# GATE Chemistry

## Sample Paper – 8

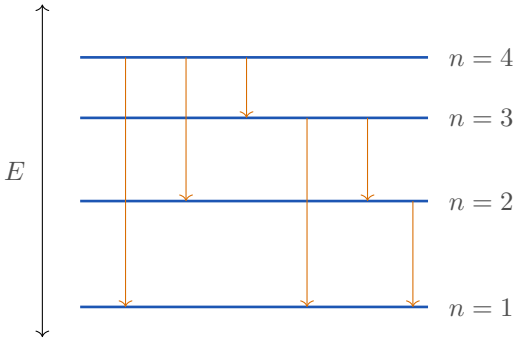
**Duration: 128 Minutes** **Maximum Marks: 72**

### 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.** An excited hydrogen atom relaxes from the $n = 4$ level, and the atom can de-excite through every allowed downward step, as sketched below. The total number of distinct emission lines that can appear when the electron cascades from $n = 4$ down to the $n = 1$ ground level is: **[1 mark]**




(A) 3

(B) 4

(C) 6

(D) 10

**Q2.** The ground-state electronic configuration of the carbon atom is $1s^2\,2s^2\,2p^2$. Applying Hund's rules to the two equivalent $2p$ electrons, the ground-state atomic term symbol ${}^{2S+1}L_J$ of carbon is: **[1 mark]**

(A) ${}^1S_0$

(B) ${}^3P_2$

(C) ${}^1D_2$

(D) ${}^3P_0$

**Q3.** The fluorine atom has the ground configuration $1s^2\,2s^2\,2p^5$, that is, one electron short of a filled $2p$ subshell (a single hole). The corresponding ground-state term symbol ${}^{2S+1}L_J$ of the fluorine atom is: **[1 mark]**

(A) ${}^2P_{1/2}$

(B) ${}^2S_{1/2}$

(C) ${}^1S_0$

(D) ${}^2P_{3/2}$

**Q4.** A molecule shows a pure rotational (microwave) absorption spectrum only if it possesses a permanent electric dipole moment. Among the gas-

phase molecules below, the one that is *microwave active* is: [1 mark]

(A) $N_2$

(B) $HCl$

(C) $O_2$

(D) $CO_2$

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

(A) $1$

(B) $0$

(C) $2$

(D) $3$

**Q6.** A coloured solution transmits $25\%$ of the incident monochromatic light, so its transmittance is $T = 0.25$. Using $A = -\log_{10} T$, the absorbance of the solution is nearest to: [1 mark]

(A) $0.60$

(B) $0.25$

(C) $1.39$

(D) $0.75$

## Physical Chemistry: Thermodynamics, Kinetics and Electrochemistry

**Q7.** A non-volatile, non-electrolyte solute is dissolved in water to give a $0.50\ \text{mol kg}^{-1}$ solution. Taking the cryoscopic constant of water as $K_f = 1.86\ \text{K kg mol}^{-1}$, the depression of the freezing point $\Delta T_f = K_f\, m$ is: [1 mark]

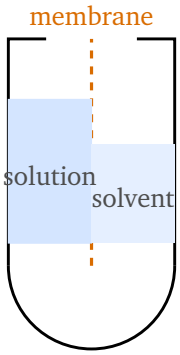
(A) $1.86\ \text{K}$

(B) $0.93\ \mathrm{K}$

(C) $0.50\ \mathrm{K}$

(D) $3.72\ \mathrm{K}$

**Q8.** A dilute aqueous solution of a non-electrolyte has a concentration of $0.10\ \mathrm{mol\,L^{-1}}$ at $300\ \mathrm{K}$, and is separated from pure solvent by a semipermeable membrane as sketched. Using $\pi = MRT$ with $R = 0.0821\ \mathrm{L\,atm\,mol^{-1}K^{-1}}$, the osmotic pressure of the solution is: **[1 mark]**




(A) $24.6\ \mathrm{atm}$

(B) $0.82\ \mathrm{atm}$

(C) $2.46\ \mathrm{atm}$

(D) $1.23\ \mathrm{atm}$

**Q9.** $\mathrm{NaCl}$ is a strong electrolyte that dissociates completely into two ions in water, so its van't Hoff factor is $i = 2$. For a $0.10\ \mathrm{mol\,kg^{-1}}$ aqueous $\mathrm{NaCl}$ solution with $K_b(\mathrm{water}) = 0.52\ \mathrm{K\,kg\,mol^{-1}}$, the elevation of boiling point $\Delta T_b = i\,K_b\,m$ is: **[1 mark]**

(A) $0.052\ \mathrm{K}$

(B) $0.104\ \mathrm{K}$

(C) $0.52\ \mathrm{K}$

(D) $0.208\ \mathrm{K}$

**Q10.** A galvanic cell has a standard cell potential $E^\circ_{\mathrm{cell}} = 0.50\ \mathrm{V}$ and its balanced reaction transfers $n = 2$ moles of electrons. Using $\Delta G^\circ = -nFE^\circ_{\mathrm{cell}}$, the standard Gibbs free-energy change is nearest to: **[1 mark]**

(A) $-48.25\ \text{kJ mol}^{-1}$

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

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

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

**Q11.** The rate law for a certain reaction is rate $= k[A]^2$, and the rate is measured in $\text{mol L}^{-1}\text{s}^{-1}$ while concentration is in $\text{mol L}^{-1}$. The units of the rate constant $k$ for this second-order reaction are: **[1 mark]**

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

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

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

(D) dimensionless

**Q12.** An endothermic reaction has $\Delta H = +30\ \text{kJ mol}^{-1}$ and $\Delta S = +100\ \text{J mol}^{-1}\text{K}^{-1}$, both taken to be temperature-independent. The temperature above which the reaction becomes spontaneous ($\Delta G = 0$ when $T = \Delta H/\Delta S$) is: **[1 mark]**

(A) $100\ \text{K}$

(B) $3000\ \text{K}$

(C) $30\ \text{K}$

(D) $300\ \text{K}$

**Q13.** A constant current of $9.65\ \text{A}$ is passed through aqueous $\text{CuSO}_4$ for $1000\ \text{s}$, depositing copper by $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ (take the molar mass of copper as $63.5\ \text{g mol}^{-1}$). The mass of copper deposited at the cathode is: **[1 mark]**

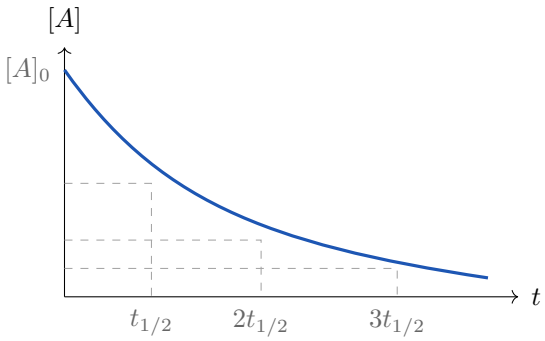
(A) $6.35\ \text{g}$

(B) $3.175\ \text{g}$

(C) $63.5\ \text{g}$

(D) $1.588\ \text{g}$

**Q14.** A first-order reaction is monitored, and its concentration decays exponentially with time as shown. After exactly three successive half-lives have elapsed, the fraction of the original reactant that still remains is: [1 mark]




(A) $25\%$

(B) $12.5\%$

(C) $6.25\%$

(D) $50\%$

## Inorganic Chemistry: Main Group and Periodic Properties

**Q15.** The electron gain enthalpy (first electron affinity) of chlorine is *more* negative than that of fluorine, which is an apparent anomaly since fluorine sits above chlorine in group 17. This anomaly is best explained by: [1 mark]

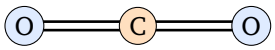
(A) the small size of the F atom, whose compact $2p$ subshell causes strong inter-electronic repulsion on adding an electron

(B) fluorine being less electronegative than chlorine

(C) the larger nuclear charge of chlorine

(D) relativistic contraction of the fluorine $1s$ shell

**Q16.** Carbon dioxide is a discrete linear gaseous molecule (shown), whereas silicon dioxide is a three-dimensional giant covalent solid. The principal reason for this striking difference between the group-14 dioxides is that: [1 mark]




O=C=O (linear)

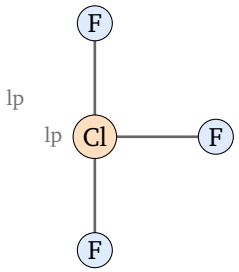
(A) carbon forms strong $p\pi$–$p\pi$ double bonds to oxygen, while silicon does not and instead forms four single $\mathrm{Si}-\mathrm{O}$ bonds

(B) silicon is more electronegative than carbon

(C) the carbon atom is larger than the silicon atom

(D) $\mathrm{SiO_2}$ is an ionic compound

**Q17.** In chlorine trifluoride $\mathrm{ClF_3}$ the central chlorine has three bonding pairs and two lone pairs (an $\mathrm{AX_3E_2}$ system), giving the geometry sketched below. The molecular shape of $\mathrm{ClF_3}$ is: **[1 mark]**




(A) trigonal planar

(B) T-shaped

(C) trigonal pyramidal

(D) trigonal bipyramidal

**Q18.** In the thiosulfate ion $\mathrm{S_2O_3^{2-}}$, each oxygen is assigned an oxidation number of $-2$ and the ion carries a charge of $-2$. The *average* oxidation state of sulfur in $\mathrm{S_2O_3^{2-}}$ is: **[1 mark]**

(A) $+6$

(B) $+4$

(C) $+2$

(D) $0$

**Q19.** The diagonal relationship in the periodic table links an element with the one placed diagonally to its lower right, on account of similar charge-to-size ratios. In its chemistry, beryllium most closely resembles: **[1 mark]**

(A) sodium

(B) calcium

(C) boron

(D) aluminium

**Q20.** Nitrogen exhibits a maximum covalency of four, whereas the heavier congener phosphorus can expand its covalency to five or six (as in $PF_5$ and $PF_6^-$). This difference is chiefly because: **[1 mark]**

(A) nitrogen has no low-lying $d$ orbitals in its valence shell, while phosphorus can use its $3d$ orbitals

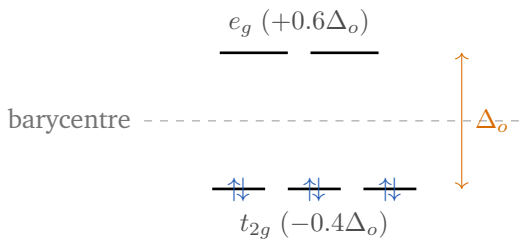
(B) nitrogen is less electronegative than phosphorus

(C) the phosphorus atom is smaller than the nitrogen atom

(D) nitrogen has more valence electrons than phosphorus

## Inorganic Chemistry: Coordination Compounds and Organometallics

**Q21.** In an octahedral field the $d$ orbitals split into a lower $t_{2g}$ set ($-0.4\Delta_o$) and an upper $e_g$ set ($+0.6\Delta_o$). For a strong-field (low-spin) $d^6$ ion, all six electrons occupy the $t_{2g}$ set as shown. Ignoring the pairing-energy term, the crystal-field stabilization energy (CFSE) is: **[2 marks]**




(A) $-1.6\,\Delta_o$

(B) $-0.6\,\Delta_o$

(C) $-2.4\,\Delta_o$

(D) $0$

**Q22.** For a high-spin (weak-field) octahedral $d^5$ ion, the five electrons are distributed as $t_{2g}^3 e_g^2$, with three electrons at $-0.4\Delta_o$ and two at $+0.6\Delta_o$. The crystal-field stabilization energy of this configuration is: **[2 marks]**

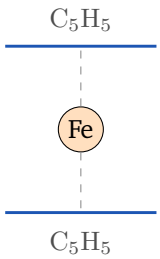
(A) $-2.0\,\Delta_o$

(B) $-1.2\,\Delta_o$

(C) $+0.5\,\Delta_o$

(D) $0$

**Q23.** Ferrocene, $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2]$, is the sandwich complex sketched below in which an iron atom lies between two cyclopentadienyl rings, each an $\eta^5$ five-electron donor (neutral counting). Its total valence-electron count, which explains its stability, is: **[2 marks]**




(A) 16

(B) 20

(C) 18

(D) 14

**Q24.** The low-spin octahedral complex $[\mathrm{Fe(CN)_6}]^{3-}$ has a $d^5$ iron(III) centre in a strong field, so its $t_{2g}^5$ configuration leaves just one unpaired electron. Using $\mu = \sqrt{n(n+2)}$ BM, its spin-only magnetic moment is nearest to: **[2 marks]**

(A) 5.92 BM

(B) 4.90 BM

(C) $3.87$ BM

(D) $1.73$ BM

**Q25.** In the complex ion $[Co(NH_3)_4Cl_2]^+$, ammonia is a neutral ligand and chloride carries a $-1$ charge. The oxidation state of the central cobalt ion is: **[2 marks]**

(A) $+1$

(B) $+2$

(C) $+3$

(D) $0$

**Q26.** Whether an octahedral complex is high-spin or low-spin depends on the field strength of its ligands in the spectrochemical series. Among the octahedral iron(III) complexes below, the one expected to be *low-spin* (fewest unpaired electrons) is: **[2 marks]**

(A) $[FeF_6]^{3-}$

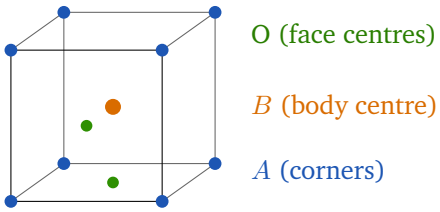
(B) $[Fe(CN)_6]^{3-}$

(C) $[Fe(H_2O)_6]^{3+}$

(D) $[FeCl_6]^{3-}$

## Inorganic Chemistry: Solid State and Bioinorganic

**Q27.** The perovskite structure, adopted by oxides such as $CaTiO_3$ and $BaTiO_3$, has the cubic unit cell sketched below: a large $A$ cation at the cube corners, a small $B$ cation at the body centre, and oxide ions at the face centres. The general stoichiometric formula of a perovskite oxide is: **[2 marks]**




(A) $ABO_3$

(B) $A_2BO_4$

(C) $AB_2O_4$

(D) $ABO_2$

**Q28.** When a superconductor such as $YBa_2Cu_3O_7$ (YBCO) is cooled below its critical temperature $T_c$, it not only loses all electrical resistance but also shows the Meissner effect. The Meissner effect refers to: **[2 marks]**

(A) a sudden rise to infinite electrical resistance

(B) the complete expulsion of magnetic flux from the interior of the material

(C) the onset of strong paramagnetism

(D) a large increase in the material's resistivity

**Q29.** Vitamin $B_{12}$ (cobalamin) is an essential biomolecule built around a corrin macrocycle that chelates a central metal ion. The metal ion at the heart of vitamin $B_{12}$ is: **[2 marks]**

(A) $Fe^{2+}$

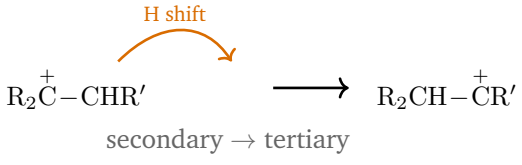
(B) $Zn^{2+}$

(C) $Co^{3+}$

(D) $Mg^{2+}$

## Organic Chemistry: Stereochemistry and Reaction Mechanisms

**Q30.** A less stable carbocation can convert into a more stable one, as illustrated below where an adjacent group migrates to the electron-deficient carbon. The rearrangement that transforms a secondary carbocation into a more stable tertiary carbocation proceeds by a: **[2 marks]**



(A) $1,2$-hydride (or $1,2$-alkyl) shift to the adjacent electron-deficient carbon

(B) $1,1$-elimination of a proton

(C) retro-aldol cleavage

(D) no rearrangement is possible for carbocations

**Q31.** A compound has two stereogenic centres bearing the *same* set of substituents, so one of the diastereomers is an achiral meso form (as in tartaric acid). Taking this internal symmetry into account, the total number of distinct stereoisomers of such a molecule is: **[2 marks]**

(A) $2$

(B) $3$

(C) $4$

(D) $1$

**Q32.** Two enantiomers of a chiral compound are non-superimposable mirror images. Under ordinary (achiral) conditions the two enantiomers are identical in every scalar physical property except one; they differ in: **[2 marks]**

(A) melting point

(B) boiling point

(C) solubility in water

(D) the direction in which they rotate plane-polarized light

**Q33.** In an $S_N1$ solvolysis the rate-determining step is unimolecular ionization to a carbocation, so the substrate that gives the most stable carbocation reacts fastest. Among the following bromides, the one that undergoes $S_N1$ solvolysis fastest is: **[2 marks]**

(A) *tert*-butyl bromide

(B) ethyl bromide

(C) methyl bromide

(D) $n$-propyl bromide

**Q34.** Carbocations are stabilized both by hyperconjugation/induction from alkyl groups and, more powerfully, by resonance delocalization of the positive charge. Among the cations below, the *most* stabilized is the: **[2 marks]**

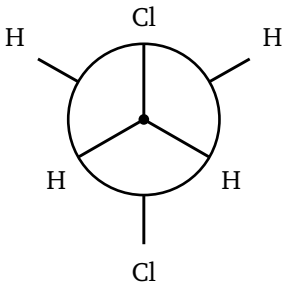
(A) ethyl cation

(B) isopropyl cation

(C) *tert*-butyl cation

(D) benzyl cation

**Q35.** The Newman projection of $1,2$-dichloroethane, viewed along the $\mathrm{C1}-\mathrm{C2}$ bond, is shown below. The conformation of *lowest* energy (minimum steric and dipole–dipole repulsion) is the staggered one in which the two chlorine atoms are: **[2 marks]**




(A) gauche ($60^\circ$ dihedral)

(B) anti ($180^\circ$ dihedral)

(C) eclipsed ($0^\circ$ dihedral)

(D) syn-periplanar eclipsed with the chlorines together

**Q36.** Propene, $\mathrm{CH_3CH{=}CH_2}$, is treated with hydrogen bromide in the *absence* of any peroxide. Following Markovnikov's rule, the hydrogen adds to the terminal ($\mathrm{CH_2}$) carbon and the bromine to the more substituted carbon, so the major product is: **[2 marks]**

(A) 1-bromopropane

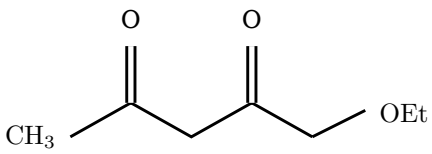
(B) 2-bromopropane

(C) 1, 2-dibromopropane

(D) propan-2-ol

## Organic Chemistry: Named Reactions and Synthesis

**Q37.** Two molecules of ethyl acetate, in the presence of sodium ethoxide, undergo self-condensation to give ethyl 3-oxobutanoate (ethyl acetoacetate), a $\beta$-keto ester whose skeleton is shown below. This ester-to-$\beta$-keto-ester condensation is the: **[2 marks]**




ethyl acetoacetate ($\beta$-keto ester)

(A) Aldol reaction

(B) Cannizzaro reaction

(C) Perkin reaction

(D) Claisen condensation

**Q38.** An aromatic aldehyde is heated with an aliphatic acid anhydride and the sodium salt of the corresponding acid, giving an $\alpha, \beta$-unsaturated aromatic acid such as cinnamic acid from benzaldehyde. This classic synthesis of $\alpha, \beta$-unsaturated acids is the: **[2 marks]**

(A) Aldol reaction

(B) Claisen condensation

(C) Perkin reaction

(D) Cannizzaro reaction

**Q39.** An aldehyde condenses with a compound bearing an active methylene group (for example malonic ester or malononitrile) in the presence of a

weak amine base to give an $\alpha,\beta$-unsaturated product. This condensation of a carbonyl with an active-methylene compound is the: [2 marks]

(A) Wittig reaction

(B) Aldol reaction

(C) Knoevenagel condensation

(D) Reformatsky reaction

**Q40.** Two molecules of benzaldehyde combine in the presence of cyanide ion (or an $N$-heterocyclic carbene catalyst) to form benzoin, $\mathrm{PhCH(OH)COPh}$, an $\alpha$-hydroxy ketone. This carbon–carbon bond-forming dimerization is the: [2 marks]

(A) benzoin condensation

(B) aldol condensation

(C) Cannizzaro reaction

(D) Claisen condensation

**Q41.** An $\alpha$-halo ester is treated with zinc metal to form an organozinc enolate, which then adds to the carbonyl of an aldehyde or ketone; acidic work-up gives a $\beta$-hydroxy ester. This synthesis of $\beta$-hydroxy esters is the: [2 marks]

(A) Reformatsky reaction

(B) Wittig reaction

(C) Grignard reaction

(D) Perkin reaction

**Q42.** A ketone bearing an $\alpha$-hydrogen reacts with formaldehyde and a secondary amine (used as its hydrochloride) to give a $\beta$-amino ketone. This amino-methylation of a carbonyl compound is the: [2 marks]

(A) Aldol reaction

(B) Michael addition

(C) Mannich reaction

(D) Cannizzaro reaction

**Q43.** A single molecule of a $1,7$-diester (for example diethyl adipate), on treatment with a strong base, undergoes an intramolecular ester condensation to form a cyclic $\beta$-keto ester. This intramolecular version of the Claisen condensation is the: **[2 marks]**

(A) Dieckmann condensation

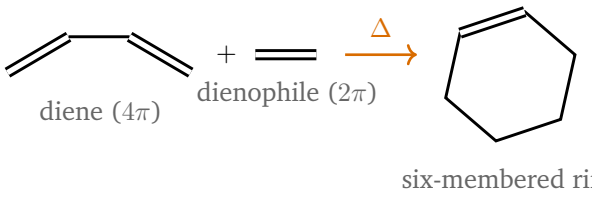
(B) Claisen–Schmidt condensation

(C) Wittig reaction

(D) Clemmensen reduction

## Organic Chemistry: Pericyclic, Photochemistry and Biomolecules

**Q44.** In the Diels–Alder reaction a conjugated diene combines with a dienophile in a thermal $[4+2]$ cycloaddition, as sketched below, forming two new $\sigma$ bonds in a single cyclic transition state. The total number of $\pi$ electrons participating in that transition state is: **[2 marks]**



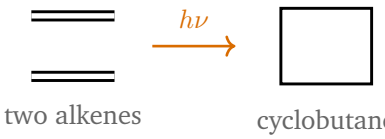

(A) $2$

(B) $8$

(C) $4$

(D) $6$

**Q45.** Two alkene molecules combine in a $[2+2]$ cycloaddition to give a cyclobutane ring. According to the Woodward–Hoffmann rules, this $4n$-electron $(4\pi)$ suprafacial–suprafacial cycloaddition is: **[2 marks]**




(A) thermally allowed in a suprafacial–suprafacial sense

(B) photochemically allowed in a suprafacial–suprafacial sense

(C) thermally allowed in a conrotatory sense

(D) forbidden under all conditions

**Q46.** In the Watson–Crick double helix of DNA, the two strands are held together by hydrogen bonds between complementary bases. Through a pair of hydrogen bonds, the base adenine specifically pairs with: **[2 marks]**

(A) guanine

(B) cytosine

(C) thymine

(D) uracil

## Detailed Solutions

### Q1.

**Solution**

**Concept – counting emission lines in a cascade:** When an electron in a hydrogen atom drops from a level $n$ down to the ground state, it can pass through every intermediate level, and the number of distinct lines equals the number of ways of choosing two levels out of $n$.

**Step 1 – write the counting formula:** Number of lines $= \dfrac{n(n-1)}{2}$.

**Step 2 – substitute the top level $n = 4$:** Number of lines $= \dfrac{4(4-1)}{2}$.

**Step 3 – evaluate the arithmetic:** $= \dfrac{4 \times 3}{2} = \dfrac{12}{2} = 6$.

**Step 4 – cross-check by listing the transitions:** $4 \to 3,\ 4 \to 2,\ 4 \to 1,\ 3 \to 2,\ 3 \to 1,\ 2 \to 1$, which is exactly $6$ lines.

**Final Answer:** $6$ emission lines $\Rightarrow$ $\boxed{\text{C}}$

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

### Q2.

**Solution**

**Concept – Russell–Saunders term symbol $^{2S+1}L_J$:** Read off the total spin $S$, total orbital angular momentum $L$, and total angular momentum $J$ for the ground state using Hund's rules.

**Step 1 – place the two equivalent $2p$ electrons:** To maximize spin, the two electrons occupy separate $p$ orbitals with parallel spins, giving $S = \frac{1}{2} + \frac{1}{2} = 1$, so the multiplicity is $2S + 1 = 3$.

**Step 2 – find the total orbital momentum $L$:** With the two electrons in $m_l = +1$ and $m_l = 0$, the maximum $M_L = 1$, so $L = 1$, which is a $P$ term.

**Step 3 – apply Hund's third rule for $J$:** The $2p$ subshell is less than half filled, so the lowest level has the minimum $J = |L - S| = |1 - 1| = 0$.

**Step 4 – assemble the term symbol:** $^3P_0$.

**Final Answer:** carbon ground term $= {}^3P_0 \Rightarrow$ $\boxed{\text{D}}$

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

## Q3.

**Solution**

**Concept – term symbol of a nearly filled subshell:** A $p^5$ configuration has a single vacancy (hole), and a hole behaves like a single electron for the purposes of $S$ and $L$.

**Step 1 – get the spin:** One unpaired electron (equivalently one hole) gives $S = \frac{1}{2}$, so the multiplicity is $2S + 1 = 2$.

**Step 2 – get the orbital momentum:** The single hole sits in a $p$ orbital, so $L = 1$, a $P$ term.

**Step 3 – apply Hund's third rule for $J$:** The $2p$ subshell is *more* than half filled, so the lowest level takes the maximum $J = L + S = 1 + \frac{1}{2} = \frac{3}{2}$.

**Step 4 – assemble the term symbol:** ${}^2P_{3/2}$.

**Final Answer:** fluorine ground term $= {}^2P_{3/2} \Rightarrow$ D

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

## Q4.

**Solution**

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

**Step 1 – test each molecule for a permanent dipole:** $N_2$ and $O_2$ are homonuclear diatomics, so they are non-polar (dipole $= 0$).

**Step 2 – consider $CO_2$:** $CO_2$ is linear and symmetric (O=C=O); the two bond dipoles cancel, so its net dipole is zero and it is microwave inactive.

**Step 3 – consider HCl:** HCl is a heteronuclear diatomic with a permanent dipole moment, so it is microwave active.

**Final Answer:** HCl is microwave active $\Rightarrow$ B

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

## Q5.

**Solution**

**Concept – radial nodes of a hydrogenic orbital:** The number of radial (spherical) nodes is $n - l - 1$.

**Step 1 – identify the quantum numbers of a $3p$ orbital:** $n = 3$ and, for a $p$ orbital, $l = 1$.

**Step 2 – substitute into the formula:** Radial nodes $= n - l - 1 = 3 - 1 - 1$.

**Step 3 – evaluate:** $= 1$.

**Step 4 – cross-check the total node count:** Total nodes $= n - 1 = 2$; of these the angular nodes $= l = 1$, leaving $2 - 1 = 1$ radial node, which is consistent.

**Final Answer:** $1$ radial node $\Rightarrow$ A

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

## Q6.

### Solution

**Concept – absorbance from transmittance:** Absorbance and transmittance are related by $A = -\log_{10} T$, where $T$ is the fraction of light transmitted.

**Step 1 – write down the transmittance:** $T = 25\% = 0.25$.

**Step 2 – substitute into $A = -\log_{10} T$:** $A = -\log_{10}(0.25)$.

**Step 3 – simplify using $0.25 = 1/4$:** $A = -\log_{10}(1/4) = \log_{10} 4$.

**Step 4 – evaluate:** $\log_{10} 4 = 2\log_{10} 2 = 2(0.301) = 0.602 \approx 0.60$.

**Final Answer:** $A \approx 0.60 \Rightarrow$ A

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

## Q7.

### Solution

**Concept – freezing-point depression (a colligative property):** $\Delta T_f = K_f\, m$, where $K_f$ is the cryoscopic constant and $m$ the molality, valid for a non-electrolyte ($i = 1$).

**Step 1 – list the data:** $K_f = 1.86\ \mathrm{K\,kg\,mol^{-1}}$ and $m = 0.50\ \mathrm{mol\,kg^{-1}}$.

**Step 2 – substitute into the formula:** $\Delta T_f = 1.86 \times 0.50$.

**Step 3 – evaluate:** $\Delta T_f = 0.93\ \mathrm{K}$.

**Step 4 – interpret:** The solution freezes $0.93$ K below the pure-solvent freezing point.

**Final Answer:** $\Delta T_f = 0.93\ \mathrm{K} \Rightarrow$ B

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

## Q8.

**Solution**

**Concept – osmotic pressure (a colligative property):** $\pi = MRT$, where $M$ is the molar concentration, $R$ the gas constant and $T$ the absolute temperature.

**Step 1 – list the data:** $M = 0.10\ \text{mol L}^{-1}$, $R = 0.0821\ \text{L atm mol}^{-1}\text{K}^{-1}$, $T = 300\ \text{K}$.

**Step 2 – substitute into $\pi = MRT$:** $\pi = 0.10 \times 0.0821 \times 300$.

**Step 3 – multiply step by step:** $0.10 \times 0.0821 = 0.00821$; then $0.00821 \times 300 = 2.463$.

**Step 4 – round to the data:** $\pi \approx 2.46\ \text{atm}$.

**Final Answer:** $\pi \approx 2.46\ \text{atm} \Rightarrow \boxed{\text{C}}$

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

## Q9.

**Solution**

**Concept – boiling-point elevation with the van't Hoff factor:** $\Delta T_b = i\,K_b\,m$, where $i$ accounts for the number of particles produced per formula unit.

**Step 1 – find $i$ for NaCl:** $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ gives two ions, so $i = 2$.

**Step 2 – list the remaining data:** $K_b = 0.52\ \text{K kg mol}^{-1}$ and $m = 0.10\ \text{mol kg}^{-1}$.

**Step 3 – substitute into the formula:** $\Delta T_b = 2 \times 0.52 \times 0.10$.

**Step 4 – evaluate:** $\Delta T_b = 0.104\ \text{K}$.

**Final Answer:** $\Delta T_b = 0.104\ \text{K} \Rightarrow \boxed{\text{B}}$

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

## Q10.

**Solution**

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

**Step 1 – list the data:** $n = 2$, $F = 96500\ \text{C mol}^{-1}$, $E^\circ_{\text{cell}} = 0.50\ \text{V}$.

**Step 2 – substitute into the formula:** $\Delta G^\circ = -(2)(96500)(0.50)$.

**Step 3 – evaluate in joules:** $\Delta G^\circ = -96500\ \text{J mol}^{-1}$.

**Step 4 – convert to kilojoules:** $\Delta G^\circ = -96.5\ \text{kJ mol}^{-1}$; the negative sign confirms a spontaneous cell reaction.

**Final Answer:** $\Delta G^\circ = -96.5\ \text{kJ mol}^{-1} \Rightarrow \boxed{\text{D}}$

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

## Q11.

### Solution

**Concept – dimensions of a rate constant:** The units of $k$ follow from making both sides of the rate law dimensionally consistent.

**Step 1 – write the rate law:** rate $= k[A]^2$, so $k = \dfrac{\text{rate}}{[A]^2}$.

**Step 2 – insert the units:** $k = \dfrac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2}$.

**Step 3 – simplify the concentration powers:** $k = \text{mol L}^{-1}\text{s}^{-1} \times \text{mol}^{-2}\text{L}^2 = \text{mol}^{-1}\text{L s}^{-1}$.

**Step 4 – write in conventional order:** $k = \text{L mol}^{-1}\text{s}^{-1}$, the standard units of a second-order rate constant.

**Final Answer:** $k$ has units $\text{L mol}^{-1}\text{s}^{-1} \Rightarrow \boxed{\text{A}}$

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

## Q12.

### Solution

**Concept – spontaneity crossover temperature:** For a reaction with positive $\Delta H$ and positive $\Delta S$, $\Delta G = \Delta H - T\Delta S$ turns negative above the temperature at which $\Delta G = 0$, i.e. $T = \Delta H/\Delta S$.

**Step 1 – convert units so they match:** $\Delta H = +30\ \text{kJ mol}^{-1} = 30000\ \text{J mol}^{-1}$ and $\Delta S = +100\ \text{J mol}^{-1}\text{K}^{-1}$.

**Step 2 – set $\Delta G = 0$ and solve for $T$:** $T = \dfrac{\Delta H}{\Delta S} = \dfrac{30000}{100}$.

**Step 3 – evaluate:** $T = 300\ \text{K}$.

**Step 4 – interpret:** Above $300\ \text{K}$ the $-T\Delta S$ term outweighs $\Delta H$, so $\Delta G < 0$ and the reaction becomes spontaneous.

**Final Answer:** $T = 300\ \text{K} \Rightarrow \boxed{\text{D}}$

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

## Q13.

**Solution**

**Concept – Faraday's laws of electrolysis:** The charge passed fixes the moles of electrons, and the electrode half-reaction fixes how many electrons deposit one mole of metal.

**Step 1 – find the charge passed:** $Q = I \times t = 9.65\ \text{A} \times 1000\ \text{s} = 9650\ \text{C}$.

**Step 2 – convert charge to moles of electrons:** $n_e = \dfrac{Q}{F} = \dfrac{9650}{96500} = 0.10\ \text{mol}$.

**Step 3 – use the half-reaction** $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$**:** Moles of $\text{Cu} = \dfrac{n_e}{2} = \dfrac{0.10}{2} = 0.05\ \text{mol}$.

**Step 4 – convert to mass:** $\text{mass} = 0.05 \times 63.5 = 3.175\ \text{g}$.

**Final Answer:** mass of $\text{Cu} = 3.175\ \text{g} \Rightarrow \boxed{\text{B}}$

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

## Q14.

**Solution**

**Concept – first-order decay in units of half-life:** After each half-life the concentration halves, so after $k$ half-lives the fraction remaining is $(1/2)^k$, independent of the initial amount.

**Step 1 – set the number of half-lives:** $k = 3$ half-lives have elapsed.

**Step 2 – write the fraction remaining:** $\text{fraction} = \left(\dfrac{1}{2}\right)^3$.

**Step 3 – evaluate:** $= \dfrac{1}{8}$.

**Step 4 – convert to a percentage:** $\dfrac{1}{8} = 0.125 = 12.5\%$, matching the third dashed drop on the decay curve.

**Final Answer:** $12.5\%$ remains $\Rightarrow \boxed{\text{B}}$

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

## Q15.

**Solution**

**Concept – why chlorine has a more negative electron affinity than fluorine:** Although electron affinity should decrease down a group, the first member (fluorine) is anomalous because its valence shell is very compact.

**Step 1 – compare the sizes:** Fluorine's incoming electron enters the small, compact $2p$ subshell, whereas chlorine's enters the larger $3p$ subshell.

**Step 2 – account for electron–electron repulsion:** In fluorine's small $2p$ shell the added electron feels strong repulsion from the electrons already crowded there, which offsets much of the energy released.

**Step 3 – conclude:** Chlorine, being larger, releases more energy on adding an electron, so its electron gain enthalpy is the more negative of the two.

**Step 4 – reject the distractors:** Fluorine is in fact more electronegative than chlorine, and chlorine's larger nuclear charge would not by itself reverse the trend; the compact-size repulsion argument is the accepted explanation.

**Final Answer:** compact $2p$ shell causes strong repulsion in F $\Rightarrow$ A

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

## Q16.

### Solution

**Concept – $p\pi$–$p\pi$ bonding and the first-row anomaly:** Second-period elements such as carbon form strong multiple bonds using $2p$–$2p$ side-on overlap; the heavier third-period elements overlap poorly and prefer single bonds.

**Step 1 – describe $CO_2$:** Carbon forms two strong $C{=}O$ double bonds ($p\pi$–$p\pi$), giving a small, self-contained linear molecule that exists as a gas.

**Step 2 – describe $SiO_2$:** Silicon's larger, more diffuse $3p$ orbitals overlap poorly side-on, so silicon avoids $Si{=}O$ double bonds and instead forms four single $Si{-}O$ bonds to four oxygens.

**Step 3 – consequence for the solid:** Each oxygen bridges two silicons, generating a three-dimensional covalent network, hence a high-melting solid.

**Step 4 – reject the distractors:** Silicon is less (not more) electronegative than carbon, carbon is smaller (not larger) than silicon, and $SiO_2$ is covalent, not ionic.

**Final Answer:** carbon's $p\pi$–$p\pi$ double bonding $\Rightarrow$ A

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

## Q17.

**Solution**

**Concept – VSEPR shape of an $AX_3E_2$ molecule:** Five electron domains adopt a trigonal-bipyramidal arrangement; lone pairs take the equatorial positions to minimize repulsion.

**Step 1 – count the domains on chlorine:** Three $Cl-F$ bonds plus two lone pairs give five electron domains (steric number $5$).

**Step 2 – place the lone pairs:** Both lone pairs occupy equatorial sites of the trigonal bipyramid, where they suffer the least repulsion.

**Step 3 – locate the atoms:** The three fluorines then sit at the two axial positions and the one remaining equatorial position.

**Step 4 – name the resulting shape:** Two axial bonds nearly collinear with one equatorial bond gives a bent "T" outline, i.e. a T-shaped molecule.

**Final Answer:** $ClF_3$ is T-shaped $\Rightarrow$ $\boxed{B}$

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

## Q18.

**Solution**

**Concept – average oxidation state from a charge balance:** The sum of oxidation numbers of all atoms equals the overall charge of the ion.

**Step 1 – assign the known oxidation numbers:** Each of the three oxygens is $-2$, contributing $3(-2) = -6$.

**Step 2 – set up the balance for $S_2O_3^{2-}$:** Let the average sulfur oxidation state be $x$; then $2x + (-6) = -2$.

**Step 3 – solve for $x$:** $2x = -2 + 6 = 4$, so $x = +2$.

**Step 4 – interpret:** The value $+2$ is the *average*; the two sulfur atoms are actually inequivalent, but their mean oxidation state is $+2$.

**Final Answer:** average sulfur oxidation state $= +2 \Rightarrow$ $\boxed{C}$

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

## Q19.

**Solution**

**Concept – the diagonal relationship:** The first element of a group often resembles the second element of the next group (diagonally down-right) because the two have comparable charge-to-radius ratios and electronegativities.

**Step 1 – locate beryllium and its diagonal partner:** Beryllium is at the top of group 2; moving one step right and down leads to aluminium in group 13.

**Step 2 – cite the shared chemistry:** Both $\mathrm{Be}$ and $\mathrm{Al}$ form amphoteric oxides, covalent halides that hydrolyze, and both are passivated by nitric acid.

**Step 3 – conclude:** Beryllium therefore most closely resembles aluminium.

**Step 4 – reject the distractors:** Calcium is Be's own group neighbour (not a diagonal analogue), sodium is a group-1 metal, and boron is Be's period neighbour, not its diagonal partner.

**Final Answer:** beryllium resembles aluminium $\Rightarrow$ $\boxed{\mathrm{D}}$

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

## Q20.

**Solution**

**Concept – covalency limited by available orbitals:** The maximum covalency of an element is set by the number of orbitals it can use for bonding in its valence shell.

**Step 1 – examine nitrogen:** Nitrogen's valence shell is the second shell $(2s, 2p)$, which offers only four orbitals, capping its covalency at four.

**Step 2 – examine phosphorus:** Phosphorus is in the third period and has energetically accessible $3d$ orbitals in addition to $3s$ and $3p$, so it can expand its valence shell.

**Step 3 – link to the observed compounds:** Using $3d$ participation, phosphorus forms five bonds in $\mathrm{PF_5}$ and six in $\mathrm{PF_6^-}$, which nitrogen cannot do.

**Step 4 – reject the distractors:** The electronegativity difference, atomic-size comparison, and valence-electron count do not by themselves explain the covalency limit; the absence of low-lying $d$ orbitals on nitrogen does.

**Final Answer:** nitrogen lacks low-lying $d$ orbitals $\Rightarrow$ $\boxed{\mathrm{A}}$

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

## Q21.

**Solution**

**Concept – crystal-field stabilization energy (CFSE):** CFSE $= \left[(-0.4)\, n_{t_{2g}} + (+0.6)\, n_{e_g}\right]\Delta_o$, where $n$ are the electron occupancies.

**Step 1 – write the low-spin $d^6$ configuration:** A strong field forces $t_{2g}^6 e_g^0$, so $n_{t_{2g}} = 6$ and $n_{e_g} = 0$.

**Step 2 – substitute into the CFSE expression:** CFSE $= \left[(-0.4)(6) + (0.6)(0)\right]\Delta_o$.

**Step 3 – evaluate the arithmetic:** $= (-2.4 + 0)\Delta_o = -2.4\,\Delta_o$.

**Step 4 – note on the pairing term:** The problem asks to ignore the pairing-energy contribution, so the orbital CFSE is $-2.4\,\Delta_o$.

**Final Answer:** CFSE $= -2.4\,\Delta_o \Rightarrow$ C

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

## Q22.

**Solution**

**Concept – CFSE of a high-spin configuration:** Use CFSE $= \left[(-0.4)\, n_{t_{2g}} + (+0.6)\, n_{e_g}\right]\Delta_o$.

**Step 1 – write the high-spin $d^5$ configuration:** A weak field gives $t_{2g}^3 e_g^2$, one electron in each of the five $d$ orbitals, so $n_{t_{2g}} = 3$ and $n_{e_g} = 2$.

**Step 2 – substitute into the formula:** CFSE $= \left[(-0.4)(3) + (0.6)(2)\right]\Delta_o$.

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

**Step 4 – add:** CFSE $= (-1.2 + 1.2)\Delta_o = 0$, as expected for a half-filled, spherically symmetric $d^5$ set.

**Final Answer:** CFSE $= 0 \Rightarrow$ D

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

## Q23.

**Solution**

**Concept – the 18-electron rule (neutral-atom counting):** Add the metal's group valence electrons to the electrons donated by each ligand; a stable organometallic often totals 18.

**Step 1 – count the iron contribution:** Iron is in group 8, so a neutral Fe atom brings 8 valence electrons.

**Step 2 – count each cyclopentadienyl ring:** In neutral counting an $\eta^5$-$C_5H_5$ ligand donates $5$ electrons; two rings give $2 \times 5 = 10$.

**Step 3 – add the contributions:** Total $= 8 + 10 = 18$ valence electrons.

**Step 4 – cross-check by ionic counting:** $Fe^{2+}$ is $d^6$ (6 electrons) and each $C_5H_5^-$ donates $6$, giving $6 + 12 = 18$; both methods agree.

**Final Answer:** electron count $= 18 \Rightarrow$ C

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

## Q24.

### Solution

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

**Step 1 – find the number of unpaired electrons:** Low-spin $d^5$ has the configuration $t_{2g}^5 e_g^0$, which leaves exactly one unpaired electron, so $n = 1$.

**Step 2 – substitute into the formula:** $\mu = \sqrt{1(1+2)}$.

**Step 3 – simplify inside the root:** $\mu = \sqrt{1 \times 3} = \sqrt{3}$.

**Step 4 – evaluate:** $\mu = 1.73$ BM.

**Final Answer:** $\mu = 1.73$ BM $\Rightarrow$ D

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

## Q25.

### Solution

**Concept – oxidation state of a metal in a complex:** The oxidation state of the metal plus the sum of the ligand charges equals the overall charge of the complex ion.

**Step 1 – assign the ligand charges:** Ammonia is neutral ($4 \times 0 = 0$) and each chloride is $-1$ ($2 \times (-1) = -2$).

**Step 2 – write the charge-balance equation:** Let the cobalt oxidation state be $x$; then $x + 0 + (-2) = +1$ (the charge on the complex).

**Step 3 – solve for $x$:** $x - 2 = +1$, so $x = +3$.

**Step 4 – interpret:** The metal centre is cobalt(III), a very common oxidation state for cobalt ammine complexes.

**Final Answer:** cobalt is $+3 \Rightarrow$ C

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

## Q26.

### Solution

**Concept – spectrochemical series and spin state:** A strong-field ligand produces a large $\Delta_o$; when $\Delta_o$ exceeds the pairing energy, electrons pair up and the complex is low-spin.

**Step 1 – rank the ligands by field strength:** The series runs $I^- < Cl^- < F^- < H_2O < CN^-$, so $CN^-$ is by far the strongest here.

**Step 2 – apply this to the $d^5$ iron(III) centre:** With the very strong-field $CN^-$, $\Delta_o >$ pairing energy, forcing the electrons into $t_{2g}^5$ (low-spin).

**Step 3 – compare the others:** $F^-$, $Cl^-$ and $H_2O$ are weaker-field ligands, giving high-spin $t_{2g}^3 e_g^2$ with five unpaired electrons.

**Step 4 – conclude:** Only $[Fe(CN)_6]^{3-}$ is low-spin.

**Final Answer:** $[Fe(CN)_6]^{3-}$ is low-spin $\Rightarrow$ B

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

## Q27.

### Solution

**Concept – counting atoms in the perovskite unit cell:** Add up the fractional contributions of atoms at corners, body centre and face centres.

**Step 1 – count the $A$ cation (corners):** Eight corner atoms, each shared by $8$ cells: $8 \times \frac{1}{8} = 1$ atom of $A$.

**Step 2 – count the $B$ cation (body centre):** One atom wholly inside the cell: $1 \times 1 = 1$ atom of $B$.

**Step 3 – count the oxide ions (face centres):** Six face-centre atoms, each shared by $2$ cells: $6 \times \frac{1}{2} = 3$ atoms of O.

**Step 4 – assemble the formula:** $A : B : O = 1 : 1 : 3$, giving the stoichiometry $ABO_3$.

**Final Answer:** perovskite formula is $ABO_3$ $\Rightarrow$ A

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

## Q28.

**Solution**

**Concept – the Meissner effect:** Below $T_c$ a superconductor is not merely a perfect conductor; it actively behaves as a perfect diamagnet.

**Step 1 – state the phenomenon:** When cooled below $T_c$ in a magnetic field, a superconductor pushes the magnetic field lines out of its bulk.

**Step 2 – name it:** This spontaneous exclusion of magnetic flux from the interior is the Meissner effect.

**Step 3 – connect to observation:** It is why a magnet levitates above a cooled YBCO pellet, the field being expelled from the superconductor's interior.

**Step 4 – reject the distractors:** A superconductor has *zero* resistance (not infinite), and it is diamagnetic (flux-expelling), not paramagnetic.

**Final Answer:** complete expulsion of magnetic flux $\Rightarrow$ $\boxed{\text{B}}$

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

## Q29.

**Solution**

**Concept – the metal ion in vitamin $\mathrm{B_{12}}$:** Vitamin $\mathrm{B_{12}}$ (cobalamin) is a coordination compound in which a corrin ring chelates a metal centre.

**Step 1 – identify the macrocycle:** The corrin ring, related to but distinct from porphyrin, provides four nitrogen donors.

**Step 2 – identify the metal:** The central ion held by the corrin nitrogens is cobalt, typically in the $+3$ oxidation state (with $\mathrm{Co^{+}/Co^{2+}}$ forms in its catalytic cycle).

**Step 3 – contrast with other biomolecules:** Heme uses $\mathrm{Fe}$, chlorophyll uses $\mathrm{Mg}$, and carbonic anhydrase uses $\mathrm{Zn}$; only cobalamin uses cobalt.

**Final Answer:** the metal is $\mathrm{Co^{3+}}$ $\Rightarrow$ $\boxed{\text{C}}$

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

## Q30.

**Solution**

**Concept – carbocation rearrangement:** An electron-deficient carbon can be stabilized when a neighbouring hydrogen or alkyl group migrates *with its bonding pair* to the positive centre.

**Step 1 – identify the driving force:** Carbocation stability increases primary $<$

secondary $<$ tertiary, so a secondary cation gains stability by becoming tertiary.

**Step 2 – describe the migration:** A hydrogen on the adjacent carbon moves, taking its bonding electrons, in a $1,2$-hydride shift (an alkyl group can migrate similarly in a $1,2$-alkyl shift).

**Step 3 – state the outcome:** The positive charge relocates to the carbon that becomes more substituted, giving the more stable tertiary carbocation.

**Step 4 – reject the distractors:** A $1,1$-elimination, a retro-aldol, or "no rearrangement possible" do not describe this well-known Wagner–Meerwein-type shift.

**Final Answer:** it is a $1,2$-hydride (or alkyl) shift $\Rightarrow$ $\boxed{\text{A}}$

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

## Q31.

### Solution

**Concept – counting stereoisomers with a meso form:** The naive maximum for $n$ stereocentres is $2^n$, but internal symmetry can make one diastereomer superimposable on its mirror image (a meso compound), reducing the count.

**Step 1 – start from the maximum:** With $n = 2$ stereocentres, $2^2 = 4$ would be the upper limit.

**Step 2 – account for identical substituents:** Because the two stereocentres carry the same substituents, the $(R, S)$ and $(S, R)$ forms are identical, being a single achiral meso compound.

**Step 3 – list the actual stereoisomers:** $(R, R)$ and $(S, S)$ form a pair of enantiomers, and the meso form is a third, optically inactive isomer.

**Step 4 – total them:** $2 + 1 = 3$ distinct stereoisomers, exactly as for tartaric acid.

**Final Answer:** $3$ stereoisomers $\Rightarrow$ $\boxed{\text{B}}$

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

## Q32.

### Solution

**Concept – physical properties of enantiomers:** Enantiomers are mirror images with identical scalar properties in an achiral environment; they differ only in their interaction with other chiral things, including plane-polarized light.

**Step 1 – compare scalar properties:** Melting point, boiling point, density and solubility in an achiral solvent are identical for the two enantiomers.

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

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

**Step 4 – note:** They also react at different rates with other chiral reagents, but among the options given only the optical-rotation direction differs.

**Final Answer:** they differ in the direction of optical rotation $\Rightarrow$ D

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

## Q33.

### Solution

**Concept – rate of $S_N1$ set by carbocation stability:** The slow step of $S_N1$ is ionization to a carbocation, so the more stable that carbocation, the faster the reaction.

**Step 1 – rank the carbocations formed:** Methyl and ethyl give unstable $1^\circ$/methyl cations, $n$-propyl gives a $1^\circ$ cation, while *tert*-butyl gives a stable $3^\circ$ cation.

**Step 2 – match stability to rate:** The $3^\circ$ *tert*-butyl cation is the most stabilized (hyperconjugation and induction from three methyls), so its bromide ionizes fastest.

**Step 3 – conclude:** *tert*-Butyl bromide undergoes $S_N1$ solvolysis fastest.

**Step 4 – reject the distractors:** Methyl and primary halides essentially do not react by $S_N1$ (they prefer $S_N2$) because their cations are too unstable.

**Final Answer:** *tert*-butyl bromide $\Rightarrow$ A

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

## Q34.

### Solution

**Concept – resonance beats hyperconjugation for cation stability:** Delocalization of the positive charge over several atoms by resonance is a stronger stabilizing effect than the hyperconjugation/induction available to simple alkyl cations.

**Step 1 – rank the alkyl cations:** Ethyl ($1^\circ$) $<$ isopropyl ($2^\circ$) $<$ *tert*-butyl ($3^\circ$), by increasing hyperconjugation.

**Step 2 – examine the benzyl cation:** In the benzyl cation the positive charge is delocalized into the aromatic ring over several carbons through resonance.

**Step 3 – compare:** This resonance stabilization is greater than the hyperconjugative stabilization of even a tertiary alkyl cation.

**Step 4 – conclude:** The benzyl cation is the most stabilized of the four.

**Final Answer:** the benzyl cation $\Rightarrow$ D

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

## Q35.

### Solution

**Concept – lowest-energy conformation about a C–C bond:** The most stable rotamer is staggered and places bulky groups as far apart as possible to minimize both steric and dipole–dipole repulsion.

**Step 1 – compare staggered and eclipsed:** Eclipsed conformations suffer torsional strain, so the minimum lies among the staggered rotamers.

**Step 2 – compare the staggered rotamers:** The staggered forms are anti (chlorines $180^\circ$ apart) and gauche (chlorines $60^\circ$ apart).

**Step 3 – choose between them:** In the anti conformation the two large chlorine atoms are farthest apart, minimizing steric clash, and their bond dipoles oppose, minimizing dipole–dipole repulsion.

**Step 4 – conclude:** The anti ($180^\circ$ dihedral) conformation is the lowest in energy.

**Final Answer:** anti ($180^\circ$) conformation $\Rightarrow$ B

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

## Q36.

### Solution

**Concept – Markovnikov addition of HBr:** In the absence of peroxides, HBr adds through the more stable carbocation intermediate, so H goes to the carbon that already has more hydrogens.

**Step 1 – protonate the double bond:** Adding $H^+$ to the terminal $CH_2$ carbon generates a secondary carbocation at C2, $CH_3\overset{+}{C}HCH_3$.

**Step 2 – compare with the alternative:** Adding $H^+$ to the internal carbon would give a less stable primary cation, which is disfavoured.

**Step 3 – add bromide to the more stable cation:** $Br^-$ attacks C2, placing bromine on the more substituted carbon.

**Step 4 – name the product:** The product is $CH_3CHBrCH_3$, i.e. 2-bromopropane.

**Final Answer:** major product is 2-bromopropane $\Rightarrow$ B

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

## Q37.

### Solution

**Concept – the Claisen ester condensation:** An ester with $\alpha$-hydrogens is deprotonated by a strong alkoxide base and its enolate attacks the carbonyl of a second ester, expelling an alkoxide to give a $\beta$-keto ester.

**Step 1 – generate the enolate:** Sodium ethoxide removes an $\alpha$-hydrogen from one ethyl acetate molecule to form the ester enolate.

**Step 2 – attack the second ester:** This enolate adds to the carbonyl carbon of a second ethyl acetate.

**Step 3 – expel ethoxide:** Collapse of the tetrahedral intermediate ejects an ethoxide ion, forming the new C–C bond and a $\beta$-keto ester.

**Step 4 – name the reaction and product:** Self-condensation of ethyl acetate gives ethyl acetoacetate; the reaction is the Claisen condensation.

**Final Answer:** it is the Claisen condensation $\Rightarrow$ D

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

## Q38.

### Solution

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

**Step 1 – form the reactive enolate:** The carboxylate base deprotonates the $\alpha$-carbon of the anhydride, generating a nucleophilic enolate.

**Step 2 – aldol-type addition:** The enolate adds to the carbonyl of benzaldehyde.

**Step 3 – dehydration:** Loss of water gives the conjugated $\alpha,\beta$-unsaturated product, and hydrolysis of the anhydride gives the free acid.

**Step 4 – name the reaction and product:** Benzaldehyde with acetic anhydride and sodium acetate gives cinnamic acid; this is the Perkin reaction.

**Final Answer:** it is the Perkin reaction $\Rightarrow$ C

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

## Q39.

**Solution**

**Concept – the Knoevenagel condensation:** A carbonyl compound condenses with an active-methylene compound (flanked by two electron-withdrawing groups) under mild amine catalysis, followed by dehydration.

**Step 1 – deprotonate the active methylene:** The weak amine base removes an acidic $CH_2$ proton from, say, malonic ester, forming a stabilized carbanion.

**Step 2 – add to the aldehyde:** The carbanion adds to the aldehyde carbonyl to give a $\beta$-hydroxy compound.

**Step 3 – eliminate water:** Dehydration gives the $\alpha,\beta$-unsaturated (alkene) product.

**Step 4 – name the reaction:** Condensation of a carbonyl with an active-methylene compound under amine catalysis is the Knoevenagel condensation.

**Final Answer:** it is the Knoevenagel condensation $\Rightarrow$ $\boxed{\text{C}}$

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

## Q40.

**Solution**

**Concept – the benzoin condensation:** Cyanide (or an $N$-heterocyclic carbene) catalyzes the coupling of two aromatic aldehyde molecules to an $\alpha$-hydroxy ketone.

**Step 1 – form the acyl anion equivalent:** Cyanide adds to one benzaldehyde and, after proton transfer, generates a nucleophilic carbanion (an "umpolung" acyl anion).

**Step 2 – attack the second aldehyde:** This carbanion adds to the carbonyl of a second benzaldehyde, forming the new C–C bond.

**Step 3 – expel the catalyst:** Loss of cyanide regenerates the catalyst and reveals the ketone, giving benzoin, $\mathrm{PhCH(OH)COPh}$.

**Step 4 – name the reaction:** This cyanide-catalyzed dimerization of benzaldehyde is the benzoin condensation.

**Final Answer:** it is the benzoin condensation $\Rightarrow$ $\boxed{\text{A}}$

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

## Q41.

**Solution**

**Concept – the Reformatsky reaction:** Zinc inserts into the C–X bond of an $\alpha$-halo ester to form an organozinc enolate, which adds to a carbonyl compound.

**Step 1 – form the zinc reagent:** Zinc reacts with the $\alpha$-halo ester to give a relatively stable, mild organozinc enolate.

**Step 2 – add to the carbonyl:** This organozinc enolate adds to the carbonyl carbon of an aldehyde or ketone.

**Step 3 – acidic work-up:** Protonation of the resulting alkoxide gives a $\beta$-hydroxy ester.

**Step 4 – name the reaction:** The overall sequence is the Reformatsky reaction, prized because the mild zinc reagent tolerates the ester group.

**Final Answer:** it is the Reformatsky reaction $\Rightarrow$ $\boxed{\text{A}}$

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

## Q42.

**Solution**

**Concept – the Mannich reaction:** An enolizable carbonyl compound, formaldehyde, and a secondary amine combine to give a $\beta$-amino carbonyl compound (a Mannich base).

**Step 1 – form the iminium electrophile:** Formaldehyde condenses with the secondary amine to give an iminium ion, $\mathrm{R_2N{=}CH_2^+}$.

**Step 2 – generate the enol/enolate:** The ketone's $\alpha$-carbon, as its enol, provides the nucleophile.

**Step 3 – form the C–C bond:** The enol attacks the iminium carbon, installing a $-\mathrm{CH_2NR_2}$ group at the $\alpha$-position.

**Step 4 – name the reaction and product:** The product is a $\beta$-amino ketone (Mannich base); the three-component amino-methylation is the Mannich reaction.

**Final Answer:** it is the Mannich reaction $\Rightarrow$ $\boxed{\text{C}}$

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

## Q43.

**Solution**

**Concept – the Dieckmann condensation:** An intramolecular Claisen condensation of a diester closes a ring to give a cyclic $\beta$-keto ester.

**Step 1 – form the enolate:** A strong base deprotonates the $\alpha$-carbon of one ester group in the diester.

**Step 2 – intramolecular attack:** This enolate reaches across the same molecule to the carbonyl of the second ester group.

**Step 3 – expel alkoxide and cyclize:** Loss of an alkoxide forms the ring and a $\beta$-keto ester; for diethyl adipate this gives a five-membered cyclic product.

**Step 4 – name the reaction:** The intramolecular Claisen condensation is called the Dieckmann condensation.

**Final Answer:** it is the Dieckmann condensation $\Rightarrow$ $\boxed{\text{A}}$

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

## Q44.

**Solution**

**Concept – $\pi$-electron count in a Diels–Alder $[4+2]$ cycloaddition:** The label $[4+2]$ refers to the number of $\pi$ electrons each partner contributes to the cyclic transition state.

**Step 1 – count the diene's contribution:** The conjugated diene brings two $\pi$ bonds, i.e. $4$ $\pi$ electrons.

**Step 2 – count the dienophile's contribution:** The dienophile brings one $\pi$ bond, i.e. $2$ $\pi$ electrons.

**Step 3 – add them:** Total $= 4 + 2 = 6$ $\pi$ electrons in the transition state.

**Step 4 – link to the selection rule:** Six is a $4n + 2$ (aromatic) count, which is exactly why the thermal Diels–Alder reaction is allowed.

**Final Answer:** $6$ $\pi$ electrons $\Rightarrow$ $\boxed{\text{D}}$

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

## Q45.

**Solution**

**Concept – Woodward–Hoffmann rule for $[2+2]$ cycloaddition:** For a suprafacial–suprafacial cycloaddition, a $4n$ $\pi$-electron system is thermally forbidden but photochemically allowed, while a $4n+2$ system is thermally allowed.

**Step 1 – count the $\pi$ electrons:** Two alkenes contribute $2+2=4$ $\pi$ electrons, a $4n$ system with $n=1$.

**Step 2 – apply the thermal rule:** For $4n$ electrons the thermal suprafacial–suprafacial pathway is forbidden.

**Step 3 – apply the photochemical rule:** Under photochemical excitation the symmetry requirement reverses, so the $[2+2]$ becomes allowed suprafacial–suprafacial.

**Step 4 – conclude:** The $[2+2]$ cycloaddition of two alkenes to a cyclobutane is photochemically allowed.

**Final Answer:** photochemically allowed (suprafacial–suprafacial) $\Rightarrow$ $\boxed{\text{B}}$

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

## Q46.

**Solution**

**Concept – complementary base pairing in DNA:** The two DNA strands pair a purine with a specific pyrimidine through a fixed number of hydrogen bonds.

**Step 1 – classify adenine:** Adenine is a purine base.

**Step 2 – identify its complement:** Adenine pairs with the pyrimidine thymine via two hydrogen bonds (A–T).

**Step 3 – contrast with the other pair:** Guanine pairs with cytosine through three hydrogen bonds (G–C), so cytosine and guanine are not adenine's partner.

**Step 4 – note on uracil:** Uracil replaces thymine only in RNA, not in DNA, so within DNA adenine pairs with thymine.

**Final Answer:** adenine pairs with thymine $\Rightarrow$ $\boxed{\text{C}}$

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

# Answer Key

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