GATE Chemistry

Sample Paper – 4

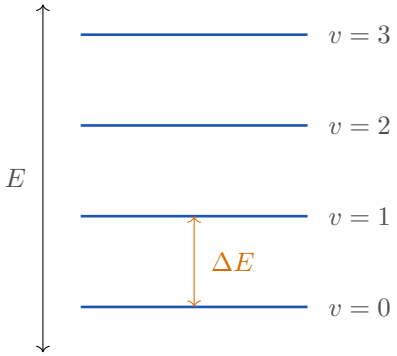
Duration: 128 Minutes **Maximum Marks: 72**

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. A diatomic molecule modelled as a one-dimensional quantum harmonic oscillator has vibrational energy levels $E_v = \left(v + \frac{1}{2}\right) h\nu$, with $v = 0, 1, 2, \ldots$ The equally spaced energy ladder is sketched below. The spacing between any two adjacent vibrational levels is: [1 mark]



(A) $\frac{1}{2}h\nu$

(B) $2h\nu$

(C) $h\nu$

(D) $\frac{3}{2}h\nu$

Q2. The gross selection rule for infrared (IR) absorption requires that a molecular vibration produce a change in the electric dipole moment of the molecule. Among the following gas-phase molecules, the one that shows a fundamental IR absorption band is: **[1 mark]**

(A) HCl

(B) N_2

(C) O_2

(D) Cl_2

Q3. For a diatomic molecule modelled as a harmonic oscillator, the vibrational wavenumber depends on the reduced mass $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$. For $H^{35}Cl$ (taking $m_H = 1$ u and $m_{Cl} = 35$ u), the reduced mass is nearest to: **[1 mark]**

(A) 36 u

(B) 18 u

(C) 1.00 u

(D) 0.97 u

Q4. For a particle of mass m confined in a one-dimensional box, the stationary-state wavefunction with quantum number n has $(n - 1)$ internal nodes

(points where $\psi = 0$, excluding the two walls). For the level $n = 4$, the number of internal nodes is: **[1 mark]**

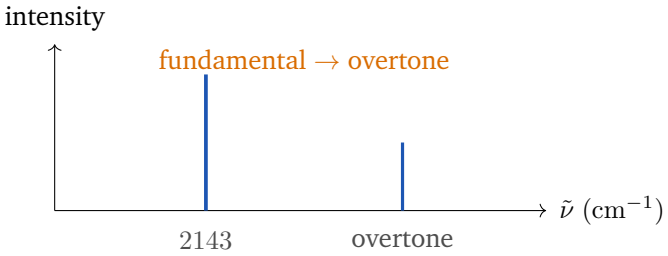
(A) 4

(B) 2

(C) 3

(D) 0

Q5. The gas-phase IR spectrum of carbon monoxide shows an intense fundamental band ($v = 0 \rightarrow 1$) at $2143\ \text{cm}^{-1}$, as sketched. If the molecule behaved as a *purely harmonic* oscillator, its first overtone ($v = 0 \rightarrow 2$) would appear at approximately: **[1 mark]**



(A) $4286\ \text{cm}^{-1}$

(B) $1072\ \text{cm}^{-1}$

(C) $2143\ \text{cm}^{-1}$

(D) $6429\ \text{cm}^{-1}$

Q6. Ignoring electron spin, the degeneracy (number of distinct orbitals) of the principal shell with quantum number n in a hydrogen atom is n^2. The degeneracy of the $n = 2$ shell is: **[1 mark]**

(A) 1

(B) 2

(C) 8

(D) 4

Physical Chemistry: Thermodynamics, Kinetics and Electrochemistry

Q7. For the gas-phase equilibrium $\mathrm{N_2(g)} + 3\,\mathrm{H_2(g)} \rightleftharpoons 2\,\mathrm{NH_3(g)}$, the equilibrium constants in terms of partial pressures (K_p) and concentrations (K_c) are related by $K_p = K_c(RT)^{\Delta n}$. For this reaction the correct relationship is: **[1 mark]**

(A) $K_p = K_c(RT)^2$

(B) $K_p = K_c$

(C) $K_p = K_c(RT)$

(D) $K_p = K_c(RT)^{-2}$

Q8. The standard Gibbs energy change of a reaction is related to its thermodynamic equilibrium constant by $\Delta G^\circ = -RT\ln K$. If a reaction has $\Delta G^\circ = 0$ at a given temperature, the value of its equilibrium constant K is: **[1 mark]**

(A) 0

(B) 1

(C) infinitely large

(D) negative

Q9. A second-order reaction $2A \rightarrow$ products obeys $t_{1/2} = \dfrac{1}{k[A]_0}$. If the rate constant is $k = 0.05\ \mathrm{L\,mol^{-1}s^{-1}}$ and the initial concentration is $[A]_0 = 0.20\ \mathrm{mol\,L^{-1}}$, the half-life of the reaction is: **[1 mark]**

(A) $10\ \mathrm{s}$

(B) $20\ \mathrm{s}$

(C) $50\ \mathrm{s}$

(D) $100\ \mathrm{s}$

Q10. For a galvanic cell the standard Gibbs energy is $\Delta G^\circ = -nFE^\circ_{\text{cell}}$. A cell transfers $n = 2$ electrons and has a standard cell potential $E^\circ_{\text{cell}} = 1.50\ \mathrm{V}$ (take $F = 96500\ \mathrm{C\,mol^{-1}}$). The value of ΔG° is: **[1 mark]**

(A) $-193\ \text{kJ mol}^{-1}$

(B) $-289.5\ \text{kJ mol}^{-1}$

(C) $+289.5\ \text{kJ mol}^{-1}$

(D) $-96.5\ \text{kJ mol}^{-1}$

Q11. One mole of A is placed in a $1\ \text{L}$ vessel where it establishes the equilibrium $A(g) \rightleftharpoons 2B(g)$. At equilibrium 50% of A has dissociated. Using $K_c = \dfrac{[B]^2}{[A]}$, the equilibrium constant K_c is: **[1 mark]**

(A) 1

(B) 2

(C) 0.5

(D) 4

Q12. For a reaction whose rate law is rate $= k[A]$, the reaction is first order overall. The SI-consistent units of the rate constant k for such a first-order reaction are: **[1 mark]**

(A) $\text{mol L}^{-1}\text{s}^{-1}$

(B) $\text{L mol}^{-1}\text{s}^{-1}$

(C) mol L^{-1}

(D) s^{-1}

Q13. In the electrolytic reduction $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$, three moles of electrons are required per mole of aluminium. Using $F = 96500\ \text{C mol}^{-1}$, the electric charge needed to deposit exactly one mole of aluminium is: **[1 mark]**

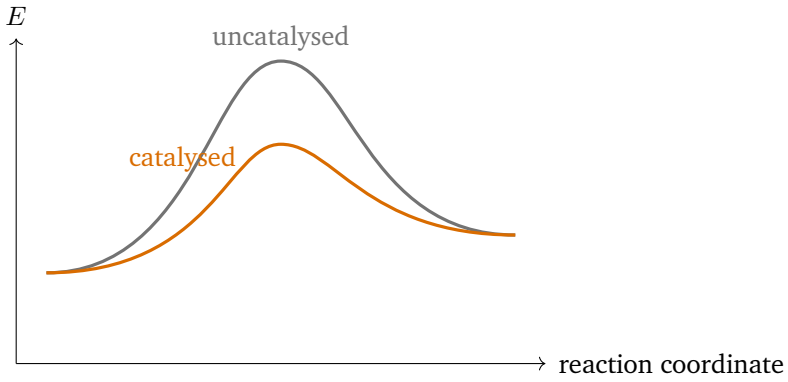
(A) $96500\ \text{C}$

(B) $289500\ \text{C}$

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

(D) $32167\ \text{C}$

Q14. The reaction-coordinate diagram below compares the same reaction run without a catalyst (upper curve) and with a catalyst (lower curve). A catalyst increases the reaction rate primarily by: **[1 mark]**



(A) increasing the enthalpy change ΔH of the reaction

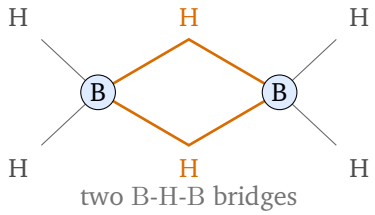
(B) raising the temperature of the system

(C) providing an alternative pathway of lower activation energy

(D) shifting the position of equilibrium towards products

Inorganic Chemistry: Main Group and Periodic Properties

Q15. Diborane, B_2H_6, is electron-deficient and adopts the bridged structure shown, in which two hydrogen atoms bridge the two boron atoms through three-centre two-electron ($3c$-$2e$) bonds. The number of such $3c$-$2e$ bridge bonds present in one B_2H_6 molecule is: **[1 mark]**



two B-H-B bridges

(A) 0

(B) 4

(C) 1

(D) 2

Q16. Owing to the inert pair effect, the stability of the lower oxidation state increases down group 14. For lead, the oxidation state in its most stable and common ionic compounds (such as $\mathrm{PbCl_2}$) is: **[1 mark]**

(A) $+2$

(B) $+4$

(C) $+3$

(D) $+1$

Q17. Orthoboric acid, $\mathrm{B(OH)_3}$, behaves as a weak monobasic acid in water even though it carries three OH groups. This acidity arises because $\mathrm{B(OH)_3}$: **[1 mark]**

(A) ionises by directly donating all three of its protons

(B) ionises by directly donating exactly one of its protons

(C) accepts a hydroxide ion from water, acting as a Lewis acid and releasing $\mathrm{H^+}$

(D) is a strong acid fully dissociated in water

Q18. Carbon monoxide, CO, does not react with either dilute acids or dilute alkalis to form a salt. On the basis of its acid–base behaviour, CO is classified as a(n): **[1 mark]**

(A) acidic oxide

(B) basic oxide

(C) neutral oxide

(D) amphoteric oxide

Q19. Although electron gain enthalpy is expected to become more negative on moving up a group, the value for fluorine is less negative than that for chlorine because of the small, compact $2p$ subshell of fluorine. Among the halogens, the element with the *most negative* electron gain enthalpy is: **[1 mark]**

(A) F

(B) Cl

(C) Br

(D) I

Q20. The tendency of an element to form long chains and rings through element–element single bonds is called catenation, and it falls sharply down group 14 as the element–element bond strength weakens. Among C, Si, Ge and Sn, the element that shows the *maximum* catenation is: **[1 mark]**

(A) Si

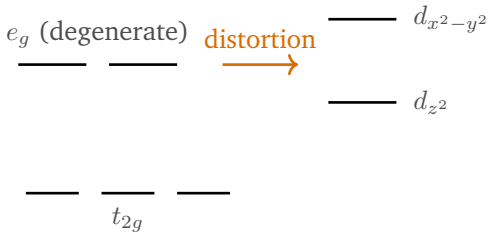
(B) Ge

(C) Sn

(D) C

Inorganic Chemistry: Coordination Compounds and Organometallics

Q21. The Jahn–Teller theorem states that a non-linear molecule in an orbitally degenerate electronic state will distort to lower its energy. The distortion is strongest when the e_g set is unevenly occupied, as illustrated by the axial elongation below. Among the following octahedral configurations, the one that shows a *strong* Jahn–Teller distortion is: **[2 marks]**



(A) high-spin d^9 (e.g. Cu^{2+})

(B) d^3

(C) low-spin d^6

(D) high-spin d^5

Q22. Iron pentacarbonyl, $[Fe(CO)_5]$, obeys the 18-electron (effective-atomic-number) rule. Taking iron(0) to contribute 8 valence electrons and each 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 two complexes $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ differ only in whether the ambidentate NO_2 ligand binds through nitrogen or through oxygen. This pair is an example of: **[2 marks]**

(A) geometrical isomerism

(B) optical isomerism

(C) linkage isomerism

(D) ionisation isomerism

Q24. Optical isomerism in a coordination compound requires that the complex be non-superimposable on its mirror image (no plane of symmetry). Among the following, the complex that exhibits optical isomerism is: **[2 marks]**

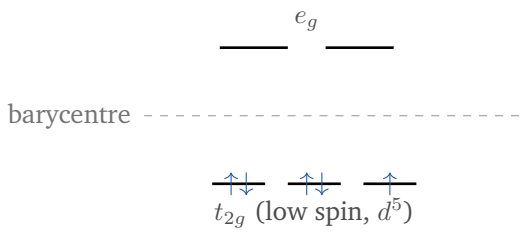
(A) $[Co(NH_3)_6]^{3+}$

(B) *trans*-$[Co(en)_2Cl_2]^{+}$

(C) $[Co(en)_3]^{3+}$

(D) $[PtCl_4]^{2-}$

Q25. The complex ion $[Fe(CN)_6]^{3-}$ contains iron(III) (d^5) with the strong-field cyanide ligand, so it is low-spin. The number of unpaired electrons on the metal centre is: **[2 marks]**



(A) 5

(B) 1

(C) 3

(D) 0

Q26. The square-planar complex $[Pt(NH_3)_2Cl_2]$ can be prepared in two distinct forms, one with the two chloride ligands adjacent (*cis*) and one with them opposite (*trans*). These two forms illustrate: **[2 marks]**

(A) optical isomerism

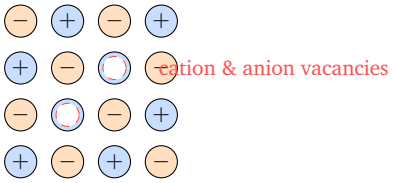
(B) geometrical (*cis–trans*) isomerism

(C) linkage isomerism

(D) no isomerism at all

Inorganic Chemistry: Solid State and Bioinorganic

Q27. The section of an ionic lattice below shows a Schottky defect: a cation vacancy and an anion vacancy created together so that overall electrical neutrality is preserved. Compared with a perfect crystal, a Schottky defect: **[2 marks]**



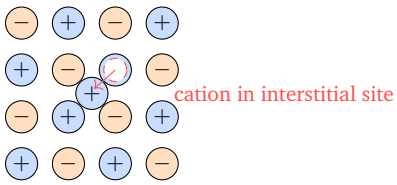
(A) decreases the density of the crystal

(B) increases the density of the crystal

(C) leaves the density unchanged and places a cation in an interstitial site

(D) creates only anion vacancies

Q28. The lattice section below shows a Frenkel defect, in which a smaller cation has left its normal lattice site and moved into an interstitial position, leaving a vacancy behind. Relative to a perfect crystal, the density of a crystal containing Frenkel defects is: [2 marks]



(A) decreased appreciably

(B) increased greatly

(C) exactly doubled

(D) unchanged

Q29. Chlorophyll, the green pigment responsible for photosynthesis in plants, is a substituted porphyrin (chlorin) that holds a single metal ion at the centre of its ring. The metal ion present at the centre of chlorophyll is: [2 marks]

(A) Fe^{2+}

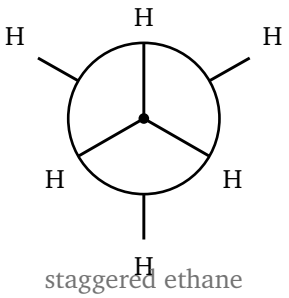
(B) Zn^{2+}

(C) Mg^{2+}

(D) Ca^{2+}

Organic Chemistry: Stereochemistry and Reaction Mechanisms

Q30. The Newman projection along the $C1-C2$ bond of ethane is shown in its staggered form below. The rotational (torsional) energy barrier separating the staggered and eclipsed conformations of ethane is closest to: [2 marks]



staggered ethane

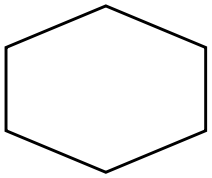
(A) about $12\ \mathrm{kJ\,mol^{-1}}$

(B) exactly $0\ \mathrm{kJ\,mol^{-1}}$

(C) about $120\ \mathrm{kJ\,mol^{-1}}$

(D) about $50\ \mathrm{kJ\,mol^{-1}}$

Q31. The chair conformation of cyclohexane, sketched below, is far more stable than the boat conformation. The principal reason the chair is preferred is that in the chair: **[2 marks]**



chair conformation of cyclohexane

(A) the ring is planar and strain-free

(B) there are strong flagpole hydrogen interactions

(C) all the adjacent $\mathrm{C-H}$ bonds are eclipsed

(D) all adjacent $\mathrm{C-H}$ bonds are staggered and there are no flagpole interactions

Q32. In methylcyclohexane the methyl group prefers the equatorial position because an axial methyl suffers $1,3$-diaxial repulsions. At room temperature, the percentage of methylcyclohexane molecules having the methyl group equatorial is closest to: **[2 marks]**

(A) 95%

(B) 50%

(C) 5%

(D) 0%

Q33. An S_N1 substitution proceeds through a rate-determining ionisation of the substrate to give a carbocation, which is then captured by the nucleophile in a fast step. Consequently, the rate of an S_N1 reaction depends on: **[2 marks]**

(A) the concentration of the substrate only

(B) the concentrations of both the substrate and the nucleophile

(C) the concentration of the nucleophile only

(D) the concentration of the solvent only

Q34. A pair of enantiomers has identical scalar physical properties such as melting point, boiling point, density and refractive index. The one property in which two enantiomers differ (in the absence of any other chiral influence) is the: **[2 marks]**

(A) melting point

(B) sign (direction) of optical rotation of plane-polarised light

(C) density

(D) solubility in ethanol

Q35. An $E1$ elimination proceeds in two steps: loss of the leaving group to form a carbocation, followed by removal of a β-proton by a base. The rate-determining (slowest) step of an $E1$ reaction is: **[2 marks]**

(A) removal of the β-proton by the base

(B) nucleophilic attack on the carbocation

(C) ionisation of the substrate to form the carbocation

(D) both steps proceed at exactly equal rates

Q36. Tartaric acid, HOOC-CHOH-CHOH-COOH, has two stereogenic centres, but one of its stereoisomers possesses an internal plane of symmetry (the *meso* form). Taking this into account, the total number of distinct stereoisomers of tartaric acid is: **[2 marks]**

(A) 4

(B) 3

(C) 2

(D) 1

Organic Chemistry: Named Reactions and Synthesis

Q37. In the Wittig reaction, an aldehyde or ketone reacts with a phosphorus ylide ($\mathrm{Ph_3P{=}CR_2}$) to give an alkene, as sketched below. The inorganic (phosphorus-containing) by-product formed alongside the alkene is: **[2 marks]**

$$\mathrm{R_2C{=}O} \;+\; \mathrm{Ph_3P{=}CR'_2} \longrightarrow \mathrm{R_2C{=}CR'_2} + \mathrm{Ph_3P{=}O}$$

carbonyl + ylide → alkene

(A) triphenylphosphine, $\mathrm{Ph_3P}$

(B) triphenylphosphine oxide, $\mathrm{Ph_3P{=}O}$

(C) water, $\mathrm{H_2O}$

(D) an alcohol, $\mathrm{R_2CHOH}$

Q38. The Horner–Wadsworth–Emmons (HWE) reaction uses a resonance-stabilised phosphonate carbanion ($(\mathrm{RO})_2\mathrm{P(O)\text{-}\bar{C}HR'}$) in place of a phosphorus ylide. With simple substrates the HWE olefination is highly selective and predominantly gives the alkene of geometry: **[2 marks]**

(A) Z (*cis*)

(B) a $50{:}50$ mixture of E and Z

(C) E (*trans*)

(D) no alkene is formed

Q39. In the classical Wittig reaction, a *non-stabilised* ylide (for example the one derived from methyltriphenylphosphonium) reacts with an aldehyde to give predominantly the alkene of geometry: **[2 marks]**

(A) E (*trans*)

(B) Z (*cis*)

(C) an alkyne

(D) an epoxide

Q40. A ketone is converted directly to the corresponding methylene ($\mathrm{C{=}O} \rightarrow \mathrm{CH_2}$) compound on heating with hydrazine ($\mathrm{NH_2NH_2}$) and a strong base such as KOH in a high-boiling solvent. This carbonyl-to-methylene reduction is the: **[2 marks]**

(A) Wolff–Kishner reduction

(B) Clemmensen reduction

(C) Rosenmund reduction

(D) Cannizzaro reaction

Q41. The base-promoted condensation of two ester molecules, in which the α-carbon of one ester attacks the carbonyl of another to give a β-keto ester, is a named carbon–carbon bond-forming reaction called the: **[2 marks]**

(A) Aldol condensation

(B) Claisen condensation

(C) Wittig reaction

(D) Cannizzaro reaction

Q42. An acid chloride (RCOCl) is reduced selectively to the corresponding aldehyde (RCHO) using hydrogen over a palladium catalyst poisoned with barium sulfate. This selective reduction of an acyl chloride to an aldehyde is the: **[2 marks]**

(A) Wolff–Kishner reduction

(B) Clemmensen reduction

(C) Stephen reduction

(D) Rosenmund reduction

Q43. In electrophilic aromatic substitution, a hydroxyl ($-\mathrm{OH}$) substituent already on the benzene ring donates electron density into the ring by resonance. As a result the $-\mathrm{OH}$ group acts as a(n): **[2 marks]**

(A) ortho- and para-directing activating group

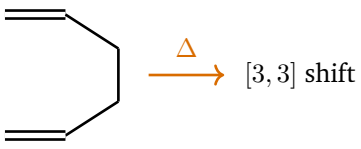
(B) meta-directing deactivating group

(C) completely unreactive (inert) group

(D) para-only directing deactivating group

Organic Chemistry: Pericyclic, Photochemistry and Biomolecules

Q44. The Cope rearrangement of $1,5$-hexadiene, sketched below, is a thermal pericyclic reaction in which a σ bond migrates while the two π bonds shift. In Woodward–Hoffmann notation, the Cope rearrangement is classified as a sigmatropic shift of order: **[2 marks]**



$1,5$-hexadiene

(A) $[1,3]$

(B) $[1,5]$

(C) $[1, 7]$

(D) $[3, 3]$

Q45. The Claisen rearrangement of an allyl vinyl ether is a thermal $[3, 3]$-sigmatropic rearrangement. Consistent with its concerted, pericyclic nature, the reaction proceeds through a transition state that is best described as a: [2 marks]

(A) six-membered cyclic (chair-like) transition state

(B) free-radical chain mechanism

(C) discrete carbocation intermediate

(D) four-membered cyclic transition state

Q46. Consider a $[1, 5]$-hydrogen sigmatropic shift in a conjugated diene system under *thermal* conditions. According to the Woodward–Hoffmann rules for a $(4n + 2)$-electron process, this thermal $[1, 5]$-H shift proceeds: [2 marks]

(A) antarafacially

(B) it is symmetry-forbidden and does not occur

(C) suprafacially

(D) through a diradical intermediate

Detailed Solutions

Q1.

Solution

Concept – energy levels of the harmonic oscillator: For a quantum harmonic oscillator the allowed energies are $E_v = \left(v + \frac{1}{2}\right) h\nu$, so the levels are equally spaced (unlike the particle in a box, whose spacing grows).

Step 1 – write two neighbouring levels: $E_{v+1} = \left(v + 1 + \frac{1}{2}\right) h\nu$

$E_v = \left(v + \frac{1}{2}\right) h\nu$

Step 2 – subtract to get the spacing: $\Delta E = E_{v+1} - E_v = \left(v + \frac{3}{2}\right) h\nu - \left(v + \frac{1}{2}\right) h\nu$

Step 3 – simplify: $\Delta E = \left(v + \frac{3}{2} - v - \frac{1}{2}\right) h\nu = h\nu$

Step 4 – interpret: The spacing is independent of v, which is why the ladder in the figure is uniform and why a harmonic oscillator has a single fundamental frequency.

Final Answer: adjacent-level spacing $= h\nu \Rightarrow \boxed{\text{C}}$

Answer: (C) Go Back to Q1

Q2.

Solution

Concept – IR activity requires a changing dipole moment: A vibration absorbs in the IR only if it changes the molecular dipole moment. Homonuclear diatomics (N_2, O_2, Cl_2) have zero dipole and remain zero throughout the stretch, so they are IR inactive.

Step 1 – test each molecule: N_2, O_2, Cl_2 are homonuclear $\Rightarrow$ no permanent dipole and no change on stretching $\Rightarrow$ IR inactive.

Step 2 – examine HCl: HCl is heteronuclear and polar; as the bond stretches and compresses, the dipole moment changes.

Step 3 – conclude: Only HCl satisfies the gross selection rule, so only HCl shows a fundamental IR band.

Why the others are wrong: being homonuclear, N_2, O_2 and Cl_2 cannot generate a dipole change and are IR silent (they are, however, Raman active).

Final Answer: HCl is IR active $\Rightarrow \boxed{\text{A}}$

Answer: (A) Go Back to Q2

Q3.

Solution

Concept – reduced mass of a diatomic: $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$.

Step 1 – insert the atomic masses: $m_{\mathrm{H}} = 1$ u and $m_{\mathrm{Cl}} = 35$ u.

$\mu = \dfrac{(1)(35)}{1 + 35}$

Step 2 – add the denominator: $\mu = \dfrac{35}{36}$

Step 3 – divide: $\mu = 0.972$ u

$\mu \approx 0.97$ u

Step 4 – sanity check: Because chlorine is so much heavier than hydrogen, μ is only slightly below the mass of the light H atom (1 u), which matches 0.97 u.

Final Answer: $\mu \approx 0.97$ u $\Rightarrow$ D

Answer: (D) Go Back to Q3

Q4.

Solution

Concept – nodes of the particle-in-a-box wavefunction: The level n has a wavefunction $\psi_n \propto \sin\left(\dfrac{n\pi x}{L}\right)$, which crosses zero $(n-1)$ times inside the box (the two walls are not counted).

Step 1 – take $n = 4$: Number of internal nodes $= n - 1$.

Step 2 – substitute: $= 4 - 1$

Step 3 – evaluate: $= 3$

Step 4 – cross-check: $\sin\left(\dfrac{4\pi x}{L}\right)$ vanishes at $x = \frac{L}{4}, \frac{L}{2}, \frac{3L}{4}$, i.e. three interior points, confirming the count.

Final Answer: number of internal nodes $= 3 \Rightarrow$ C

Answer: (C) Go Back to Q4

Q5.

Solution

Concept – overtones of a harmonic oscillator: For an ideal (harmonic) oscillator the levels are evenly spaced, so the transition $v = 0 \rightarrow 2$ has exactly twice the energy of the fundamental $v = 0 \rightarrow 1$; the overtone falls at $2\tilde{\nu}_0$.

Step 1 – write the fundamental: $\tilde{\nu}_0 = 2143\ \text{cm}^{-1}$ (the $v = 0 \to 1$ band).

Step 2 – express the harmonic overtone: $\tilde{\nu}_{0\to 2} = 2 \times \tilde{\nu}_0$

Step 3 – substitute: $\tilde{\nu}_{0\to 2} = 2 \times 2143$

Step 4 – evaluate: $\tilde{\nu}_{0\to 2} = 4286\ \text{cm}^{-1}$

Step 5 – note the real-world caveat: A real molecule is slightly anharmonic, so the observed overtone lies a little below $4286\ \text{cm}^{-1}$; the question specifies a purely harmonic oscillator, so the exact double is required.

Final Answer: first overtone $= 4286\ \text{cm}^{-1} \Rightarrow \boxed{\text{A}}$

Answer: (A) Go Back to Q5

Q6.

Solution

Concept – orbital degeneracy of a hydrogenic shell: Ignoring spin, the number of orbitals in the shell of principal quantum number n is n^2.

Step 1 – take $n = 2$: Degeneracy $= n^2 = 2^2$.

Step 2 – evaluate: $= 4$

Step 3 – verify by listing the orbitals: The $n = 2$ shell contains one $2s$ orbital and three $2p$ orbitals, i.e. $1 + 3 = 4$ orbitals in all.

Why (C) is wrong: 8 counts spin ($2n^2$); the question explicitly ignores spin, so the answer is $n^2 = 4$.

Final Answer: degeneracy of $n = 2 = 4 \Rightarrow \boxed{\text{D}}$

Answer: (D) Go Back to Q6

Q7.

Solution

Concept – relating K_p and K_c: $K_p = K_c(RT)^{\Delta n}$, where $\Delta n =$ (moles of gaseous products) $-$ (moles of gaseous reactants).

Step 1 – count gaseous moles: Products: 2 mol NH_3. Reactants: 1 mol $\text{N}_2 + 3$ mol $\text{H}_2 = 4$ mol.

Step 2 – compute Δn: $\Delta n = 2 - 4 = -2$

Step 3 – substitute into the relation: $K_p = K_c(RT)^{-2}$

Step 4 – interpret: Since the forward reaction reduces the number of gas moles, the (RT) factor carries a negative exponent.

Final Answer: $K_p = K_c(RT)^{-2} \Rightarrow$ D

Answer: (D) Go Back to Q7

Q8.

Solution

Concept – link between ΔG° and K: $\Delta G^\circ = -RT\ln K$, so the equilibrium constant is $K = e^{-\Delta G^\circ/RT}$.

Step 1 – set $\Delta G^\circ = 0$: $0 = -RT\ln K$

Step 2 – divide through by $-RT$ (non-zero): $\ln K = 0$

Step 3 – exponentiate: $K = e^0 = 1$

Step 4 – interpret: $\Delta G^\circ = 0$ describes a reaction poised exactly at the standard-state balance, so products and reactants are equally favoured and $K = 1$.

Final Answer: $K = 1 \Rightarrow$ B

Answer: (B) Go Back to Q8

Q9.

Solution

Concept – half-life of a second-order reaction: For a second-order reaction, $t_{1/2} = \dfrac{1}{k[A]_0}$, which (unlike first order) depends on the initial concentration.

Step 1 – write the formula: $t_{1/2} = \dfrac{1}{k[A]_0}$

Step 2 – substitute the data: $t_{1/2} = \dfrac{1}{(0.05)(0.20)}$

Step 3 – multiply the denominator: $(0.05)(0.20) = 0.010$

Step 4 – divide: $t_{1/2} = \dfrac{1}{0.010} = 100\ \text{s}$

Final Answer: $t_{1/2} = 100\ \text{s} \Rightarrow$ D

Answer: (D) Go Back to Q9

Q10.

Solution

Concept – Gibbs energy of a cell reaction: $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and $F = 96500\ \text{C mol}^{-1}$.

Step 1 – insert the values: $\Delta G^\circ = -(2)(96500)(1.50)$

Step 2 – multiply n and F: $2 \times 96500 = 193000$

Step 3 – multiply by E°: $193000 \times 1.50 = 289500\ \text{J mol}^{-1}$

Step 4 – apply the negative sign and convert to kJ: $\Delta G^\circ = -289500\ \text{J mol}^{-1} = -289.5\ \text{kJ mol}^{-1}$

Step 5 – sanity check: $E^\circ_{\text{cell}} > 0$ gives $\Delta G^\circ < 0$, so the cell reaction is spontaneous, as expected.

Final Answer: $\Delta G^\circ = -289.5\ \text{kJ mol}^{-1} \Rightarrow \boxed{\text{B}}$

Answer: (B) Go Back to Q10

Q11.

Solution

Concept – equilibrium constant from a degree of dissociation: Set up an ICE table for $A(g) \rightleftharpoons 2B(g)$ in a 1 L vessel and use $K_c = \dfrac{[B]^2}{[A]}$.

Step 1 – amount of A that dissociates: 50% of 1 mol dissociates $\Rightarrow 0.5$ mol of A reacts.

Step 2 – equilibrium amount of A: $[A] = 1 - 0.5 = 0.5\ \text{mol L}^{-1}$

Step 3 – equilibrium amount of B: Each mole of A gives 2 mol B, so $[B] = 2 \times 0.5 = 1.0\ \text{mol L}^{-1}$.

Step 4 – substitute into K_c: $K_c = \dfrac{[B]^2}{[A]} = \dfrac{(1.0)^2}{0.5}$

Step 5 – evaluate: $K_c = \dfrac{1.0}{0.5} = 2$

Final Answer: $K_c = 2 \Rightarrow \boxed{\text{B}}$

Answer: (B) Go Back to Q11

Q12.

Solution

Concept – units of a rate constant: For an overall order m, the rate constant carries units of $(\text{concentration})^{1-m}(\text{time})^{-1}$.

Step 1 – write the rate law: rate $= k[A]$, which is first order, so $m = 1$.

Step 2 – balance the units: Rate has units $\text{mol L}^{-1}\text{s}^{-1}$; $[A]$ has units mol L^{-1}.

Step 3 – solve for the units of k: $k = \dfrac{\text{rate}}{[A]} = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol L}^{-1}}$

Step 4 – cancel: k has units s^{-1}.

Why the others are wrong: $\text{mol L}^{-1}\text{s}^{-1}$ belongs to a zero-order k and $\text{L mol}^{-1}\text{s}^{-1}$ to a second-order k.

Final Answer: units of k are $\text{s}^{-1} \Rightarrow \boxed{\text{D}}$

Answer: (D) Go Back to Q12

Q13.

Solution

Concept – Faraday's law of electrolysis: The charge to deposit one mole of a metal is (number of electrons per ion) $\times F$.

Step 1 – read the half-reaction: $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$, so 3 mol of electrons are required per mole of aluminium.

Step 2 – write the charge: $Q = 3 \times F$

Step 3 – substitute $F = 96500\ \text{C mol}^{-1}$: $Q = 3 \times 96500$

Step 4 – evaluate: $Q = 289500\ \text{C}$

Final Answer: $Q = 289500\ \text{C} \Rightarrow \boxed{\text{B}}$

Answer: (B) Go Back to Q13

Q14.

Solution

Concept – how a catalyst works: A catalyst offers a different reaction pathway with a lower activation energy, so a larger fraction of collisions succeeds and the rate rises.

Step 1 – read the diagram: The catalysed (orange) curve has a lower barrier than the uncatalysed (grey) curve, while both start and end at the same energies.

Step 2 – note what is unchanged: The reactant and product energies coincide for both curves, so ΔH is identical; the catalyst does not alter the thermodynamics.

Step 3 – identify the effect: Only the peak (activation energy) is lowered, which is exactly how a catalyst speeds the reaction.

Why the others are wrong: a catalyst does not change ΔH, does not require heating, and does not shift the equilibrium position (it speeds forward and reverse equally).

Final Answer: it provides a lower-activation-energy pathway $\Rightarrow$ C

Answer: (C) Go Back to Q14

Q15.

Solution

Concept – bonding in electron-deficient diborane: B_2H_6 has only 12 valence electrons but 8 bonds to accommodate, so it uses two three-centre two-electron B-H-B bridge bonds.

Step 1 – describe the structure: Four terminal B-H bonds are ordinary $2c$-$2e$ bonds; the two bridging hydrogens each hold the two borons together.

Step 2 – count the bridge bonds: There are exactly two bridging hydrogens, giving two $3c$-$2e$ bonds, as the figure shows.

Step 3 – electron book-keeping: 4 terminal bonds use 8 electrons; the remaining 4 electrons make the two $3c$-$2e$ bridges (2 electrons each).

Final Answer: number of $3c$-$2e$ bridge bonds $= 2 \Rightarrow$ D

Answer: (D) Go Back to Q15

Q16.

Solution

Concept – inert pair effect down group 14: As we descend from C to Pb, the ns^2 electrons become increasingly reluctant to take part in bonding, so the oxidation state two units below the group value ($+2$) grows more stable.

Step 1 – identify the group valency: Group 14 has a maximum oxidation state of $+4$.

Step 2 – apply the inert pair effect to lead: For lead, the $6s^2$ pair is held tightly, so Pb^{2+} (state $+2$) is the stable, common form; Pb^{4+} is strongly oxidising.

Step 3 – match to the example: $PbCl_2$ is stable, whereas $PbCl_4$ is unstable and

decomposes, confirming $+2$.

Final Answer: most stable oxidation state of Pb $= +2 \Rightarrow$ A

Answer: (A) Go Back to Q16

Q17.

Solution

Concept – boric acid as a Lewis (not Bronsted) acid: $B(OH)_3$ does not release its own protons. Instead the electron-deficient boron accepts a hydroxide ion from water, and it is that removal of OH^- which leaves behind H^+.

Step 1 – write the reaction with water: $B(OH)_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$

Step 2 – identify the acidic behaviour: Boron completes its octet by binding OH^-; the freed proton makes the solution acidic. Only one H^+ appears, so the acid is monobasic.

Step 3 – rule out proton donation: The three O-H bonds of $B(OH)_3$ do not ionise directly, so it is not a triprotic Bronsted acid.

Final Answer: it acts as a Lewis acid, accepting OH^- and releasing $H^+ \Rightarrow$ C

Answer: (C) Go Back to Q17

Q18.

Solution

Concept – classifying oxides by acid–base behaviour: An oxide is acidic if it reacts with base, basic if it reacts with acid, amphoteric if it reacts with both, and neutral if it reacts with neither.

Step 1 – test CO against acids and bases: CO does not form a carbonate/bicarbonate salt with alkali under ordinary conditions, and it forms no salt with acids.

Step 2 – classify: Reacting with neither acids nor bases makes CO a neutral oxide (like N_2O and NO).

Step 3 – contrast with CO_2: CO_2, by comparison, is acidic and reacts with alkali to give carbonates; CO does not, underscoring its neutral character.

Final Answer: CO is a neutral oxide $\Rightarrow$ C

Answer: (C) Go Back to Q18

Q19.

Solution

Concept – the electron-gain-enthalpy anomaly in group 17: Electron gain enthalpy generally becomes less negative down a group, which would make fluorine the most negative. But fluorine's very small $2p$ shell is so compact that the incoming electron feels strong electron–electron repulsion, making its value less negative than expected.

Step 1 – compare F and Cl: Experimentally, $\Delta_{eg}H(\mathrm{Cl}) \approx -349\ \mathrm{kJ\,mol^{-1}}$ is more negative than $\Delta_{eg}H(\mathrm{F}) \approx -328\ \mathrm{kJ\,mol^{-1}}$.

Step 2 – order the halogens: The magnitude order is $\mathrm{Cl} > \mathrm{F} > \mathrm{Br} > \mathrm{I}$, so chlorine's value is the most negative.

Step 3 – conclude: Chlorine has the most negative electron gain enthalpy.

Final Answer: Cl has the most negative $\Delta_{eg}H \Rightarrow \boxed{\mathrm{B}}$

Answer: (B) Go Back to Q19

Q20.

Solution

Concept – catenation in group 14: Catenation depends on the strength of the element–element single bond, which falls sharply down the group as atoms get larger and orbital overlap weakens.

Step 1 – compare bond strengths: $\mathrm{C\text{-}C}$ ($\approx 348\ \mathrm{kJ\,mol^{-1}}$) is far stronger than $\mathrm{Si\text{-}Si}$, $\mathrm{Ge\text{-}Ge}$ or $\mathrm{Sn\text{-}Sn}$.

Step 2 – link strength to catenation: The stronger the E–E bond, the longer and more stable the chains, so carbon forms the most extensive chains and rings.

Step 3 – conclude: Carbon shows the maximum catenation of the group, which underlies the whole of organic chemistry.

Final Answer: maximum catenation is shown by $\mathrm{C} \Rightarrow \boxed{\mathrm{D}}$

Answer: (D) Go Back to Q20

Q21.

Solution

Concept – Jahn–Teller distortion: A strong Jahn–Teller effect arises when the e_g orbitals (which point directly at the ligands) are unequally occupied, because that asymmetry can be relieved by distorting the octahedron.

Step 1 – examine each configuration's e_g occupancy: High-spin d^9 (Cu^{2+}): $t_{2g}^6 e_g^3$, i.e. e_g holds 3 electrons unevenly (d_{z^2} vs $d_{x^2-y^2}$) $\Rightarrow$ strong distortion.

Step 2 – check the alternatives: d^3 ($t_{2g}^3 e_g^0$) has an empty, symmetric e_g; low-spin d^6 ($t_{2g}^6 e_g^0$) also has an empty e_g; high-spin d^5 ($t_{2g}^3 e_g^2$) has a half-filled, symmetric e_g. None of these gives a strong effect.

Step 3 – conclude: Only d^9 has the uneven e_g filling needed for a strong Jahn–Teller distortion, giving the axial elongation drawn in the figure.

Final Answer: strong Jahn–Teller for high-spin d^9 (Cu^{2+}) $\Rightarrow$ $\boxed{A}$

Answer: (A) Go Back to Q21

Q22.

Solution

Concept – the 18-electron rule: Count the metal's valence electrons plus the electrons donated by all ligands.

Step 1 – electrons from the metal: Iron(0) has the configuration $[Ar]3d^6 4s^2$, giving 8 valence electrons.

Step 2 – electrons from the ligands: Each CO donates 2 electrons; five carbonyls give $5 \times 2 = 10$.

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

Step 4 – interpret: 18 electrons corresponds to a filled valence shell, so $[Fe(CO)_5]$ is a stable, closed-shell organometallic.

Final Answer: total valence electron count $= 18 \Rightarrow$ $\boxed{A}$

Answer: (A) Go Back to Q22

Q23.

Solution

Concept – linkage (ambidentate) isomerism: Linkage isomers arise when an ambidentate ligand can coordinate through either of two different donor atoms.

Step 1 – identify the ligand: The nitrite ligand can bind through nitrogen (nitro, $-NO_2$) or through oxygen (nitrito, $-ONO$).

Step 2 – compare the two complexes: $[Co(NH_3)_5(NO_2)]^{2+}$ (N-bound) and $[Co(NH_3)_5(ONO)]^{2+}$ (O-bound) have the same formula but differ only in the donor atom.

Step 3 – classify: Same composition, different point of attachment $\Rightarrow$ linkage isomerism.

Why the others are wrong: the two are not related as spatial (geometrical/optical) arrangements, nor do they exchange ions between the coordination and outer spheres (ionisation isomerism).

Final Answer: the pair shows linkage isomerism $\Rightarrow$ C

Answer: (C) Go Back to Q23

Q24.

Solution

Concept – optical isomerism needs chirality: A complex is optically active only if it lacks any plane or centre of symmetry, so that it and its mirror image cannot be superimposed.

Step 1 – test $[Co(en)_3]^{3+}$: Three bidentate en ligands wrap around the metal as a three-bladed propeller with no plane of symmetry, giving Δ and Λ enantiomers.

Step 2 – test the others: $[Co(NH_3)_6]^{3+}$ is highly symmetric (achiral); *trans*-$[Co(en)_2Cl_2]^{+}$ has a plane of symmetry (achiral); square-planar $[PtCl_4]^{2-}$ is planar and achiral.

Step 3 – conclude: Only $[Co(en)_3]^{3+}$ is chiral and shows optical isomerism.

Final Answer: $[Co(en)_3]^{3+}$ is optically active $\Rightarrow$ C

Answer: (C) Go Back to Q24

Q25.

Solution

Concept – low-spin d^5 electron count: For a strong-field octahedral complex the t_{2g} orbitals fill completely before any electron enters the higher e_g set.

Step 1 – find the d count: Iron(III) is d^5.

Step 2 – apply the strong field of CN^-: CN^- is a strong-field ligand, so all five electrons pair up in t_{2g}: $t_{2g}^5 e_g^0$.

Step 3 – count unpaired electrons: Three t_{2g} orbitals hold 5 electrons as (2, 2, 1), leaving exactly one unpaired electron, as the diagram shows.

Step 4 – cross-check: A single unpaired electron gives a spin-only moment $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73$ BM, consistent with the low-spin $[Fe(CN)_6]^{3-}$.

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

Answer: (B) Go Back to Q25

Q26.

Solution

Concept – geometrical isomerism in square-planar complexes: A square-planar MA_2B_2 complex can place the two identical ligands either next to each other (*cis*) or across the square (*trans*).

Step 1 – identify the type: $[Pt(NH_3)_2Cl_2]$ is a square-planar MA_2B_2 system.

Step 2 – draw the two arrangements: *cis* has the two Cl at adjacent corners; *trans* has them at opposite corners.

Step 3 – classify: Same connectivity, different spatial arrangement about the metal $\Rightarrow$ geometrical (*cis–trans*) isomerism. (Both forms have a plane of symmetry, so neither is optically active.)

Final Answer: the two forms are geometrical (*cis–trans*) isomers $\Rightarrow$ B

Answer: (B) Go Back to Q26

Q27.

Solution

Concept – effect of a Schottky defect on density: A Schottky defect removes one cation and one anion together, so the crystal loses ions (and mass) while keeping the same volume.

Step 1 – note what is missing: Equal numbers of cation and anion sites are

vacant, preserving neutrality (see the two dashed vacancies).

Step 2 – relate to density: density $= \dfrac{\text{mass}}{\text{volume}}$. Missing ions lower the mass while the volume is essentially unchanged.

Step 3 – conclude: A Schottky defect therefore *decreases* the density of the crystal.

Why the others are wrong: it does not put a cation in an interstitial site (that is a Frenkel defect), and it involves both cation and anion vacancies, not anion-only.

Final Answer: a Schottky defect decreases the density $\Rightarrow \boxed{\text{A}}$

Answer: (A) Go Back to Q27

Q28.

Solution

Concept – effect of a Frenkel defect on density: In a Frenkel defect an ion merely moves from its lattice site into an interstitial hole; no ion leaves the crystal, so neither the mass nor the volume changes.

Step 1 – describe the defect: The smaller cation shifts to an interstitial position, leaving a vacancy behind (see the arrow in the figure).

Step 2 – account for mass and volume: The same number of ions occupy the same overall volume; only the internal position of one ion has changed.

Step 3 – conclude: Since mass and volume are both unchanged, the density is unchanged.

Why the others are wrong: Frenkel defects (unlike Schottky) neither remove ions nor lower the density; the density is not doubled or greatly increased.

Final Answer: a Frenkel defect leaves the density unchanged $\Rightarrow \boxed{\text{D}}$

Answer: (D) Go Back to Q28

Q29.

Solution

Concept – metal centres in biological porphyrins: Different porphyrin cofactors carry different central metals: heme uses iron, vitamin B_{12} uses cobalt, and chlorophyll uses magnesium.

Step 1 – identify chlorophyll's cofactor: Chlorophyll is a magnesium chlorin (a modified porphyrin).

Step 2 – name the central ion: The metal ion held in the ring is Mg^{2+}.

Step 3 – contrast with heme: Haemoglobin's heme uses Fe^{2+} to bind oxygen;

chlorophyll instead uses Mg^{2+} for light harvesting, so the two must not be confused.

Final Answer: the central ion in chlorophyll is $Mg^{2+} \Rightarrow \boxed{C}$

Answer: (C) Go Back to Q29

Q30.

Solution

Concept – torsional (rotational) barrier in ethane: Rotating one CH_3 relative to the other converts the low-energy staggered form into the higher-energy eclipsed form; the energy difference is the torsional barrier, caused mainly by torsional (bond–bond) strain.

Step 1 – recall the accepted value: The staggered→eclipsed barrier in ethane is about $12\ \text{kJ mol}^{-1}$ ($\approx 2.9\ \text{kcal mol}^{-1}$), i.e. roughly $4\ \text{kJ mol}^{-1}$ per eclipsing H-H pair.

Step 2 – reject the impossible options: A barrier of 0 would mean free, unhindered rotation (not observed); $120\ \text{kJ mol}^{-1}$ or $50\ \text{kJ mol}^{-1}$ are far too large for simple single-bond rotation.

Step 3 – conclude: The staggered conformation shown is the minimum, lying about $12\ \text{kJ mol}^{-1}$ below the eclipsed maximum.

Final Answer: rotational barrier $\approx 12\ \text{kJ mol}^{-1} \Rightarrow \boxed{A}$

Answer: (A) Go Back to Q30

Q31.

Solution

Concept – why the chair is the most stable conformation: The chair form of cyclohexane is strain-minimised: every pair of adjacent C-H bonds is staggered and there are no flagpole (transannular) hydrogen clashes.

Step 1 – assess torsional strain: In the chair, looking along any C-C bond the substituents are perfectly staggered, so torsional strain is essentially zero.

Step 2 – assess steric strain: The chair has no flagpole interactions, unlike the boat, where two "flagpole" hydrogens are pushed close together.

Step 3 – conclude: Staggered bonds plus the absence of flagpole strain make the chair the global energy minimum.

Why the others are wrong: cyclohexane is not planar (that would give large

angle and torsional strain); flagpole clashes and eclipsing describe the higher-energy boat, not the chair.

Final Answer: all adjacent C-H bonds staggered with no flagpole strain $\Rightarrow$ D

Answer: (D) Go Back to Q31

Q32.

Solution

Concept – equatorial preference from the A-value: An axial methyl suffers two $1,3$-diaxial interactions; the resulting energy penalty (the A-value, about $7.3\ \text{kJ mol}^{-1}$ for methyl) strongly favours the equatorial conformer.

Step 1 – relate the A-value to the equilibrium constant: $\Delta G^\circ \approx -7.3\ \text{kJ mol}^{-1}$ (equatorial favoured); $K = e^{-\Delta G^\circ/RT}$ at 298 K.

Step 2 – estimate the ratio: $K = e^{7300/(8.314\times298)} = e^{2.95} \approx 19$, i.e. about 19 equatorial for every 1 axial.

Step 3 – convert to a percentage: $\dfrac{19}{19+1} \times 100 \approx 95\%$ equatorial.

Final Answer: about 95% of molecules have methyl equatorial $\Rightarrow$ A

Answer: (A) Go Back to Q32

Q33.

Solution

Concept – kinetics of S_N1: An S_N1 reaction has a unimolecular, rate-determining ionisation step; the nucleophile enters only in the subsequent fast step, so it does not appear in the rate law.

Step 1 – identify the slow step: $\text{R-X} \rightarrow \text{R}^+ + \text{X}^-$ (slow, rate-determining).

Step 2 – write the rate law: rate $= k[\text{R-X}]$, first order in substrate only.

Step 3 – conclude: The rate depends solely on the concentration of the substrate and is independent of the nucleophile's concentration.

Why the others are wrong: dependence on both substrate and nucleophile is the hallmark of S_N2, not S_N1.

Final Answer: the rate depends on the substrate concentration only $\Rightarrow$ A

Answer: (A) Go Back to Q33

Q34.

Solution

Concept – how enantiomers differ: Enantiomers are non-superimposable mirror images. They share all scalar physical properties and differ only in chiral contexts, the simplest being their interaction with plane-polarised light.

Step 1 – list identical properties: Melting point, boiling point, density, refractive index and (achiral) solubility are the same for both enantiomers.

Step 2 – identify the difference: They rotate plane-polarised light by equal magnitudes but in opposite directions (one $+$, one $-$).

Step 3 – conclude: The distinguishing property is the sign (direction) of the optical rotation.

Why the others are wrong: melting point, density and solubility in an achiral solvent are identical for a pair of enantiomers.

Final Answer: they differ in the sign of optical rotation $\Rightarrow$ $\boxed{\text{B}}$

Answer: (B) Go Back to Q34

Q35.

Solution

Concept – rate-determining step of $E1$: Like S_N1, an $E1$ reaction begins with a slow, unimolecular ionisation to a carbocation; the fast second step is loss of a β-proton to a base.

Step 1 – write the two steps: Step 1 (slow): $\text{R-X} \rightarrow \text{R}^+ + \text{X}^-$.

Step 2 (fast): base removes a β-H to give the alkene.

Step 2 – identify the slowest step: The energetically costly carbocation-forming ionisation is rate-determining.

Step 3 – conclude: The rate law is rate $= k[\text{R-X}]$, controlled by the ionisation step.

Why the others are wrong: proton removal is the fast step, and there is no nucleophilic attack in an elimination; the two steps are not equal in rate.

Final Answer: the rate-determining step is ionisation to the carbocation $\Rightarrow$ $\boxed{\text{C}}$

Answer: (C) Go Back to Q35

Q36.

Solution

Concept – stereoisomers of tartaric acid: Two stereocentres would normally give $2^2 = 4$ stereoisomers, but an internal mirror plane makes one pair identical (the *meso* form), reducing the count.

Step 1 – apply the 2^n maximum: With $n = 2$, the naive maximum is 4.

Step 2 – account for internal symmetry: The (R, S) and (S, R) forms are superimposable (one and the same *meso* compound), so they count as a single achiral isomer.

Step 3 – tally the distinct isomers: (R, R) and (S, S) are a pair of enantiomers (2 isomers) plus one *meso* form $= 3$ distinct stereoisomers.

Final Answer: tartaric acid has 3 distinct stereoisomers $\Rightarrow$ B

Answer: (B) Go Back to Q36

Q37.

Solution

Concept – the Wittig reaction and its by-product: A phosphorus ylide adds to a carbonyl to form a four-membered oxaphosphetane, which collapses to the alkene. The very strong $\mathrm{P{=}O}$ bond that forms drives the reaction.

Step 1 – write the transformation: $\mathrm{R_2C{=}O + Ph_3P{=}CR'_2 \rightarrow R_2C{=}CR'_2 + Ph_3P{=}O}$

Step 2 – identify the driving force: Formation of the extremely stable phosphorus–oxygen double bond (triphenylphosphine oxide) makes the reaction essentially irreversible.

Step 3 – name the by-product: The phosphorus-containing by-product is triphenylphosphine oxide, $\mathrm{Ph_3P{=}O}$.

Why the others are wrong: $\mathrm{Ph_3P}$ is the precursor to the ylide, not the product; no water or alcohol is released.

Final Answer: the by-product is triphenylphosphine oxide $\Rightarrow$ B

Answer: (B) Go Back to Q37

Q38.

Solution

Concept – stereoselectivity of the HWE reaction: The Horner–Wadsworth–Emmons olefination uses a stabilised phosphonate carbanion, which reacts through an equilibrating intermediate that channels the product toward the more stable trans arrangement.

Step 1 – recall the selectivity: Stabilised phosphonate carbanions give predominantly the thermodynamically favoured E (*trans*) alkene.

Step 2 – contrast with non-stabilised Wittig ylides: Non-stabilised ylides give mainly Z; the phosphonate's ester groups reverse this preference to E.

Step 3 – conclude: The HWE reaction is prized as a reliable route to E-alkenes.

Why the others are wrong: Z selectivity and a $50:50$ mixture do not describe the HWE reaction, and an alkene is certainly formed.

Final Answer: the HWE reaction gives mainly the E (*trans*) alkene $\Rightarrow$ $\boxed{\text{C}}$

Answer: (C) Go Back to Q38

Q39.

Solution

Concept – stereochemistry of the classical Wittig reaction: A non-stabilised ylide reacts quickly and irreversibly through a *cis*-oxaphosphetane, which decomposes to give predominantly the Z alkene.

Step 1 – classify the ylide: An ylide with no anion-stabilising group (e.g. from $CH_3PPh_3^+$) is non-stabilised (reactive).

Step 2 – recall the outcome: Such ylides give mainly the Z (*cis*) alkene under kinetic control.

Step 3 – conclude: The major product is the Z (*cis*) alkene.

Why the others are wrong: stabilised ylides (and the HWE variant) give E; the Wittig reaction forms alkenes, not alkynes or epoxides.

Final Answer: a non-stabilised Wittig ylide gives mainly the Z (*cis*) alkene $\Rightarrow$ $\boxed{\text{B}}$

Answer: (B) Go Back to Q39

Q40.

Solution

Concept – carbonyl-to-methylene reductions: Two classic methods reduce $C{=}O$ to CH_2: the Wolff–Kishner (basic, hydrazine) and the Clemmensen (acidic, $Zn(Hg)/HCl$).

Step 1 – read the conditions: Hydrazine (NH_2NH_2) plus a strong base (KOH), heated in a high-boiling solvent, are the Wolff–Kishner conditions.

Step 2 – name the reaction: This is the Wolff–Kishner reduction, in which the carbonyl first forms a hydrazone that is then decomposed by base to the alkane.

Step 3 – distinguish from Clemmensen: The Clemmensen reduction achieves the same overall change but uses acidic $Zn(Hg)/HCl$; it is chosen for base-sensitive substrates, whereas Wolff–Kishner suits acid-sensitive ones.

Why the others are wrong: Rosenmund reduces acid chlorides to aldehydes; Cannizzaro is a disproportionation, not a $C{=}O \rightarrow CH_2$ reduction.

Final Answer: hydrazine/KOH is the Wolff–Kishner reduction $\Rightarrow$ $\boxed{A}$

Answer: (A) Go Back to Q40

Q41.

Solution

Concept – the Claisen ester condensation: Under base, the α-carbanion of one ester attacks the carbonyl carbon of a second ester; loss of alkoxide gives a β-keto ester.

Step 1 – identify the reactants and product: Two ester molecules combine to give a β-keto ester (e.g. ethyl acetate $\rightarrow$ ethyl acetoacetate).

Step 2 – name the reaction: This ester–ester condensation is the Claisen condensation.

Step 3 – distinguish from the aldol: The aldol reaction couples aldehydes/ketones to give a β-hydroxy carbonyl; the Claisen couples esters to give a β-keto ester, expelling an alkoxide.

Why the others are wrong: Wittig forms alkenes, and Cannizzaro is a disproportionation of non-enolisable aldehydes.

Final Answer: coupling two esters to a β-keto ester is the Claisen condensation $\Rightarrow$ $\boxed{B}$

Answer: (B) Go Back to Q41

Q42.

Solution

Concept – selective reduction of an acid chloride to an aldehyde: The Rosenmund reduction hydrogenates an acyl chloride over palladium poisoned with $BaSO_4$, stopping cleanly at the aldehyde stage.

Step 1 – read the conditions: H_2 over $Pd/BaSO_4$ (a poisoned, deactivated catalyst).

Step 2 – name the reaction: This is the Rosenmund reduction, $RCOCl \xrightarrow{H_2,\,Pd/BaSO_4} RCHO$.

Step 3 – explain the selectivity: Poisoning the palladium tempers its activity so the aldehyde is not over-reduced to the alcohol.

Why the others are wrong: Wolff–Kishner and Clemmensen reduce $C{=}O$ to CH_2; the Stephen reduction converts nitriles (not acid chlorides) to aldehydes.

Final Answer: $H_2/Pd\text{-}BaSO_4$ on an acid chloride is the Rosenmund reduction $\Rightarrow$ $\boxed{D}$

Answer: (D) Go Back to Q42

Q43.

Solution

Concept – directing effect of $-OH$ in EAS: Groups with a lone pair on the atom attached to the ring donate electron density by resonance, activating the ring and directing incoming electrophiles to the ortho and para positions.

Step 1 – classify $-OH$: The oxygen lone pair conjugates into the ring, raising the electron density at the ortho and para carbons.

Step 2 – state the consequences: The ring is activated (reacts faster than benzene) and substitution is directed ortho/para.

Step 3 – conclude: $-OH$ is an ortho- and para-directing activating group.

Why the others are wrong: meta-directing deactivators are electron-withdrawing groups (e.g. $-NO_2$); $-OH$ is neither inert nor a deactivator.

Final Answer: $-OH$ is an ortho/para-directing activator $\Rightarrow$ $\boxed{A}$

Answer: (A) Go Back to Q43

Q44.

Solution

Concept – classifying a sigmatropic shift: The order $[i, j]$ counts the number of atoms over which each end of the migrating σ bond moves, starting from the original bond termini.

Step 1 – locate the breaking σ bond: In $1,5$-hexadiene the C3-C4 σ bond breaks.

Step 2 – track each terminus: One end migrates from C3 to C1 (positions $3 \to 1$, i.e. 3 atoms) and the other from C4 to C6 (positions $3 \to 1$ on that fragment).

Step 3 – assign the order: Both termini move by three atoms, so the Cope rearrangement is a $[3, 3]$-sigmatropic shift.

Why the others are wrong: $[1, 3]$, $[1, 5]$ and $[1, 7]$ describe hydrogen or alkyl shifts where only one terminus migrates; the Cope shifts both.

Final Answer: the Cope rearrangement is a $[3, 3]$-sigmatropic shift $\Rightarrow \boxed{\text{D}}$

Answer: (D) Go Back to Q44

Q45.

Solution

Concept – transition state of the Claisen rearrangement: The Claisen rearrangement of an allyl vinyl ether is a concerted $[3, 3]$-sigmatropic process; its six reorganising atoms pass through a cyclic, chair-like transition state.

Step 1 – count the atoms in the array: Three atoms from the allyl unit and three from the vinyl-oxygen unit make a six-atom cyclic array.

Step 2 – identify the geometry: These six atoms adopt a six-membered, chair-like transition state (as in the Cope rearrangement).

Step 3 – conclude: The reaction is concerted through a six-membered cyclic transition state, giving a γ, δ-unsaturated carbonyl product.

Why the others are wrong: being a concerted pericyclic reaction, it involves no radicals or carbocations, and the array is six-membered, not four.

Final Answer: it proceeds via a six-membered cyclic (chair-like) transition state $\Rightarrow \boxed{\text{A}}$

Answer: (A) Go Back to Q45

Q46.

Solution

Concept – Woodward–Hoffmann rule for sigmatropic H-shifts: For a thermal sigmatropic hydrogen shift, a $(4n + 2)$-electron process is suprafacial-allowed, whereas a $4n$ process would have to be antarafacial (geometrically hard for H).

Step 1 – count the electrons: A $[1, 5]$-H shift involves 6 electrons in the cyclic transition state ($4n + 2$ with $n = 1$).

Step 2 – apply the thermal selection rule: For $4n + 2$ electrons under thermal conditions, the allowed mode is suprafacial.

Step 3 – conclude: The thermal $[1, 5]$-H shift proceeds suprafacially, which is why it occurs readily (e.g. in cyclopentadienes).

Why the others are wrong: the antarafacial mode belongs to thermal $[1, 3]$-H shifts (which are therefore rare); the $[1, 5]$-H shift is symmetry-allowed and needs no diradical.

Final Answer: the thermal $[1, 5]$-H shift proceeds suprafacially $\Rightarrow$ $\boxed{\text{C}}$

Answer: (C) Go Back to Q46

Answer Key

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