# GATE Chemistry

## Sample Paper – 2

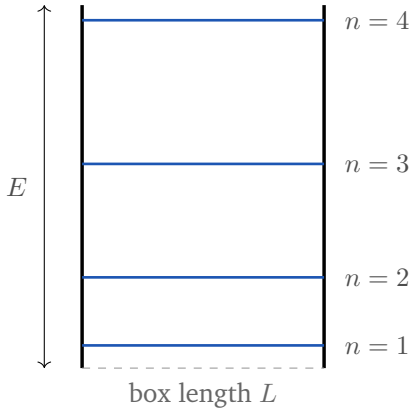
**Duration: 128 Minutes** **Maximum Marks: 72**

### Instructions

- This paper contains **46 questions** covering the core **Chemistry (CY)** subject of the GATE paper conducted by the IITs and IISc (General Aptitude and Engineering Mathematics are provided as separate papers).
- **Q1–Q20 carry 1 mark each** and **Q21–Q46 carry 2 marks each**, for a total of **72 marks**.
- Each question carries **negative marking of one-third of its allotted marks**: a wrong 1-mark question costs **0.33** and a wrong 2-mark question costs **0.67**. Unattempted questions carry no penalty.
- Every question here is a single-correct **MCQ**. The real GATE paper also has Multiple Select (MSQ) and Numerical Answer Type (NAT) questions, and **those carry no negative marking**.
- Attempt this paper in one timed sitting of about **128 minutes**, the share this core subject earns at GATE's overall pace of 180 minutes for 65 questions. Take $R = 8.314\ \mathrm{J\,mol^{-1}K^{-1}}$, $F = 96500\ \mathrm{C\,mol^{-1}}$ and $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$ unless stated otherwise.

## Physical Chemistry: Quantum Chemistry and Spectroscopy

**Q1.** For a particle of mass $m$ confined in a one-dimensional box of length $L$, the allowed energies are $E_n = \dfrac{n^2h^2}{8mL^2}$, with $n = 1, 2, 3, \ldots$ The energy-level ladder is sketched below. The ratio of the energy of the fourth level to that of the second level, $E_4/E_2$, is: **[1 mark]**



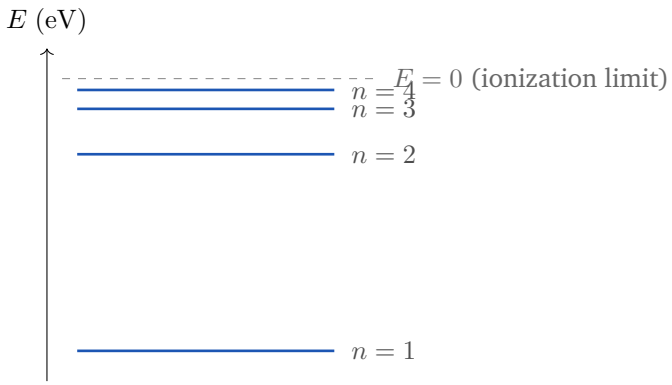

(A) 2

(B) 4

(C) 8

(D) 16

**Q2.** The bound-state energy levels of the hydrogen atom are given by $E_n = -\dfrac{13.6}{n^2}\ \text{eV}$, with $n = 1, 2, 3, \ldots$, converging to the ionization limit at $E = 0$ as sketched below. The energy of the $n = 2$ level of the hydrogen atom is: **[1 mark]**




(A) $-13.6$ eV

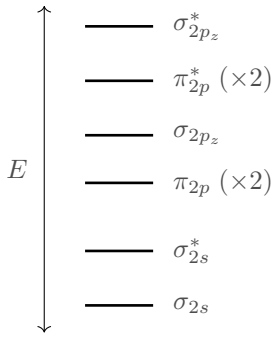
(B) $-3.4$ eV

(C) $-1.51$ eV

(D) $-0.85$ eV

**Q3.** The molecular-orbital energy ordering for the second-period homonuclear diatomic $N_2$ is shown below. Using molecular-orbital theory (bond-

ing electrons $= 10$, antibonding electrons $= 4$), the bond order of the $N_2$ molecule is: **[1 mark]**




(A) $1$

(B) $2$

(C) $2.5$

(D) $3$

**Q4.** The number of normal (fundamental) modes of vibration of a bent (non-linear) triatomic molecule such as $H_2O$ (with $N = 3$ atoms) is given by $3N - 6$. This number is: **[1 mark]**

(A) $4$

(B) $3$

(C) $6$

(D) $5$

**Q5.** For a hydrogen-atom orbital, the number of radial (spherical) nodes is given by $n - l - 1$, where $n$ is the principal quantum number and $l$ the azimuthal quantum number. The number of radial nodes in the $3s$ orbital is: **[1 mark]**

(A) $0$

(B) $1$

(C) $2$

(D) $3$

**Q6.** A molecule shows a pure rotational (microwave) absorption spectrum only if it possesses a permanent electric dipole moment. Among the following gas-phase molecules, the one that does *not* show a pure rotational spectrum is: **[1 mark]**

(A) $\mathrm{HCl}$

(B) $\mathrm{CO}$

(C) $\mathrm{N_2}$

(D) $\mathrm{HF}$

## Physical Chemistry: Thermodynamics, Kinetics and Electrochemistry

**Q7.** A closed system absorbs $200\ \mathrm{J}$ of heat from its surroundings and, in the same process, does $80\ \mathrm{J}$ of work *on* the surroundings. Using the first law of thermodynamics, $\Delta U = q + w$ (with $w$ the work done on the system), the change in internal energy $\Delta U$ of the system is: **[1 mark]**

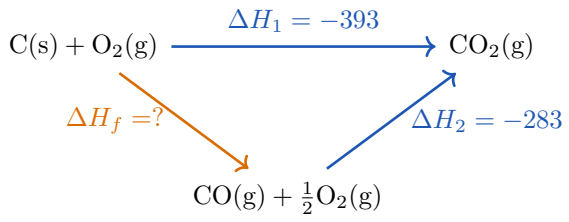
(A) $280\ \mathrm{J}$

(B) $-120\ \mathrm{J}$

(C) $200\ \mathrm{J}$

(D) $120\ \mathrm{J}$

**Q8.** Using Hess's law and the enthalpy cycle sketched below, the standard enthalpy of formation of carbon monoxide, $\mathrm{C(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)}$, is to be found from $\Delta H_1$ for $\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}$ $(= -393\ \mathrm{kJ\,mol^{-1}})$ and $\Delta H_2$ for $\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)}$ $(= -283\ \mathrm{kJ\,mol^{-1}})$. The value of $\Delta H_f(\mathrm{CO})$ is: **[1 mark]**




(A) $-110\ \mathrm{kJ\,mol^{-1}}$

(B) $-676\ \text{kJ mol}^{-1}$

(C) $+110\ \text{kJ mol}^{-1}$

(D) $-283\ \text{kJ mol}^{-1}$

**Q9.** A first-order reaction has a rate constant $k = 0.0231\ \text{min}^{-1}$. Using $t_{1/2} = \dfrac{0.693}{k}$, the half-life of the reaction is nearest to: **[1 mark]**

(A) $30\ \text{min}$

(B) $0.693\ \text{min}$

(C) $15\ \text{min}$

(D) $60\ \text{min}$

**Q10.** Copper is electrodeposited from a solution of $\text{Cu}^{2+}$ by the reduction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$. Using $Q = nF$, the quantity of electric charge required to deposit exactly $0.5$ mole of copper is: **[1 mark]**

(A) $48250\ \text{C}$

(B) $193000\ \text{C}$

(C) $96500\ \text{C}$

(D) $24125\ \text{C}$

**Q11.** The experimentally measured rate constant of a certain reaction is found to have the units $\text{mol L}^{-1}\,\text{s}^{-1}$. From the units of the rate constant, the overall order of this reaction is: **[1 mark]**

(A) first order

(B) zero order

(C) second order

(D) third order

**Q12.** A reaction at $400\ \text{K}$ has $\Delta H = -60\ \text{kJ mol}^{-1}$ and $\Delta S = -100\ \text{J mol}^{-1}\text{K}^{-1}$. Using $\Delta G = \Delta H - T\Delta S$, the Gibbs free-energy change of the reaction is: **[1 mark]**

(A) $-20\ \text{kJ mol}^{-1}$

(B) $-100\ \text{kJ mol}^{-1}$

(C) $+20\ \text{kJ mol}^{-1}$

(D) $-60\ \text{kJ mol}^{-1}$

**Q13.** A combustion reaction is carried out in a sealed bomb calorimeter, which holds the volume of the system *constant*. Under these constant-volume conditions, the heat exchanged by the reaction is equal to: **[1 mark]**

(A) the change in internal energy, $\Delta U$

(B) the change in enthalpy, $\Delta H$

(C) the change in Gibbs energy, $\Delta G$

(D) the change in entropy, $\Delta S$

**Q14.** For a first-order reaction the half-life is $10$ minutes. Since each successive half-life reduces the reactant to half of its value, the time required for the reaction to reach $75\%$ completion is: **[1 mark]**

(A) $10$ min

(B) $40$ min

(C) $30$ min

(D) $20$ min

## Inorganic Chemistry: Main Group and Periodic Properties

**Q15.** Among the third-period elements $\text{Na}$, $\text{Mg}$, $\text{Al}$ and $\text{Si}$, the element having the *largest* atomic radius is: **[1 mark]**

(A) $\text{Si}$

(B) $\text{Na}$

(C) $\text{Al}$

(D) $\text{Mg}$

**Q16.** Among the hydrogen halides $HF$, $HCl$, $HBr$ and $HI$, the strongest acid in aqueous solution (the one that ionizes most completely) is: **[1 mark]**

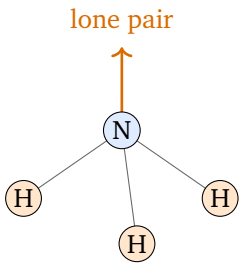
(A) $HF$

(B) $HI$

(C) $HCl$

(D) $HBr$

**Q17.** In the ammonia molecule $NH_3$ the central nitrogen atom has three bonding pairs and one lone pair, as shown. According to VSEPR theory, the molecular shape of $NH_3$ is: **[1 mark]**




(A) trigonal pyramidal

(B) tetrahedral

(C) trigonal planar

(D) T-shaped

**Q18.** In phosphine, $PH_3$, phosphorus is more electronegative than hydrogen, so each hydrogen is assigned an oxidation number of $+1$. Using the fact that the molecule is neutral, the oxidation state of phosphorus in $PH_3$ is: **[1 mark]**

(A) $-3$

(B) $+3$

(C) $+5$

(D) $0$

**Q19.** On moving across the third period from sodium ($Na$) to chlorine ($Cl$), the electronegativity of the elements generally: **[1 mark]**

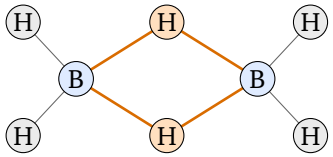
(A) decreases

(B) increases

(C) stays essentially constant

(D) first decreases and then increases

**Q20.** Diborane, $B_2H_6$, is electron-deficient and adopts a bridged structure in which two hydrogen atoms bridge the two boron atoms through three-centre two-electron ($3c-2e$) bonds, as sketched below. The number of such $3c-2e$ bridge bonds in one $B_2H_6$ molecule is: **[1 mark]**




bridging H atoms

(A) $0$

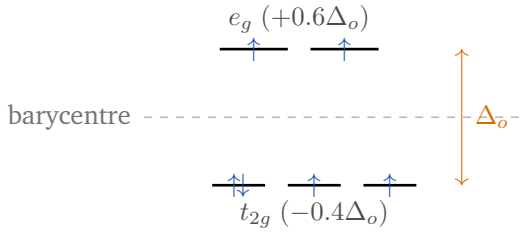
(B) $1$

(C) $2$

(D) $4$

## Inorganic Chemistry: Coordination Compounds and Organometallics

**Q21.** In an octahedral crystal field the five $d$ orbitals split into a lower $t_{2g}$ set at $-0.4\Delta_o$ and an upper $e_g$ set at $+0.6\Delta_o$ relative to the barycentre, as shown. For a high-spin $d^6$ ion (configuration $t_{2g}^4 e_g^2$), the crystal-field stabilization energy (CFSE), ignoring the pairing-energy term, is: **[2 marks]**




(A) $-2.4\,\Delta_o$

(B) $0$

(C) $-1.2\,\Delta_o$

(D) $-0.4\,\Delta_o$

**Q22.** The pentacarbonyliron(0) complex $[\mathrm{Fe(CO)_5}]$ obeys the effective-atomic-number (18-electron) rule. Taking iron(0) to contribute $8$ valence electrons and each $\mathrm{CO}$ ligand to donate $2$ electrons, the total valence electron count of the complex is: **[2 marks]**

(A) $18$

(B) $16$

(C) $20$

(D) $17$

**Q23.** The octahedral complex $[\mathrm{V(H_2O)_6}]^{3+}$ contains a $d^2$ vanadium(III) centre with two unpaired electrons. Using the spin-only formula $\mu = \sqrt{n(n+2)}\,\mathrm{BM}$, the magnetic moment of the complex is nearest to: **[2 marks]**

(A) $1.73\ \mathrm{BM}$

(B) $5.92\ \mathrm{BM}$

(C) $3.87\ \mathrm{BM}$

(D) $2.83\ \mathrm{BM}$

**Q24.** According to Werner's coordination theory, every metal ion has a fixed *secondary* valence (satisfied by directly bonded ligands) in addition to its *primary* valence (its oxidation state). For the complex ion $[\mathrm{Co(NH_3)_6}]^{3+}$, the secondary valence of the central cobalt ion is: **[2 marks]**

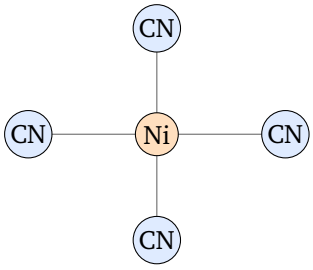
(A) $6$

(B) $3$

(C) $4$

(D) $2$

**Q25.** The tetracyanonickelate(II) ion $[\mathrm{Ni(CN)_4}]^{2-}$ has a $d^8$ nickel(II) centre with the strong-field cyanide ligand, giving a diamagnetic, $\mathrm{dsp^2}$ complex whose four ligands lie at the corners of a plane, as shown. The geometry of $[\mathrm{Ni(CN)_4}]^{2-}$ is: **[2 marks]**



four ligands in one plane

(A) square planar

(B) tetrahedral

(C) octahedral

(D) linear

**Q26.** The complex ion $[\mathrm{Fe(CN)_6}]^{3-}$ contains a low-spin $d^5$ iron(III) centre, since cyanide is a strong-field ligand. In the low-spin arrangement the five $d$ electrons occupy the $t_{2g}$ set as $t_{2g}^5 e_g^0$. The number of unpaired electrons in $[\mathrm{Fe(CN)_6}]^{3-}$ is: **[2 marks]**

(A) $5$

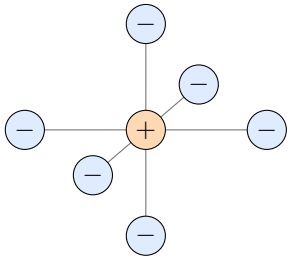
(B) $3$

(C) $1$

(D) $0$

## Inorganic Chemistry: Solid State and Bioinorganic

**Q27.** In an ionic crystal the coordination number of a cation is governed by the radius ratio $r_+/r_-$. A cation surrounded octahedrally by six anions, as sketched below, corresponds to which radius-ratio range and coordination number? **[2 marks]**



six anions around one cation

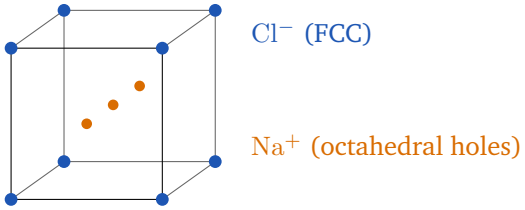
(A) $0.414$–$0.732$, coordination number $6$ (octahedral)

(B) $0.225$–$0.414$, coordination number $4$ (tetrahedral)

(C) $0.732$–$1.000$, coordination number $8$ (cubic)

(D) $0.155$–$0.225$, coordination number $3$ (trigonal)

**Q28.** Sodium chloride crystallizes in the rock-salt structure, in which the chloride ions form a face-centred cubic (FCC) lattice and the sodium ions occupy all the octahedral holes, as sketched below. The number of $\mathrm{NaCl}$ formula units contained in one conventional unit cell is: **[2 marks]**




(A) $1$

(B) $8$

(C) $2$

(D) $4$

**Q29.** Chlorophyll, the green pigment responsible for photosynthesis in plants, is a metal–porphyrin complex in which a single metal ion sits at the centre of the porphyrin ring. The metal ion present at the centre of chlorophyll is: **[2 marks]**

(A) $\mathrm{Fe}^{2+}$

(B) $\mathrm{Cu}^{2+}$

(C) $\mathrm{Zn}^{2+}$

(D) $Mg^{2+}$

## Organic Chemistry: Stereochemistry and Reaction Mechanisms

**Q30.** The tertiary alkyl halide tert-butyl bromide, $(CH_3)_3CBr$, undergoes solvolysis in aqueous ethanol. Because a stable tertiary carbocation forms readily, the substitution proceeds predominantly by which mechanism? **[2 marks]**

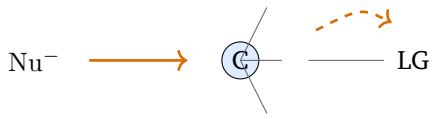
(A) $S_N2$

(B) $E2$

(C) $S_N1$

(D) $E1cb$

**Q31.** When a chiral secondary alkyl halide reacts through the concerted, one-step $S_N2$ pathway, the nucleophile attacks the carbon from the side opposite the leaving group. The stereochemical outcome at the reacting carbon is: **[2 marks]**




backside attack

(A) retention of configuration

(B) complete racemization

(C) no change in configuration

(D) inversion of configuration

**Q32.** A molecule contains three dissimilar (non-equivalent) stereogenic centres and possesses no internal symmetry, so that the maximum number of stereoisomers is $2^n$ with $n$ the number of such centres. The maximum number of stereoisomers possible for this molecule is: **[2 marks]**

(A) 3

(B) $6$

(C) $8$

(D) $4$

**Q33.** An $S_N1$ substitution proceeds through a rate-determining ionization step that forms a carbocation before the nucleophile adds. Consequently, the rate of an $S_N1$ reaction depends on the concentration of: **[2 marks]**

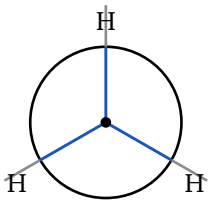
(A) both the substrate and the nucleophile

(B) the nucleophile only

(C) the substrate only

(D) the solvent only

**Q34.** The Newman projection of ethane, viewed along the $\mathrm{C}-\mathrm{C}$ bond, is shown below with the front and back hydrogens aligned. Among the conformations of ethane, the arrangement of *highest* torsional energy is the: **[2 marks]**




eclipsed Newman projection

(A) staggered conformation

(B) eclipsed conformation

(C) gauche conformation

(D) anti conformation

**Q35.** In an $S_N2$ reaction the rate falls as steric crowding around the reacting carbon increases, following the reactivity order $\mathrm{CH_3X} > 1^\circ > 2^\circ > 3^\circ$. Among the following substrates, the one that reacts *fastest* by the $S_N2$ mechanism is: **[2 marks]**

(A) a methyl halide, $\mathrm{CH_3Br}$

(B) a tertiary halide, $(CH_3)_3CBr$

(C) a secondary halide, $(CH_3)_2CHBr$

(D) neopentyl bromide, $(CH_3)_3CCH_2Br$

**Q36.** The molecule 2-chlorobutane, $CH_3CHClCH_2CH_3$, is found to be optically active. The structural feature that makes this molecule optically active is that it contains: **[2 marks]**

(A) an internal plane of symmetry

(B) no stereogenic centre at all

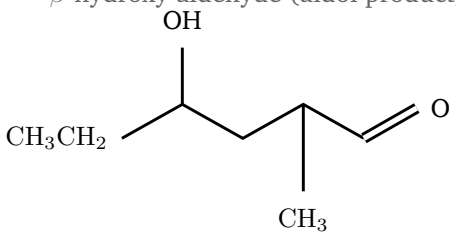
(C) a carbon atom bonded to four different groups

(D) a centre of inversion

## Organic Chemistry: Named Reactions and Synthesis

**Q37.** Two molecules of propanal ($CH_3CH_2CHO$) undergo base-catalysed self-condensation to give the $\beta$-hydroxy aldehyde 3-hydroxy-2-methylpentanal (the skeletal structure of the product is shown below). This carbon–carbon bond-forming reaction is known as the: **[2 marks]**

$\beta$-hydroxy aldehyde (aldol product)




(A) Cannizzaro reaction

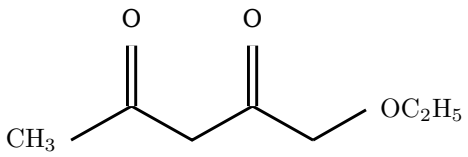
(B) Aldol reaction

(C) Claisen condensation

(D) Perkin reaction

**Q38.** Two molecules of ethyl acetate ($CH_3COOC_2H_5$), on treatment with sodium ethoxide followed by acidification, condense to give ethyl 3-oxobutanoate

(ethyl acetoacetate), a $\beta$-keto ester whose skeleton is shown below. This ester–ester condensation is known as the: **[2 marks]**




ethyl acetoacetate ($\beta$-keto ester)

(A) Aldol reaction

(B) Cannizzaro reaction

(C) Wittig reaction

(D) Claisen condensation

**Q39.** An aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the corresponding acid, giving an $\alpha,\beta$-unsaturated aromatic acid (for example benzaldehyde giving cinnamic acid). This condensation is the: **[2 marks]**

(A) Aldol condensation

(B) Perkin reaction

(C) Claisen condensation

(D) Cannizzaro reaction

**Q40.** In the Friedel–Crafts alkylation of benzene, an alkyl halide is activated by an anhydrous aluminium chloride ($AlCl_3$) catalyst. The actual electrophile that attacks the aromatic ring in this reaction is: **[2 marks]**

(A) an alkyl carbanion, $R^-$

(B) a carbocation, $R^+$

(C) a free radical, $R^\bullet$

(D) the intact $AlCl_3$ molecule

**Q41.** A Grignard reagent ($\mathrm{RMgX}$) is added to formaldehyde ($\mathrm{HCHO}$) and the adduct is then worked up with dilute acid. The organic product of this sequence is: **[2 marks]**

(A) a carboxylic acid ($\mathrm{RCOOH}$)

(B) a ketone ($\mathrm{RCOR'}$)

(C) a primary alcohol ($\mathrm{RCH_2OH}$)

(D) a tertiary alcohol ($\mathrm{R_3COH}$)

**Q42.** An acid chloride ($\mathrm{RCOCl}$) is reduced selectively to the corresponding aldehyde ($\mathrm{RCHO}$) by hydrogen over a palladium catalyst poisoned with barium sulfate ($\mathrm{Pd/BaSO_4}$). This selective reduction of an acid chloride to an aldehyde is the: **[2 marks]**

(A) Clemmensen reduction

(B) Wolff–Kishner reduction

(C) Birch reduction

(D) Rosenmund reduction

**Q43.** Propene ($\mathrm{CH_3CH{=}CH_2}$) is treated with hydrogen bromide ($\mathrm{HBr}$) in the presence of an organic peroxide. Under these radical (anti-Markovnikov) conditions, the major product is: **[2 marks]**

(A) $2$-bromopropane

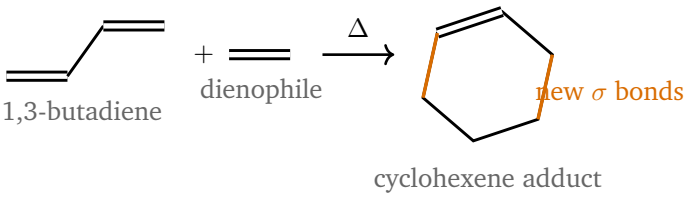
(B) $1$-bromopropane

(C) propan-2-ol

(D) $2,2$-dibromopropane

## Organic Chemistry: Pericyclic, Photochemistry and Biomolecules

**Q44.** $1,3$-Butadiene (the diene) reacts with maleic anhydride (the dienophile) in a thermal $[4+2]$ Diels–Alder cycloaddition, as sketched below, to give a six-membered ring adduct. The number of *new* $\sigma$ bonds formed in this cycloaddition is: **[2 marks]**




(A) $0$

(B) $1$

(C) $2$

(D) $3$

**Q45.** $1,3$-Butadiene is a conjugated diene with a $4\pi$-electron system ($4n$, $n = 1$). Under *photochemical* conditions it undergoes an electrocyclic ring closure to cyclobutene. According to the Woodward–Hoffmann rules, the stereochemical mode of this photochemical $4\pi$ electrocyclization is: **[2 marks]**

(A) conrotatory

(B) forbidden (does not occur)

(C) suprafacial–antarafacial

(D) disrotatory

**Q46.** In a disaccharide such as sucrose or maltose, two monosaccharide units are joined together through an oxygen bridge formed by a condensation between their hydroxyl (anomeric) groups. Chemically, this linkage between the two sugar units is a(n): **[2 marks]**

(A) glycosidic bond

(B) peptide bond

(C) ester bond

(D) phosphodiester bond

## Detailed Solutions

### Q1.

**Solution**

**Concept – particle-in-a-box energy scales as $n^2$:** The allowed energies are $E_n = \frac{n^2h^2}{8mL^2}$, so each level is fixed by the quantum number $n$ through $n^2$.

**Step 1 – write the two energies of interest:** $E_4 = \frac{4^2h^2}{8mL^2}$

$E_2 = \frac{2^2h^2}{8mL^2}$

**Step 2 – form the ratio:** $\frac{E_4}{E_2} = \frac{4^2}{2^2}$

**Step 3 – evaluate the squares:** $\frac{E_4}{E_2} = \frac{16}{4}$

**Step 4 – simplify:** $\frac{E_4}{E_2} = 4$

**Final Answer:** $E_4/E_2 = 4 \Rightarrow \boxed{\text{B}}$

**Answer: (B)** Go Back to Q1

### Q2.

**Solution**

**Concept – hydrogen-atom energy levels:** The bound-state energies are $E_n = -\frac{13.6}{n^2}$ eV, becoming less negative as $n$ increases and approaching $0$ at the ionization limit.

**Step 1 – put in the level of interest:** For $n = 2$, $E_2 = -\frac{13.6}{2^2}$ eV.

**Step 2 – evaluate the denominator:** $2^2 = 4$.

**Step 3 – divide:** $E_2 = -\frac{13.6}{4}$ eV

$E_2 = -3.4$ eV

**Step 4 – cross-check the neighbours:** $E_1 = -13.6$ eV, $E_3 = -1.51$ eV, $E_4 = -0.85$ eV; the $n = 2$ value sits correctly between $E_1$ and $E_3$, matching the level diagram.

**Final Answer:** $E_2 = -3.4$ eV $\Rightarrow \boxed{\text{B}}$

**Answer: (B)** Go Back to Q2

## Q3.

**Solution**

**Concept – bond order from molecular-orbital populations:** Bond order $= \frac{N_b - N_a}{2}$, where $N_b$ and $N_a$ are the numbers of electrons in bonding and antibonding MOs.

**Step 1 – count the electrons in $N_2$:** $N_2$ has $14$ electrons; filling the MO ladder gives $N_b = 10$ bonding and $N_a = 4$ antibonding electrons.

**Step 2 – substitute into the bond-order formula:** Bond order $= \frac{10 - 4}{2}$

**Step 3 – evaluate the numerator:** $= \frac{6}{2}$

**Step 4 – divide:** Bond order $= 3$

**Step 5 – cross-check:** A bond order of $3$ matches the $N{\equiv}N$ triple bond, consistent with the very high bond dissociation energy and the diamagnetism of $N_2$ (all electrons paired).

**Final Answer:** bond order $= 3 \Rightarrow \boxed{D}$

**Answer: (D)** Go Back to Q3

## Q4.

**Solution**

**Concept – vibrational degrees of freedom:** A non-linear molecule has $3N - 6$ vibrational modes; a linear molecule has $3N - 5$.

**Step 1 – identify the geometry:** $H_2O$ is bent (non-linear), so the correct formula is $3N - 6$.

**Step 2 – put in the number of atoms:** $N = 3$, so number of modes $= 3(3) - 6$.

**Step 3 – evaluate:** $= 9 - 6 = 3$

**Step 4 – name the three modes:** symmetric stretch, asymmetric stretch, and the bending (scissoring) mode $= 3$ in all, which matches.

**Final Answer:** number of vibrational modes $= 3 \Rightarrow \boxed{B}$

**Answer: (B)** Go Back to Q4

## Q5.

**Solution**

**Concept – radial nodes of a hydrogenic orbital:** Number of radial nodes $= n - l - 1$.

**Step 1 – read the quantum numbers for $3s$:** $n = 3$ and, for an $s$ orbital, $l = 0$.

**Step 2 – substitute into the formula:** radial nodes $= 3 - 0 - 1$

**Step 3 – evaluate:** $= 2$

**Step 4 – cross-check (total nodes):** Total nodes $= n - 1 = 2$; angular nodes $= l = 0$; so radial nodes $= 2 - 0 = 2$, consistent.

**Final Answer:** radial nodes in $3s = 2 \Rightarrow$ C

**Answer: (C)** Go Back to Q5

## Q6.

**Solution**

**Concept – gross selection rule for pure rotation:** A molecule is microwave (rotationally) active only if it has a *permanent* electric dipole moment.

**Step 1 – test each molecule for a permanent dipole:** HCl, CO and HF are heteronuclear and polar, so each has a permanent dipole.

**Step 2 – examine $N_2$:** $N_2$ is homonuclear; its two identical atoms give zero permanent dipole moment.

**Step 3 – apply the selection rule:** With no permanent dipole, $N_2$ cannot show a pure rotational (microwave) absorption spectrum.

**Final Answer:** the microwave-inactive molecule is $N_2 \Rightarrow$ C

**Answer: (C)** Go Back to Q6

## Q7.

**Solution**

**Concept – first law of thermodynamics:** $\Delta U = q + w$, where $q$ is heat added to the system and $w$ is work done *on* the system.

**Step 1 – assign the heat term:** The system absorbs heat, so $q = +200$ J.

**Step 2 – assign the work term:** The system does $80$ J of work *on* the surroundings, so the work done *on* the system is $w = -80$ J.

**Step 3 – substitute into the first law:** $\Delta U = (+200) + (-80)$

**Step 4 – evaluate:** $\Delta U = 120$ J

**Why the other options are wrong:** adding $200 + 80 = 280$ J mishandles the sign of the work; $-120$ J reverses both signs.

**Final Answer:** $\Delta U = 120$ J $\Rightarrow$ D

**Answer: (D)** Go Back to Q7

## Q8.

### Solution

**Concept – Hess's law:** Enthalpy is a state function, so the enthalpy of a target reaction can be obtained by algebraically combining the enthalpies of reactions that add up to it.

**Step 1 – write the two known reactions:** (1) $C + O_2 \rightarrow CO_2$, $\Delta H_1 = -393$ kJ mol$^{-1}$.

(2) $CO + \frac{1}{2}O_2 \rightarrow CO_2$, $\Delta H_2 = -283$ kJ mol$^{-1}$.

**Step 2 – write the target reaction:** $C + \frac{1}{2}O_2 \rightarrow CO$, $\Delta H_f = ?$

**Step 3 – combine: target = (1) − (2):** Reversing (2) and adding to (1) cancels $CO_2$ and one $\frac{1}{2}O_2$, leaving exactly the target.

**Step 4 – combine the enthalpies:** $\Delta H_f = \Delta H_1 - \Delta H_2 = (-393) - (-283)$

**Step 5 – evaluate:** $\Delta H_f = -393 + 283 = -110$ kJ mol$^{-1}$

**Final Answer:** $\Delta H_f(CO) = -110$ kJ mol$^{-1}$ $\Rightarrow$ A

**Answer: (A)** Go Back to Q8

## Q9.

### Solution

**Concept – half-life of a first-order reaction:** $t_{1/2} = \dfrac{0.693}{k}$, independent of the initial concentration.

**Step 1 – write the relation:** $t_{1/2} = \dfrac{0.693}{k}$

**Step 2 – substitute** $k = 0.0231$ min$^{-1}$**:** $t_{1/2} = \dfrac{0.693}{0.0231}$

**Step 3 – evaluate:** $t_{1/2} = 30$ min

**Final Answer:** $t_{1/2} = 30$ min $\Rightarrow$ A

**Answer: (A)** Go Back to Q9

## Q10.

**Solution**

**Concept – Faraday's law of electrolysis:** Depositing $n_{\text{mol}}$ moles of a species that each needs $z$ electrons requires charge $Q = n_{\text{mol}}\, z\, F$.

**Step 1 – write the reduction:** $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$, so $z = 2$ electrons per copper atom.

**Step 2 – insert the amounts:** $Q = n_{\text{mol}} \times z \times F = 0.5 \times 2 \times 96500$

**Step 3 – multiply the first two factors:** $0.5 \times 2 = 1$

**Step 4 – complete the product:** $Q = 1 \times 96500 = 96500\ \text{C}$

**Final Answer:** $Q = 96500\ \text{C} \Rightarrow \boxed{\text{C}}$

**Answer: (C)** Go Back to Q10

## Q11.

**Solution**

**Concept – order of a reaction from the units of $k$:** For a rate law rate $= k[A]^m$, the units of $k$ are $(\text{mol}\,\text{L}^{-1})^{1-n}\,\text{s}^{-1}$, where $n$ is the overall order.

**Step 1 – state the general unit relation:** The units of $k$ are $\text{mol}^{(1-\text{n})}\,\text{L}^{-(1-\text{n})}\,\text{s}^{-1}$.

**Step 2 – compare with the given units:** Here $k$ has units $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1} = \text{mol}^1\,\text{L}^{-1}\,\text{s}^{-1}$.

**Step 3 – match the exponents:** We need $1 - n = 1$, which gives $n = 0$.

**Step 4 – interpret:** The rate constant of a zero-order reaction has exactly the units of a rate, $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$, so the reaction is zero order.

**Final Answer:** the reaction is zero order $\Rightarrow \boxed{\text{B}}$

**Answer: (B)** Go Back to Q11

## Q12.

**Solution**

**Concept – Gibbs free energy:** $\Delta G = \Delta H - T\Delta S$, using consistent (joule) units.

**Step 1 – convert to joules:** $\Delta H = -60\ \text{kJ}\,\text{mol}^{-1} = -60000\ \text{J}\,\text{mol}^{-1}$, $\Delta S = -100\ \text{J}\,\text{mol}^{-1}\text{K}^{-1}$, $T = 400\ \text{K}$.

**Step 2 – compute the $T\Delta S$ term:** $T\Delta S = 400 \times (-100) = -40000\ \text{J}\,\text{mol}^{-1}$

**Step 3 – substitute into $\Delta G = \Delta H - T\Delta S$:** $\Delta G = -60000 - (-40000)$

**Step 4 – simplify the double negative:** $\Delta G = -60000 + 40000$

**Step 5 – evaluate:** $\Delta G = -20000\ \text{J mol}^{-1} = -20\ \text{kJ mol}^{-1}$

The negative sign shows the reaction is spontaneous at $400$ K.

**Final Answer:** $\Delta G = -20\ \text{kJ mol}^{-1} \Rightarrow \boxed{\text{A}}$

**Answer: (A)** Go Back to Q12

## Q13.

### Solution

**Concept – heat at constant volume:** From the first law, at constant volume no pressure–volume work is done ($w = -p\,\Delta V = 0$), so the heat exchanged equals the internal-energy change.

**Step 1 – write the first law:** $\Delta U = q + w$

**Step 2 – apply the constant-volume condition:** A sealed bomb calorimeter keeps $V$ fixed, so $\Delta V = 0$ and $w = -p\,\Delta V = 0$.

**Step 3 – reduce the first law:** $\Delta U = q_V + 0 = q_V$

**Step 4 – interpret:** The measured heat at constant volume, $q_V$, is exactly the change in internal energy $\Delta U$ (whereas heat at constant pressure would give $\Delta H$).

**Final Answer:** the heat equals $\Delta U \Rightarrow \boxed{\text{A}}$

**Answer: (A)** Go Back to Q13

## Q14.

### Solution

**Concept – first-order decay by successive half-lives:** After each half-life the reactant concentration halves; $75\%$ completion means $25\%$ (one quarter) of the reactant remains.

**Step 1 – relate remaining fraction to half-lives:** After one $t_{1/2}$, $50\%$ remains; after two $t_{1/2}$, $25\%$ remains.

**Step 2 – identify the number of half-lives for $75\%$ completion:** $75\%$ reacted $\Rightarrow$ $25\%$ left $\Rightarrow$ two half-lives.

**Step 3 – compute the time:** $t = 2 \times t_{1/2} = 2 \times 10\ \text{min}$

**Step 4 – evaluate:** $t = 20\ \text{min}$

**Final Answer:** time for $75\%$ completion $= 20\ \text{min} \Rightarrow \boxed{\text{D}}$

**Answer: (D)** Go Back to Q14

## Q15.

**Solution**

**Concept – atomic-radius trend across a period:** Across a period the atomic radius decreases; the earliest (left-most) element in the set is the largest.

**Step 1 – order the elements by position:** Going $\mathrm{Na} \to \mathrm{Mg} \to \mathrm{Al} \to \mathrm{Si}$, nuclear charge increases while electrons enter the same third shell.

**Step 2 – account for the size change:** The rising effective nuclear charge pulls the electron cloud inward, so radius decreases left to right.

**Step 3 – pick the largest:** $\mathrm{Na}$, sitting at the far left, is the least contracted and therefore has the largest atomic radius.

**Final Answer:** largest atomic radius $= \mathrm{Na} \Rightarrow \boxed{\mathrm{B}}$

**Answer: (B)** Go Back to Q15

## Q16.

**Solution**

**Concept – acid strength of the hydrogen halides:** Down the halogen group the $\mathrm{H-X}$ bond gets weaker (larger, more diffuse halogen), so the acid dissociates more easily and acid strength increases: $\mathrm{HF} < \mathrm{HCl} < \mathrm{HBr} < \mathrm{HI}$.

**Step 1 – identify the controlling factor:** Acid strength here is governed mainly by the $\mathrm{H-X}$ bond dissociation energy, not by electronegativity.

**Step 2 – order the bond strengths:** $\mathrm{H-I}$ is the weakest bond (longest, poorest overlap), so it breaks most readily.

**Step 3 – pick the strongest acid:** $\mathrm{HI}$ ionizes most completely in water and is therefore the strongest acid of the four.

**Why $\mathrm{HF}$ is weakest:** the very strong $\mathrm{H-F}$ bond makes $\mathrm{HF}$ only a weak acid despite fluorine's high electronegativity.

**Final Answer:** strongest acid $= \mathrm{HI} \Rightarrow \boxed{\mathrm{B}}$

**Answer: (B)** Go Back to Q16

## Q17.

**Solution**

**Concept – VSEPR shape versus electron-domain geometry:** The molecular shape counts only the positions of the atoms; lone pairs occupy space but are not part of the named shape.

**Step 1 – count the domains on nitrogen in $NH_3$:** Three $N-H$ bonding pairs and one lone pair, so the steric number is $4$.

**Step 2 – assign the electron geometry:** Four domains give a tetrahedral electron-pair geometry.

**Step 3 – deduce the molecular shape:** With one of the four domains being a lone pair, the three hydrogens form a trigonal pyramid below the nitrogen.

**Step 4 – match the figure:** The lone pair points up and the three $N-H$ bonds splay downward, exactly a trigonal-pyramidal shape.

**Final Answer:** shape of $NH_3$ is trigonal pyramidal $\Rightarrow$ $\boxed{A}$

**Answer: (A)** Go Back to Q17

## Q18.

**Solution**

**Concept – oxidation state from a neutral molecule:** The oxidation states of all atoms in a neutral molecule sum to zero.

**Step 1 – assign hydrogen:** Phosphorus is more electronegative than hydrogen, so each $H$ is $+1$; there are three of them.

**Step 2 – let the oxidation state of phosphorus be $x$:** $x + 3(+1) = 0$

**Step 3 – simplify:** $x + 3 = 0$

**Step 4 – solve for $x$:** $x = -3$

**Final Answer:** oxidation state of $P$ in $PH_3 = -3 \Rightarrow$ $\boxed{A}$

**Answer: (A)** Go Back to Q18

## Q19.

**Solution**

**Concept – electronegativity trend across a period:** Moving left to right, nuclear charge increases and atomic size decreases, so the atom pulls bonding electrons more strongly and electronegativity rises.

**Step 1 – track the nuclear charge:** From $\mathrm{Na}$ ($\mathrm{Z} = 11$) to $\mathrm{Cl}$ ($\mathrm{Z} = 17$), nuclear charge steadily increases.

**Step 2 – track the size:** The atoms get smaller across the period, so the nucleus is closer to the bonding electrons.

**Step 3 – conclude the trend:** Stronger pull on the bonding pair means electronegativity *increases* from $\mathrm{Na}$ to $\mathrm{Cl}$.

**Final Answer:** electronegativity increases $\Rightarrow$ $\boxed{\mathrm{B}}$

**Answer: (B)** Go Back to Q19

## Q20.

### Solution

**Concept – bonding in electron-deficient diborane:** $\mathrm{B_2H_6}$ has only $12$ valence electrons, too few for eight ordinary two-centre bonds, so two of the hydrogens bridge the borons through three-centre two-electron ($\mathrm{3c-2e}$) "banana" bonds.

**Step 1 – classify the hydrogens:** Four hydrogens are terminal (normal $\mathrm{B-H}$ bonds); two hydrogens are bridging.

**Step 2 – count the bridge bonds:** Each bridging hydrogen forms one $\mathrm{B-H-B}$ three-centre two-electron bond, so two bridging hydrogens give two such bonds.

**Step 3 – confirm the electron bookkeeping:** The two $\mathrm{3c-2e}$ bridges use $2\times2 = 4$ electrons; the four terminal $\mathrm{B-H}$ bonds use $4\times2 = 8$; total $= 12$ valence electrons, exactly what $\mathrm{B_2H_6}$ has.

**Final Answer:** number of $\mathrm{3c-2e}$ bridge bonds $= 2 \Rightarrow$ $\boxed{\mathrm{C}}$

**Answer: (C)** Go Back to Q20

## Q21.

### Solution

**Concept – CFSE in an octahedral field:** $\mathrm{CFSE} = \big[-0.4\,n(t_{2g}) + 0.6\,n(e_g)\big]\Delta_o$, using the electron occupancies of the two sets.

**Step 1 – place the high-spin $d^6$ electrons:** The configuration is $t_{2g}^4 e_g^2$, so $n(t_{2g}) = 4$ and $n(e_g) = 2$.

**Step 2 – substitute into the CFSE expression:** $\mathrm{CFSE} = \big[-0.4(4) + 0.6(2)\big]\Delta_o$

**Step 3 – evaluate each term:** $-0.4(4) = -1.6$ and $0.6(2) = +1.2$.

**Step 4 – add the terms:** $\mathrm{CFSE} = (-1.6 + 1.2)\Delta_o$

**Step 5 – write the result:** $\mathrm{CFSE} = -0.4\,\Delta_o$ (the pairing-energy term is neglected

as stated).

**Final Answer:** CFSE $= -0.4\,\Delta_o \Rightarrow$ D

**Answer: (D)** Go Back to Q21

## Q22.

### Solution

**Concept – the 18-electron (EAN) rule:** Total valence electron count = metal $d$-electrons + electrons donated by the ligands.

**Step 1 – count the metal contribution:** Fe is in group 8; as Fe(0) it contributes 8 valence electrons.

**Step 2 – count the ligand contribution:** Each CO donates 2 electrons; five CO give $5 \times 2 = 10$.

**Step 3 – add:** Total $= 8 + 10 = 18$

**Step 4 – interpret:** An 18-electron count is a filled, noble-gas-like valence shell, which is why $[Fe(CO)_5]$ is a stable, well-defined carbonyl.

**Final Answer:** valence electron count $= 18 \Rightarrow$ A

**Answer: (A)** Go Back to Q22

## Q23.

### Solution

**Concept – spin-only magnetic moment:** $\mu = \sqrt{n(n+2)}$ BM, with $n$ the number of unpaired electrons.

**Step 1 – find $n$ for $V^{3+}$:** $V^{3+}$ is $d^2$; the two electrons occupy separate $t_{2g}$ orbitals, giving $n = 2$.

**Step 2 – substitute into the formula:** $\mu = \sqrt{2(2+2)}$

**Step 3 – evaluate inside the root:** $\mu = \sqrt{2 \times 4} = \sqrt{8}$

**Step 4 – take the square root:** $\mu = 2.828$

$\mu \approx 2.83$ BM

**Final Answer:** $\mu \approx 2.83$ BM $\Rightarrow$ D

**Answer: (D)** Go Back to Q23

## Q24.

**Solution**

**Concept – Werner's primary and secondary valences:** In Werner's theory the *primary* valence is the oxidation state (satisfied by anions) and the *secondary* valence is the coordination number (satisfied by directly bonded ligands, giving the fixed geometry).

**Step 1 – identify the ligands bonded to cobalt:** In $[\mathrm{Co(NH_3)_6}]^{3+}$, six ammonia molecules are directly bonded to the cobalt centre.

**Step 2 – read off the secondary valence:** The secondary valence equals the number of donor atoms directly attached, which is $6$.

**Step 3 – note the consequence:** A secondary valence of $6$ fixes an octahedral arrangement of the six $\mathrm{NH_3}$ ligands (the primary valence of $3$ is satisfied separately by the three counter-anions).

**Final Answer:** secondary valence of cobalt $= 6 \Rightarrow \boxed{\text{A}}$

**Answer: (A)** Go Back to Q24

## Q25.

**Solution**

**Concept – geometry of a four-coordinate $d^8$ complex with a strong-field ligand:** A $d^8$ metal ion with a strong-field ligand adopts a diamagnetic, $\mathrm{dsp^2}$ (square-planar) geometry rather than tetrahedral.

**Step 1 – identify the $d$-count:** $\mathrm{Ni^{2+}}$ is $d^8$.

**Step 2 – assess the ligand field:** Cyanide is a strong-field ligand, so it forces the eight $d$ electrons to pair up, emptying one $d$ orbital.

**Step 3 – deduce the hybridization and shape:** The empty $d_{x^2-y^2}$ mixes with $s$ and two $p$ orbitals to give $\mathrm{dsp^2}$ hybridization, and the four cyanides sit at the corners of a square.

**Step 4 – match the figure:** The four ligands lying in one plane about the metal is exactly a square-planar arrangement.

**Final Answer:** geometry of $[\mathrm{Ni(CN)_4}]^{2-}$ is square planar $\Rightarrow \boxed{\text{A}}$

**Answer: (A)** Go Back to Q25

## Q26.

**Solution**

**Concept – unpaired electrons in a low-spin $d^5$ octahedral complex:** With a strong-field ligand the five $d$ electrons pack into the lower $t_{2g}$ set before any go to $e_g$.

**Step 1 – assign the $d$-count:** $Fe^{3+}$ is $d^5$.

**Step 2 – fill the $t_{2g}$ set (low spin):** Cyanide is a strong field, so the configuration is $t_{2g}^5 e_g^0$.

**Step 3 – count unpaired electrons:** Filling three $t_{2g}$ orbitals with five electrons gives two pairs and one single electron, so $n = 1$ unpaired electron.

**Step 4 – cross-check:** This predicts $\mu = \sqrt{1(1+2)} = \sqrt{3} \approx 1.73$ BM, the observed low-spin value for $[Fe(CN)_6]^{3-}$.

**Final Answer:** number of unpaired electrons $= 1 \Rightarrow$ C

**Answer: (C)** Go Back to Q26

## Q27.

**Solution**

**Concept – radius ratio and coordination number:** The radius ratio $r_+/r_-$ sets how many anions can pack around a cation without the anions touching each other; each range maps to a fixed coordination number and geometry.

**Step 1 – recall the standard ranges:** $0.155$–$0.225 \rightarrow 3$ (trigonal); $0.225$–$0.414 \rightarrow 4$ (tetrahedral); $0.414$–$0.732 \rightarrow 6$ (octahedral); $0.732$–$1.000 \rightarrow 8$ (cubic).

**Step 2 – match the figure:** The sketch shows six anions surrounding one cation octahedrally, i.e. coordination number $6$.

**Step 3 – select the corresponding ratio range:** A coordination number of $6$ (octahedral) corresponds to the radius-ratio range $0.414$–$0.732$.

**Final Answer:** $0.414$–$0.732$, coordination number $6$ (octahedral) $\Rightarrow$ A

**Answer: (A)** Go Back to Q27

## Q28.

**Solution**

**Concept – counting formula units in the rock-salt cell:** Count the chloride ions (FCC lattice) and the sodium ions (octahedral holes) separately, then divide by the ions per formula unit.

**Step 1 – count the $Cl^-$ ions (FCC positions):** $8$ corners $\times\frac{1}{8}+6$ faces $\times\frac{1}{2} = 1+3 = 4$ chloride ions.

**Step 2 – count the $Na^+$ ions (octahedral holes):** $12$ edge-centres $\times\frac{1}{4} + 1$ body-centre $\times 1 = 3 + 1 = 4$ sodium ions.

**Step 3 – form the number of formula units:** There are $4$ $Na^+$ and $4$ $Cl^-$, i.e. $4$ $NaCl$ units per unit cell.

**Final Answer:** formula units per unit cell $= 4 \Rightarrow$ D

**Answer: (D)** Go Back to Q28

## Q29.

**Solution**

**Concept – metal centre of chlorophyll:** Chlorophyll is a magnesium–porphyrin complex; the central metal is essential for capturing light in photosynthesis.

**Step 1 – identify the prosthetic ring:** Chlorophyll contains a porphyrin-type (chlorin) ring with a metal ion at its centre.

**Step 2 – identify the metal:** The central ion is magnesium, $Mg^{2+}$.

**Step 3 – reject the distractors:** $Fe^{2+}$ is in haemoglobin, $Cu^{2+}$ in haemocyanin, and $Zn^{2+}$ in carbonic anhydrase, not in chlorophyll.

**Final Answer:** metal in chlorophyll $= Mg^{2+} \Rightarrow$ D

**Answer: (D)** Go Back to Q29

## Q30.

**Solution**

**Concept – mechanism selection for a tertiary substrate:** A tertiary carbon forms a stable carbocation, and solvolysis (a weak nucleophile that is also the solvent) favours the stepwise ionization pathway $S_N1$.

**Step 1 – assess the substrate:** $(CH_3)_3CBr$ is tertiary; the three alkyl groups stabilize the resulting tertiary carbocation.

**Step 2 – assess the conditions:** Aqueous ethanol is a polar protic solvent and

a weak nucleophile, which stabilizes ions and cannot push a concerted backside attack.

**Step 3 – rule out $S_N2$:** The bulky tertiary carbon blocks backside approach, so $S_N2$ is negligible.

**Step 4 – conclude:** Ionization to the carbocation is rate-determining, so substitution proceeds by the two-step $S_N1$ mechanism.

**Final Answer:** mechanism is $S_N1 \Rightarrow \boxed{\text{C}}$

**Answer: (C)** Go Back to Q30

## Q31.

### Solution

**Concept – stereochemistry of the $S_N2$ reaction:** The nucleophile attacks $180°$ opposite the leaving group, so the other three groups flip through, like an umbrella in the wind.

**Step 1 – describe the geometry of attack:** The nucleophile approaches from the back face, exactly opposite the departing leaving group.

**Step 2 – follow the transition state:** At the transition state the carbon is trigonal-bipyramidal, with the three remaining groups in a plane.

**Step 3 – complete the inversion:** As the leaving group departs, the three groups swing to the far side, inverting the configuration at the carbon (Walden inversion).

**Step 4 – state the outcome:** A single, chiral $S_N2$ substrate therefore gives the product with inverted configuration.

**Final Answer:** the outcome is inversion of configuration $\Rightarrow \boxed{\text{D}}$

**Answer: (D)** Go Back to Q31

## Q32.

### Solution

**Concept – counting stereoisomers:** For $n$ non-equivalent stereogenic centres with no internal symmetry, the maximum number of stereoisomers is $2^n$.

**Step 1 – set the number of centres:** $n = 3$ dissimilar stereocentres.

**Step 2 – apply the $2^n$ rule:** Maximum stereoisomers $= 2^3$

**Step 3 – evaluate the power:** $2^3 = 2 \times 2 \times 2 = 8$

**Step 4 – note:** Because the centres are dissimilar and there is no symmetry, no meso forms collapse the count, so all $8$ are distinct.

**Final Answer:** maximum number of stereoisomers $= 8 \Rightarrow \boxed{\text{C}}$

**Answer: (C)** Go Back to Q32

## Q33.

### Solution

**Concept – rate law of the $S_N1$ reaction:** The slow, rate-determining step of $S_N1$ is ionization of the substrate to a carbocation; the nucleophile enters only in a later, fast step.

**Step 1 – identify the rate-determining step:** $\mathrm{R{-}LG} \rightarrow \mathrm{R^+ + LG^-}$ is slow and involves only the substrate.

**Step 2 – write the rate law:** rate $= k[\text{substrate}]$, first order overall.

**Step 3 – note the nucleophile's role:** Because the nucleophile attacks after the rate-determining step, its concentration does not appear in the rate law.

**Step 4 – conclude:** The $S_N1$ rate depends only on the concentration of the substrate.

**Final Answer:** the rate depends on the substrate only $\Rightarrow \boxed{\text{C}}$

**Answer: (C)** Go Back to Q33

## Q34.

### Solution

**Concept – torsional strain in ethane conformations:** Ethane rotates between staggered (lowest energy) and eclipsed (highest energy) conformations; eclipsing brings the front and back $\mathrm{C{-}H}$ bonds into alignment, maximizing torsional strain.

**Step 1 – compare the two limiting forms:** In the staggered form the $\mathrm{C{-}H}$ bonds are $60^\circ$ apart (minimum repulsion); in the eclipsed form they are $0^\circ$ apart (maximum repulsion).

**Step 2 – locate the energy maximum:** The eclipsed conformation sits at the top of the torsional-energy curve, about $12\ \mathrm{kJ\,mol^{-1}}$ above the staggered form.

**Step 3 – match the figure:** The Newman projection with the front and back hydrogens aligned is the eclipsed conformation.

**Why gauche/anti are wrong:** these terms describe butane's conformations; for ethane the two extremes are simply staggered and eclipsed.

**Final Answer:** highest-energy form is the eclipsed conformation $\Rightarrow \boxed{\text{B}}$

**Answer: (B)** Go Back to Q34

## Q35.

### Solution

**Concept – steric control of $S_N2$ rate:** $S_N2$ needs an open backside for the nucleophile, so reactivity falls as substitution at the reacting carbon increases: $CH_3X > 1^\circ > 2^\circ > 3^\circ$.

**Step 1 – rank the substrates by crowding:** The methyl halide has the least steric bulk; the tertiary halide is fully blocked; neopentyl bromide, though primary, is hindered by its bulky adjacent quaternary carbon.

**Step 2 – pick the least hindered:** $CH_3Br$ offers the most open backside for nucleophilic attack.

**Step 3 – conclude:** The methyl halide reacts fastest by $S_N2$.

**Why the others are slower:** the tertiary halide essentially does not undergo $S_N2$, the secondary is intermediate, and neopentyl is anomalously slow because of $\beta$-branching.

**Final Answer:** fastest $S_N2$ substrate is the methyl halide $\Rightarrow$ $\boxed{A}$

**Answer: (A)** Go Back to Q35

## Q36.

### Solution

**Concept – origin of optical activity:** A molecule is chiral (and hence optically active) when it has a stereogenic carbon bonded to four *different* groups and lacks any improper symmetry element.

**Step 1 – examine C2 of 2-chlorobutane:** The second carbon carries four different substituents: H, Cl, $CH_3$ and $C_2H_5$.

**Step 2 – test for a symmetry element:** With four different groups there is no plane or centre of symmetry, so the molecule is non-superimposable on its mirror image.

**Step 3 – conclude:** The presence of a carbon bonded to four different groups makes the molecule chiral and therefore optically active.

**Why the others are wrong:** a plane of symmetry or a centre of inversion would make the molecule achiral, and it does have a stereocentre.

**Final Answer:** it contains a carbon bonded to four different groups $\Rightarrow$ $\boxed{C}$

**Answer: (C)** Go Back to Q36

## Q37.

### Solution

**Concept – the aldol reaction:** A base removes an $\alpha$-hydrogen from one aldehyde to give an enolate, which adds to the carbonyl carbon of a second aldehyde, producing a $\beta$-hydroxy aldehyde.

**Step 1 – form the enolate:** Hydroxide removes an $\alpha$-hydrogen of propanal to give its enolate.

**Step 2 – nucleophilic addition:** The enolate adds to the carbonyl carbon of a second propanal molecule.

**Step 3 – identify the product:** Protonation gives the $\beta$-hydroxy aldehyde (3-hydroxy-2-methylpentanal) shown, the hallmark "aldol".

**Step 4 – name the reaction:** This carbon–carbon bond-forming step is the aldol reaction (further heating would give the aldol *condensation* enal).

**Final Answer:** the reaction is the Aldol reaction $\Rightarrow$ B

**Answer: (B)** Go Back to Q37

## Q38.

### Solution

**Concept – the Claisen condensation:** Two ester molecules condense under a strong base (an alkoxide): the enolate of one ester attacks the carbonyl of the second, expelling an alkoxide to give a $\beta$-keto ester.

**Step 1 – form the ester enolate:** Ethoxide removes an $\alpha$-hydrogen of one ethyl acetate to give its enolate.

**Step 2 – nucleophilic acyl substitution:** The enolate attacks the carbonyl carbon of a second ethyl acetate, and ethoxide leaves.

**Step 3 – identify the product:** The product is ethyl acetoacetate (ethyl 3-oxobutanoate), the $\beta$-keto ester shown.

**Step 4 – name the reaction:** This ester–ester self-condensation is the Claisen condensation.

**Why "Aldol" is wrong:** the aldol reaction joins aldehydes/ketones to give a $\beta$-hydroxy carbonyl, whereas here two esters give a $\beta$-keto ester with loss of alkoxide.

**Final Answer:** the reaction is the Claisen condensation $\Rightarrow$ $\boxed{\text{D}}$

**Answer: (D)** Go Back to Q38

## Q39.

### Solution

**Concept – the Perkin reaction:** An aromatic aldehyde condenses with an acid anhydride in the presence of the corresponding carboxylate salt to give an $\alpha,\beta$-unsaturated aromatic acid.

**Step 1 – form the reactive enolate:** The carboxylate base removes an $\alpha$-hydrogen from the anhydride to give an enolate.

**Step 2 – aldol-type addition and dehydration:** The enolate adds to the aromatic aldehyde and the intermediate loses water to install a $\text{C}{=}\text{C}$ double bond conjugated to the ring.

**Step 3 – identify the product and name it:** Benzaldehyde thus gives cinnamic acid; this synthesis of an $\alpha,\beta$-unsaturated acid is the Perkin reaction.

**Final Answer:** the reaction is the Perkin reaction $\Rightarrow$ $\boxed{\text{B}}$

**Answer: (B)** Go Back to Q39

## Q40.

### Solution

**Concept – electrophile in Friedel–Crafts alkylation:** Anhydrous $\text{AlCl}_3$ abstracts the halide from the alkyl halide, generating a carbocation that acts as the electrophile.

**Step 1 – generate the electrophile:** $\text{R}{-}\text{Cl} + \text{AlCl}_3 \rightarrow \text{R}^+ + \text{AlCl}_4^-$

**Step 2 – identify the active species:** The carbocation $\text{R}^+$ is the electrophile that attacks the benzene ring.

**Step 3 – complete the mechanism (conceptually):** The ring $\pi$-electrons attack $\text{R}^+$ to form an arenium ion, which loses a proton to restore aromaticity, giving the alkylbenzene.

**Final Answer:** the electrophile is the carbocation $\text{R}^+$ $\Rightarrow$ $\boxed{\text{B}}$

**Answer: (B)** Go Back to Q40

## Q41.

**Solution**

**Concept – Grignard addition to formaldehyde:** The carbanionic carbon of $\mathrm{RMgX}$ adds to the carbonyl carbon of an aldehyde; formaldehyde (the simplest aldehyde) uniquely gives a *primary* alcohol.

**Step 1 – nucleophilic addition:** $\mathrm{R-MgX}$ adds to $\mathrm{H_2C{=}O}$ to give the magnesium alkoxide $\mathrm{R-CH_2-OMgX}$.

**Step 2 – acidic work-up:** $\mathrm{R-CH_2-OMgX + H^+ \rightarrow R-CH_2-OH}$.

**Step 3 – classify the product:** The carbon bearing $\mathrm{OH}$ carries two hydrogens, so the product $\mathrm{RCH_2OH}$ is a primary alcohol.

**Why the other options are wrong:** a higher aldehyde would give a secondary alcohol, a ketone a tertiary alcohol, and $\mathrm{CO_2}$ a carboxylic acid; only formaldehyde gives a primary alcohol.

**Final Answer:** the product is a primary alcohol $\Rightarrow$ $\boxed{\mathrm{C}}$

**Answer: (C)** Go Back to Q41

## Q42.

**Solution**

**Concept – the Rosenmund reduction:** Hydrogen over a poisoned palladium catalyst ($\mathrm{Pd/BaSO_4}$) reduces an acid chloride only as far as the aldehyde, stopping before over-reduction to the alcohol.

**Step 1 – write the transformation:** $\mathrm{R-COCl \xrightarrow{H_2,\ Pd/BaSO_4} R-CHO}$

**Step 2 – note the role of the poison:** Barium sulfate (with quinoline) partially deactivates the palladium so the reaction halts at the aldehyde stage.

**Step 3 – name the reaction:** This selective acid chloride $\rightarrow$ aldehyde reduction is the Rosenmund reduction.

**Why the others are wrong:** Clemmensen and Wolff–Kishner reduce a carbonyl all the way to $\mathrm{CH_2}$, and Birch reduces aromatic rings.

**Final Answer:** the reaction is the Rosenmund reduction $\Rightarrow$ $\boxed{\mathrm{D}}$

**Answer: (D)** Go Back to Q42

## Q43.

**Solution**

**Concept – anti-Markovnikov (peroxide) addition of HBr:** With peroxides, $\mathrm{HBr}$ adds by a free-radical chain, so bromine adds to the *less* substituted carbon (the Kharasch or peroxide effect); this reversal is specific to $\mathrm{HBr}$.

**Step 1 – generate the bromine radical:** The peroxide initiates formation of $\mathrm{Br}^{\bullet}$.

**Step 2 – add the radical for the more stable intermediate:** $\mathrm{Br}^{\bullet}$ adds to the terminal $\mathrm{CH_2}$ of propene, giving the more stable secondary carbon radical $\mathrm{CH_3-\overset{\bullet}{C}H-CH_2Br}$.

**Step 3 – abstract hydrogen:** The radical takes a hydrogen from $\mathrm{HBr}$, placing $\mathrm{H}$ on the middle carbon and $\mathrm{Br}$ on the terminal carbon.

**Step 4 – name the product:** Bromine ends up on carbon-1, giving 1-bromopropane (the anti-Markovnikov product).

**Final Answer:** major product $=$ 1-bromopropane $\Rightarrow \boxed{\mathrm{B}}$

**Answer: (B)** Go Back to Q43

## Q44.

**Solution**

**Concept – bond changes in the Diels–Alder $[4+2]$ cycloaddition:** The diene $(4\pi)$ and dienophile $(2\pi)$ combine so that two new $\sigma$ bonds close a six-membered ring, while one new $\pi$ bond remains inside the ring.

**Step 1 – count the $\pi$ systems consumed:** Three $\pi$ bonds react (two from the diene, one from the dienophile).

**Step 2 – identify the bonds formed:** Two of the reacting $\pi$ bonds become two new $\sigma$ bonds at the ends of the diene, joining it to the dienophile.

**Step 3 – account for the remaining bond:** The third electron pair becomes the new $\pi$ (double) bond in the middle of the ring.

**Step 4 – state the count of new $\sigma$ bonds:** Exactly two new $\sigma$ bonds are formed, closing the cyclohexene ring.

**Final Answer:** number of new $\sigma$ bonds $= 2 \Rightarrow \boxed{\mathrm{C}}$

**Answer: (C)** Go Back to Q44

## Q45.

**Solution**

**Concept – Woodward–Hoffmann rules for electrocyclic reactions:** For a $4n$ $\pi$-electron system, the thermal mode is conrotatory and the *photochemical* mode is disrotatory (the selection rule reverses on going from heat to light).

**Step 1 – count the $\pi$ electrons:** $1,3$-butadiene has $4$ $\pi$ electrons, so it is a $4n$ system with $n = 1$.

**Step 2 – recall the thermal rule:** Thermally, a $4n$ system closes conrotatory.

**Step 3 – apply the photochemical reversal:** Under photochemical excitation the symmetry of the reacting orbital changes, so the allowed mode becomes disrotatory.

**Step 4 – conclude:** The photochemical $4\pi$ electrocyclization of butadiene to cyclobutene is disrotatory.

**Final Answer:** the photochemical $4\pi$ closure is disrotatory $\Rightarrow$ $\boxed{\text{D}}$

**Answer: (D)** Go Back to Q45

## Q46.

**Solution**

**Concept – the glycosidic bond:** Two monosaccharides join when the anomeric hydroxyl of one sugar condenses with a hydroxyl of the other, eliminating water and forming a $\text{C}-\text{O}-\text{C}$ acetal linkage.

**Step 1 – identify the groups joined:** The anomeric $-\text{OH}$ of one sugar reacts with an $-\text{OH}$ of the second sugar.

**Step 2 – classify the resulting linkage:** The $\text{C}-\text{O}-\text{C}$ bridge between two sugar units is, by definition, a glycosidic bond.

**Step 3 – reject the distractors:** A peptide bond joins amino acids, an ester bond joins an acid and an alcohol, and a phosphodiester bond links nucleotides; none of these describes a sugar–sugar linkage.

**Final Answer:** the linkage is a glycosidic bond $\Rightarrow$ $\boxed{\text{A}}$

**Answer: (A)** Go Back to Q46

# Answer Key

| Q | Ans | Q | Ans | Q | Ans | Q | Ans | Q | Ans |
|---|---|---|---|---|---|---|---|---|---|
| 1 | B | 2 | B | 3 | D | 4 | B | 5 | C |
| 6 | C | 7 | D | 8 | A | 9 | A | 10 | C |
| 11 | B | 12 | A | 13 | A | 14 | D | 15 | B |
| 16 | B | 17 | A | 18 | A | 19 | B | 20 | C |
| 21 | D | 22 | A | 23 | D | 24 | A | 25 | A |
| 26 | C | 27 | A | 28 | D | 29 | D | 30 | C |
| 31 | D | 32 | C | 33 | C | 34 | B | 35 | A |
| 36 | C | 37 | B | 38 | D | 39 | B | 40 | B |
| 41 | C | 42 | D | 43 | B | 44 | C | 45 | D |
| 46 | A | | | | | | | | |