10.7 g cm⁻³ to three significant figures (approximately 10.72 g cm⁻³).

Quick Tip to Solve: For fcc, convert nearest-neighbour distance to the edge using $a = \sqrt{2}d$, then cube the edge in centimetres.

18. Two elements A and B form compounds having molecular formulae AB_2 and AB_4 . Dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate the atomic masses of A and B. [3 marks]

Solution:

Concept:

- For a dilute solution of a non-electrolyte, freezing-point depression is $\Delta T_f = K_f m$, where m is the number of moles of solute per kilogram of solvent.
- If solute mass is w , molar mass is M , and solvent mass in kilograms is W , then $m = w/(MW)$. Molecular masses are sums of the constituent atomic masses.

Step 1: Find the molar mass of each compound The mass of benzene in each experiment is 20 g = 0.020 kg. Rearranging the depression equation gives

$$M = \frac{K_f w}{\Delta T_f W}.$$

Thus, for the two solutes,

$$M(AB_2) = \frac{5.1 \times 1}{2.3 \times 0.020} = 110.87 \text{ g mol}^{-1},$$
$$M(AB_4) = \frac{5.1 \times 1}{1.3 \times 0.020} = 196.15 \text{ g mol}^{-1}.$$

The smaller depression for the same solute mass therefore corresponds to the larger molar mass.

Step 2: Solve the simultaneous atomic-mass equations Let the atomic masses of A and B be a and b , respectively, in atomic mass units. The molecular formulae require

$$a + 2b = 110.87, \quad a + 4b = 196.15.$$

Subtracting the first equation from the second isolates the contribution of two B atoms:

$$2b = 85.28, \quad b = 42.64.$$

Substituting this into the first equation gives

$$a = 110.87 - 2(42.64) = 25.59.$$

Substitution into the second equation also gives $25.59 + 4(42.64) = 196.15$, confirming consistency with both experiments.

Step 3: Conclusion The atomic masses are approximately $A = 25.6 \text{ u}$, $B = 42.6 \text{ u}$.

Quick Tip to Solve: Calculate both molecular masses first, then subtract their formula equations to isolate two B atoms.

19. Calculate the standard Gibbs energy change for the formation of propane at 298 K.



$\Delta_f H^\circ$ for propane, $\text{C}_3\text{H}_8(\text{g})$, is $-103.85 \text{ kJ mol}^{-1}$. **Given:** $S_m^\circ[\text{C}_3\text{H}_8(\text{g})] = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_m^\circ[\text{C}(\text{graphite})] = 5.70 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S_m^\circ[\text{H}_2(\text{g})] = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$. [3 marks]

Solution:

Concept:

- The standard reaction entropy is $\Delta_r S^\circ = \sum \nu S_m^\circ(\text{products}) - \sum \nu S_m^\circ(\text{reactants})$, with stoichiometric coefficients ν .
- At temperature T , the standard Gibbs energy change is $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$. Enthalpy and the entropy term must use the same energy units.

Step 1: Calculate the entropy change for formation The reaction forms one mole of propane from three moles of graphite and four moles of hydrogen gas. Using the printed standard molar entropies,

$$\begin{aligned}\Delta_f S^\circ &= 270.2 - [3(5.70) + 4(130.68)] \\ &= 270.2 - (17.10 + 522.72) \\ &= -269.62 \text{ J K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

The negative sign is consistent with a decrease from four moles of gaseous hydrogen to one mole of gaseous propane. Graphite also contributes to the entropy balance even though it is a solid.

Step 2: Combine enthalpy and entropy at 298 K The supplied formation enthalpy is $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$. Convert the entropy change to $-0.26962 \text{ kJ K}^{-1} \text{ mol}^{-1}$ before substitution. Therefore,

$$\begin{aligned}\Delta_f G^\circ &= -103.85 - 298(-0.26962) \\ &= -103.85 + 80.34676 \\ &= -23.50324 \text{ kJ mol}^{-1}.\end{aligned}$$

Because the entropy change is negative, the term $-T\Delta_f S^\circ$ is positive; it makes formation less favourable than the enthalpy change alone would suggest.

Step 3: Conclusion At 298 K, the required value is $\Delta_f G^\circ = -23.50 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Convert entropy from joules to kilojoules before combining it with the given formation enthalpy.

20. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant? [3 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} .
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$. For a monobasic acid, $K_a = c\alpha^2/(1 - \alpha)$.

Step 1: Calculate the molar conductivity The given concentration is $c = 0.00241 \text{ mol L}^{-1}$, and the conductivity is $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$. Thus

$$\Lambda_m = \frac{1000(7.896 \times 10^{-5})}{0.00241} = 32.7635 \text{ S cm}^2 \text{ mol}^{-1}.$$

The factor 1000 converts the concentration expressed per litre into concentration per cubic centimetre, keeping the centimetre-based conductivity units consistent.

Step 2: Find the fraction of acid dissociated At infinite dilution the acid is completely dissociated, so its limiting molar conductivity provides the reference for complete ion formation. Hence

$$\alpha = \frac{32.7635}{390.5} = 0.0839014.$$

Approximately 8.39% of the acid is dissociated at the specified concentration.

Step 3: Apply the acid dissociation equilibrium For $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$, the equilibrium concentrations are $c(1 - \alpha)$ for undissociated acid and $c\alpha$ for each ion. Therefore

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha^2}{1 - \alpha} = \frac{0.00241(0.0839014)^2}{0.916099} = 1.8519 \times 10^{-5}.$$

Retaining the denominator avoids an unnecessary small-dissociation approximation.

Step 4: Conclusion $\Lambda_m = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$, and the dissociation constant is $K_a = 1.85 \times 10^{-5}$ (concentration convention: mol L^{-1}).

Quick Tip to Solve: Use the conductivity ratio to find alpha, then retain the factor one minus alpha in the equilibrium expression.

21. A reaction is first order in A and second order in B.

(i) Write differential rate equation.

(ii) How is the rate affected if the concentration of B is tripled?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

What is the significance of rate constant in the rate expression?

[3 marks]

Solution:

Concept:

- The order with respect to a reactant is the exponent of its concentration in the experimentally determined rate law. Here the exponents of $[A]$ and $[B]$ are 1 and 2.
- At fixed temperature, $r = k[A][B]^2$, where r is reaction rate and k is the rate constant. Ratios of rates eliminate the unchanged value of k .

Step 1: (i) Write the differential rate equation The differential rate law is

$$r = k[A][B]^2.$$

For a reactant A with stoichiometric coefficient a , the reaction rate is $r = -\frac{1}{a} \frac{d[A]}{dt}$. Thus the concentration dependence of this differential rate is first order in A and second order in B; the overall order is $1 + 2 = 3$.

Step 2: (ii) Triple the concentration of B Keep $[A]$ and temperature unchanged. Replacing $[B]$ by $3[B]$ gives

$$r_1 = k[A](3[B])^2 = 9k[A][B]^2 = 9r.$$

Thus the rate becomes nine times its original value. The factor is squared because the order with respect to B is two.

Step 3: (iii) Double both concentrations At the same temperature, replace both concentrations by twice their original values:

$$r_2 = k(2[A])(2[B])^2 = 2 \times 4 k[A][B]^2 = 8r.$$

The factor of two from A and the factor of four from B multiply.

Step 4: Explain the rate constant The rate constant is the proportionality constant relating the rate to the appropriate product of reactant concentrations. It equals the numerical rate when the concentrations of both reactants are unity in the chosen concentration units. At fixed temperature it is independent of reactant concentrations and characterises the reaction under the specified conditions. For this third-order reaction, if rate is measured in $\text{mol L}^{-1} \text{s}^{-1}$, the units of k are $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$.

Step 5: Conclusion The differential law is $r = k[A][B]^2$. Tripling B makes the rate $9r$, while doubling both A and B makes it $8r$. The constant k expresses the rate at unit reactant concentrations for the given conditions.

Quick Tip to Solve: For a concentration change, raise each multiplying factor to its own order and then multiply the factors.

22(a). How are the colloids classified on the basis of the nature of interaction between dispersed phase and dispersion medium? Describe an important characteristic of each class. Which of these sols need stabilising agents for preservation? [3 marks]

Solution:

Concept:

- Colloids contain a dispersed phase distributed through a dispersion medium. Their classification here depends on the affinity between these two components.
- Strong solvation promotes stability, whereas weak interaction with the medium makes a sol more readily coagulated.

Step 1: Classify and describe lyophilic sols Lyophilic (solvent-loving) sols have a strong affinity between the dispersed phase and the dispersion medium. The dispersed particles become strongly solvated; in water this is called hydration. They form relatively easily by mixing the substance with a suitable medium. An important characteristic is reversibility: after separation, the dispersed phase can generally be brought back into the sol by adding the dispersion medium. Starch or gelatin in water is an example.

Step 2: Describe lyophobic sols Lyophobic (solvent-hating) sols have little affinity between the dispersed phase and the dispersion medium. They require special methods of preparation and are comparatively unstable. An important characteristic is irreversibility: once coagulated, the separated material cannot ordinarily be converted back into the sol merely by adding the medium. Gold sol and arsenic sulphide sol are examples. Small additions of suitable electrolytes can cause coagulation.

Step 3: Identify the class needing preservation Lyophobic sols need stabilising agents for preservation. Their stability commonly depends on the charge carried by the colloidal particles, which produces mutual repulsion. A protective lyophilic colloid, such as gelatin, can form a solvated protective layer around lyophobic particles and reduce their tendency to aggregate. Lyophilic sols are comparatively stable because of their strong interaction with the medium.

Step 4: Conclusion The classes are lyophilic and lyophobic sols. Lyophilic sols are generally reversible and readily stable; lyophobic sols are generally irreversible and need stabilising agents for preservation.

Quick Tip to Solve: Link solvent affinity to solvation: stronger solvation explains why lyophilic sols are more stable and reversible.

OR

22(b). What are detergents? Give their scheme of classification. Why are the detergents preferred over soaps? [3 marks]

Solution:

Concept:

- Detergents are synthetic cleansing agents with a hydrophobic hydrocarbon portion and a hydrophilic portion. They loosen greasy dirt and allow it to be dispersed in water.
- The classification is based on the charge of the active hydrophilic part: anionic, cationic or

non-ionic.

Step 1: Define detergents and classify anionic detergents Synthetic detergents are cleansing agents that can act effectively even in hard water. Anionic detergents have a negatively charged active cleansing ion. They include sodium salts of long-chain alkyl sulphates and alkylbenzene sulphonates. Sodium lauryl sulphate, $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$, is an example; its long hydrocarbon chain associates with grease and its sulphate end interacts with water.

Step 2: Describe cationic and non-ionic detergents Cationic detergents have a positively charged active ion. They are commonly quaternary ammonium salts with one or more long hydrocarbon chains; cetyltrimethylammonium bromide is an example. Non-ionic detergents have no charged groups in their molecules. Their water-loving portion generally contains several oxygen atoms or hydroxyl groups; polyethylene glycol stearate is an example. Thus the three classes differ in the nature of the hydrophilic portion, not in the presence of the grease-loving chain.

Step 3: Explain the preference over soaps Soaps form insoluble calcium and magnesium salts in hard water, producing scum and wasting soap. Detergents generally do not form such insoluble precipitates with Ca^{2+} and Mg^{2+} , so they retain cleansing action in hard water. Many detergents, particularly sulphonate detergents, can also function in acidic water, where soap is converted into poorly soluble free fatty acids. Their usefulness therefore extends to conditions in which soaps clean inefficiently.

Step 4: Conclusion Detergents are synthetic cleansing agents, classified as anionic, cationic and non-ionic. They are preferred for effective cleaning in hard water because they do not produce the insoluble scum formed by soaps.

Quick Tip to Solve: Classify a detergent by the charge on its active head group; explain hard-water cleaning using calcium and magnesium ions.

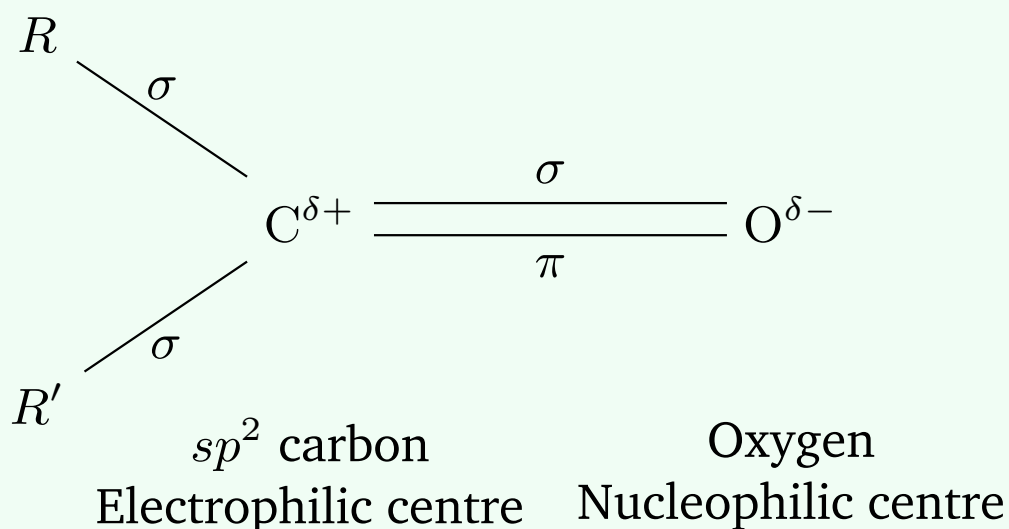
23. Draw the structure of a carbonyl group and indicate clearly (i) the hybridized state of carbon, (ii) the σ and π bonds present and (iii) the electrophilic and nucleophilic centres in it. [3 marks]

Solution:

Concept:

- A carbonyl group is $>\text{C}=\text{O}$. Its carbon atom is sp^2 -hybridized and has a trigonal planar arrangement of three sigma bonds, with bond angles approximately 120° .
- A double bond consists of one σ bond from head-on orbital overlap and one π bond from sideways overlap of parallel unhybridized p orbitals.

Step 1: Draw the structure and identify the hybridization The structure below represents a general carbonyl compound; R and R' may represent hydrogen or carbon-containing groups. Carbon uses three coplanar sp^2 orbitals to form sigma bonds with oxygen and the two attached groups. The remaining unhybridized p orbital on carbon is perpendicular to this plane.



Planar carbonyl group with bond types and reactive centres

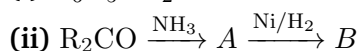
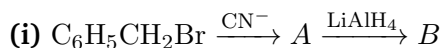
Step 2: Identify the sigma and pi bonds In the carbonyl double bond, head-on overlap of an sp^2 orbital of carbon with an orbital of oxygen forms the C – O sigma bond. Sideways overlap of the unhybridized p orbitals on carbon and oxygen gives the pi bond. Thus the C = O linkage contains exactly one σ and one π bond. The two single bonds from carbon to R and R' are also sigma bonds.

Step 3: Locate the electrophilic and nucleophilic centres Oxygen is more electronegative than carbon and attracts the shared electrons towards itself. Consequently the bond is polarized as $C^{\delta+} = O^{\delta-}$. The electron-deficient carbon is the electrophilic centre and is attacked by nucleophiles. Oxygen, with its partial negative charge and lone pairs, is the nucleophilic centre and can interact with electrophiles such as H^+ .

Step 4: Conclusion Carbonyl carbon is sp^2 -hybridized; C = O has one σ and one π bond. Carbon is electrophilic and oxygen is nucleophilic.

Quick Tip to Solve: Mark the partial charges first: oxygen attracts electrons, so the carbonyl carbon receives nucleophilic attack.

24. (a) Identify A and B in the following:



(b) Explain why the aromatic amines are less basic than ammonia and aliphatic amines. [3 marks]

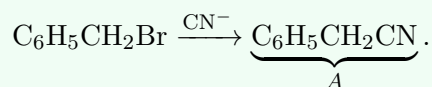
Solution:

Concept:

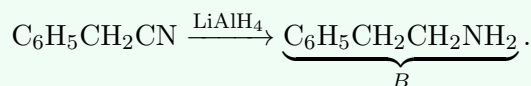
- Cyanide substitutes a halide to form a nitrile, adding one carbon to the chain. Lithium aluminium hydride reduces $-C \equiv N$ to $-CH_2NH_2$.
- A ketone condenses with ammonia to give an imine, which on catalytic hydrogenation gives a

primary amine. Basicity depends on the availability of the nitrogen lone pair for protonation.

Step 1: Identify A and B in sequence (i) Cyanide attacks through carbon and replaces bromide in benzyl bromide, producing benzyl cyanide (phenylacetonitrile):

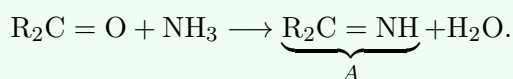


Reduction of the nitrile group by LiAlH_4 , followed by hydrolytic work-up, gives the corresponding primary amine:

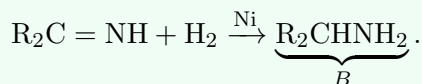


Thus B is 2-phenylethan-1-amine. The nitrile carbon remains in the product, so the chain now contains two carbon atoms between the phenyl ring and nitrogen.

Step 2: Identify A and B in sequence (ii) The ketone reacts with ammonia by condensation with loss of water, producing the imine:



Hydrogenation over nickel adds hydrogen across the carbon-nitrogen double bond:



The nitrogen bears two hydrogens in B, so it is a primary amine even though the carbon bonded to nitrogen has two R groups.

Step 3: Explain the lower basicity of aromatic amines In an aromatic amine such as aniline, the nitrogen lone pair is delocalized into the benzene ring by resonance. It is therefore less readily available to bind a proton. Protonation removes this lone pair from conjugation, so the resonance stabilization of the free amine also opposes proton acceptance. The phenyl group's electron-withdrawing inductive effect further reduces electron density on nitrogen. In ammonia the lone pair is localized on nitrogen. In aliphatic amines, alkyl groups donate electron density by their positive inductive effect, making the lone pair more available. Hence ordinary aromatic amines are less basic than ammonia and aliphatic amines.

Step 4: Conclusion (i) $A = \text{C}_6\text{H}_5\text{CH}_2\text{CN}$, $B = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$. (ii) $A = \text{R}_2\text{C} = \text{NH}$, $B = \text{R}_2\text{CHNH}_2$. Aromatic amines have a less available nitrogen lone pair owing chiefly to resonance delocalization.

Quick Tip to Solve: Count the cyanide carbon when reducing a nitrile: the product is one carbon longer than the original alkyl halide.

25. (a) Assign appropriate reason for each of the following:

- (i) Aluminium is highly electropositive yet it is used as a structural metal.
- (ii) White phosphorus is much more reactive than red phosphorus.
- (iii) Hydrogen fluoride is a much weaker acid than HCl in aqueous solution.
- (iv) Sulphur in vapour state exhibits some paramagnetic behaviour.

(b) Draw the structure of SiF_6^{2-} or XeF_4 .

[5 marks]

Solution:

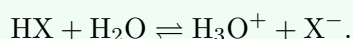
Concept:

- Chemical reactivity depends on both thermodynamic tendency and kinetic protection. A compact surface oxide can protect a highly electropositive metal from further attack.
- Molecular strain, bond strength and electron configuration explain the contrasting properties of phosphorus allotropes, hydrogen halides and sulphur vapour.
- In VSEPR theory, bonding pairs and lone pairs arrange to minimise repulsion. Molecular shape describes the positions of bonded atoms, whereas electron-pair geometry includes lone pairs.

Step 1: (a)(i) Aluminium as a structural metal Aluminium has a strong tendency to lose electrons, but exposure to air rapidly forms a thin, compact and adherent layer of aluminium oxide, Al_2O_3 , on its surface. This protective film prevents air and moisture from reaching the underlying metal and checks further corrosion. Thus, despite its electropositive character, aluminium is corrosion-resistant in ordinary conditions. Its low density and the strength of its alloys also make it suitable for structural use.

Step 2: (a)(ii) Greater reactivity of white phosphorus White phosphorus consists of discrete tetrahedral P_4 molecules. Each phosphorus atom is bonded to the other three, giving a $\text{P} - \text{P} - \text{P}$ angle of approximately 60° . This small angle produces considerable angular strain, making the molecule less stable and more reactive. Red phosphorus has a polymeric network with much less strained bonding; it is consequently more stable and less reactive than white phosphorus.

Step 3: (a)(iii) Weaker acidity of hydrogen fluoride In water, acidity depends on the ease of ionisation of the hydrogen halide:

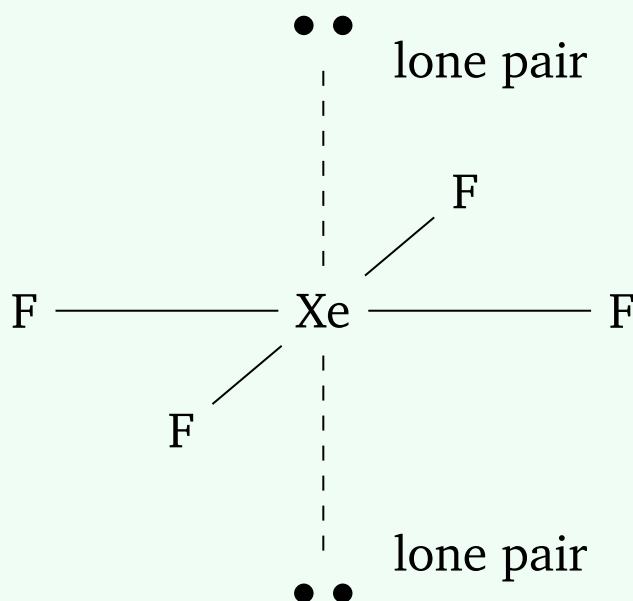


The $\text{H} - \text{F}$ bond is exceptionally strong because the fluorine atom is very small. Breaking this bond requires substantially more energy than breaking the weaker $\text{H} - \text{Cl}$ bond. Although the fluoride ion is strongly hydrated, this does not sufficiently compensate for the high bond dissociation energy. Therefore HF ionises only partially in water, while HCl ionises almost completely, making HF the weaker aqueous acid.

Step 4: (a)(iv) Paramagnetism of sulphur vapour At sufficiently 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 cause attraction towards a magnetic field. The presence of this diatomic species therefore accounts for the paramagnetic behaviour of sulphur vapour; this explanation does not assign unpaired electrons to the usual cyclic S_8 molecule.

Step 5: (b) Structure of xenon tetrafluoride Choosing the XeF_4 alternative, xenon has eight valence electrons. Formation of four single $\text{Xe} - \text{F}$ bonds leaves two lone pairs on xenon. There are thus six

electron domains around the central atom: four bond pairs and two lone pairs. Their electron-pair arrangement is octahedral, with the lone pairs occupying opposite positions to minimise repulsion. The four fluorine atoms consequently lie in one square plane, with adjacent $F - Xe - F$ angles of 90° and opposite angles of 180° . The molecular shape is square planar, not octahedral.



Square-planar XeF_4 ; the two lone pairs occupy positions above and below the fluorine plane.

Step 6: Conclusion Aluminium is protected by an oxide film; strained P_4 is more reactive than polymeric red phosphorus; the strong $H - F$ bond makes HF a weak aqueous acid; and unpaired electrons in S_2 cause sulphur-vapour paramagnetism. The chosen structure, XeF_4 , is square planar with two opposite lone pairs on xenon.

Quick Tip to Solve: For XeF_4 , count six electron domains first, then remove the two opposite lone-pair positions to obtain the square-planar molecular shape.

26(a). Name the products obtained on complete hydrolysis of DNA. Enumerate the structural differences between DNA and RNA. In what way is a nucleotide different from a nucleoside? Illustrate with examples. [5 marks]

Solution:

Concept:

- Nucleic acids are polynucleotides: each nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- Hydrolysis breaks the links between these constituents. A nucleoside contains only sugar and base; adding phosphate gives a nucleotide.
- DNA and RNA differ in their pentose sugars, one of their pyrimidine bases and their usual chain arrangement.

Step 1: Products of complete hydrolysis of DNA Complete hydrolysis of deoxyribonucleic acid (DNA) gives 2-deoxy-D-ribose, phosphoric acid and the nitrogenous bases adenine (A), guanine (G), cytosine (C) and thymine (T). Adenine and guanine are purines, whereas cytosine and thymine are pyrimidines. Thus the products include the sugar and phosphate components as well as all four kinds of bases; nucleotides are intermediate products rather than the final products of complete hydrolysis.

Step 2: Compare the structures of DNA and RNA The structural differences are as follows.

(i) DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. At the 2' carbon of the sugar, DNA has a hydrogen atom in place of the hydroxyl group present in RNA.

(ii) DNA contains adenine, guanine, cytosine and thymine. RNA contains adenine, guanine, cytosine and uracil: uracil replaces thymine, while the other three bases are common to both.

(iii) DNA normally consists of two antiparallel polynucleotide strands wound into a double helix. Complementary bases on opposite strands are held together by hydrogen bonds, with A paired with T and G paired with C. RNA is usually a single polynucleotide strand, although regions of the strand can fold and form base-paired segments. Where such pairing occurs in RNA, A pairs with U and G with C.

Step 3: Distinguish a nucleoside from a nucleotide using examples A nucleoside consists of a nitrogenous base linked to the 1' carbon of a pentose sugar through an N-glycosidic bond. It contains no phosphate group. For example, adenine joined to ribose forms the nucleoside adenosine; adenine joined to deoxyribose forms deoxyadenosine.

A nucleotide is the phosphate ester of a nucleoside: it contains a base, a pentose sugar and one or more phosphate groups. For example, adenosine 5'-monophosphate (AMP) is formed when the 5'-hydroxyl group of adenosine is esterified with phosphoric acid. Similarly, deoxyadenosine 5'-monophosphate (dAMP) is a DNA nucleotide. Hence adenosine and AMP provide a corresponding nucleoside-nucleotide pair, differing by the phosphate group.

Step 4: Conclusion DNA yields deoxyribose, phosphoric acid and A, G, C and T on complete hydrolysis. DNA differs from RNA in sugar, thymine versus uracil, and its usual double-stranded structure. A nucleoside is sugar plus base; a nucleotide is its phosphate ester, as illustrated by adenosine and AMP.

Quick Tip to Solve: Remember the components in order: base plus sugar gives a nucleoside; adding phosphate gives a nucleotide. For DNA versus RNA, compare sugar, base and strands.

OR

26(b). Define and classify vitamins. Name the diseases caused due to lack of any three of them.

[5 marks]

Solution:

Concept:

- Vitamins are organic compounds required in very small amounts for normal growth, metabolism and maintenance of health. Most cannot be synthesised by the human body in sufficient amounts and must therefore be supplied through the diet.
- Vitamins are classified according to their solubility: fat-soluble vitamins dissolve in fats and oils,

whereas water-soluble vitamins dissolve in water. A deficiency of a particular vitamin produces characteristic disorders.

Step 1: Define vitamins and explain their importance Vitamins are essential organic micronutrients needed in small quantities for the proper functioning of the body. They help regulate metabolic processes; many act as parts of coenzymes. They are required for normal growth and maintenance of good health, although they are not primarily energy-yielding nutrients like carbohydrates and fats. An adequate, balanced diet normally provides these substances. Prolonged inadequate intake of a vitamin can result in a specific deficiency disease.

Step 2: Classify vitamins on the basis of solubility The two classes are:

1. **Fat-soluble vitamins:** vitamins A, D, E and K. They are soluble in fats and oils and can be stored in the liver and fatty tissues.
2. **Water-soluble vitamins:** the B-group vitamins and vitamin C. They dissolve in water and generally require regular dietary supply because excess amounts are usually excreted in urine. Vitamin B₁₂ is an important exception to the general rule of limited storage.

Step 3: Name three deficiency diseases Any three appropriate vitamin–disease pairs answer this part. Three standard examples are:

1. **Vitamin A deficiency:** night blindness, in which vision in dim light is impaired.
2. **Vitamin B₁ (thiamine) deficiency:** beriberi, which affects the nervous and muscular systems.
3. **Vitamin C (ascorbic acid) deficiency:** scurvy, associated with bleeding gums and poor wound healing because normal collagen formation is impaired.

Step 4: Conclusion Vitamins are organic micronutrients essential for normal growth and health. They are classified into **fat-soluble vitamins A, D, E and K** and **water-soluble B-group vitamins and C**. Three deficiency diseases are **night blindness (A), beriberi (B₁) and scurvy (C)**.

Quick Tip to Solve: Remember the fat-soluble set as A, D, E, K; then link A with night vision, B₁ with beriberi and C with scurvy.

27. (a) How would you account for the following:

- (i) The transition elements exhibit high enthalpies of atomization.
 - (ii) The 4d and 5d series of the transition metals have more frequent metal-metal bonding in their compounds than do the 3d metals.
 - (iii) There is a greater range of oxidation states among the actinoids than that in the lanthanoids.
- (b) Write the complete chemical equation for each of the following:
- (i) An alkaline solution of KMnO₄ reacts with an iodide.
 - (ii) An excess of SnCl₂ solution is added to a solution of mercury(II) chloride.

[5 marks]

Solution:

Concept:

- Enthalpy of atomization measures the energy required to separate a metal into gaseous atoms; strong metallic bonding therefore gives a high value.

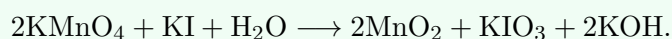
- The extent of overlap of metal orbitals controls the strength of metal-metal bonds, while the relative energies of valence orbitals determine which electrons can participate in bonding.
- Redox equations must conserve both atoms and charge. Permanganate oxidizes iodide to iodate in alkaline solution, whereas excess tin(II) chloride reduces mercury(II) chloride to mercury metal.

Step 1: (a)(i) High enthalpies of atomization Transition metals have several valence electrons available for metallic bonding, including electrons of the $(n - 1)d$ and ns orbitals. The participation of these electrons, particularly the large number of unpaired d electrons in many transition metals, produces strong interatomic attraction in the metallic lattice. Considerable energy is therefore required to separate the solid into individual gaseous atoms. This accounts for their generally high enthalpies of atomization.

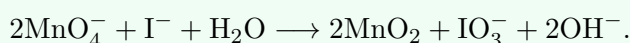
Step 2: (a)(ii) More frequent metal-metal bonding in the heavier series The $4d$ and $5d$ orbitals are more spatially extended than the $3d$ orbitals. Their greater radial extension permits more effective overlap between orbitals on neighbouring metal atoms. Consequently, strong direct metal-metal bonds form more readily in compounds of the $4d$ and $5d$ metals than in corresponding compounds of $3d$ metals. The explanation concerns orbital overlap between metal centres, rather than merely the number of valence electrons.

Step 3: (a)(iii) Greater range of actinoid oxidation states In actinoids, the energies of the $5f$, $6d$ and $7s$ subshells are relatively close. Different numbers of electrons from these subshells can therefore participate in bonding, giving a wide range of oxidation states. In lanthanoids the $4f$ electrons are more deeply buried and less readily available for bonding; the $+3$ state predominates, with only a few $+2$ and $+4$ exceptions. Thus actinoids exhibit more variable oxidation states than lanthanoids.

Step 4: (b)(i) Alkaline permanganate and iodide Iodide is oxidized from oxidation state -1 to $+5$ in iodate, losing six electrons. Each permanganate ion is reduced from manganese(VII) to manganese(IV) in manganese dioxide, gaining three electrons. Thus two permanganate ions are needed per iodide ion. Taking potassium iodide as the iodide, the complete equation is

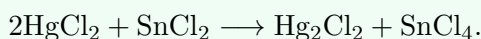


The corresponding net ionic equation is

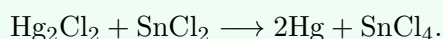


Both sides of the ionic equation have charge -3 ; manganese dioxide is a brown precipitate.

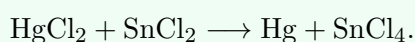
Step 5: (b)(ii) Excess tin(II) chloride and mercury(II) chloride Reduction first gives a white precipitate of mercury(I) chloride:



Excess tin(II) chloride reduces this precipitate further to grey metallic mercury:



Adding the two stages and cancelling the intermediate gives the overall equation required for excess reagent:



Tin is oxidized from +2 to +4, while mercury is finally reduced from +2 to zero.

Step 6: Conclusion Strong metallic bonding explains (a)(i), greater orbital overlap explains (a)(ii), and the close energies of $5f$, $6d$ and $7s$ orbitals explain (a)(iii). In (b), alkaline permanganate produces iodate and MnO_2 , while excess SnCl_2 gives metallic mercury.

Quick Tip to Solve: In the mercury reaction, the word “excess” means that reduction proceeds beyond white mercury(I) chloride to grey mercury metal.