GAT B Chemistry

Sample Paper – 7

Duration: 23 Minutes **Maximum Marks: 15**

Instructions

- This paper contains **15** Multiple Choice Questions (Single Correct Answer), modelled on the Chemistry portion of **GAT B** entrance.
- Each correct answer carries **+1 marks**. There is **a deduction of 0.5 marks for each incorrect answer**.
- Only **one** option is correct. Choose carefully.
- Syllabus level: **NCERT Class 11 & 12 Chemistry — Physical, Organic, and Inorganic Chemistry.**
- Use of mobile phones, calculators, or electronic gadgets is strictly prohibited.

Questions

Q1. Which of the following amino acids is **achiral** (optically inactive), because its α-carbon does *not* bear four different substituents?

(A) Glycine

(B) Alanine

(C) Valine

(D) Leucine

Q2. The Meselson–Stahl experiment (1958) provided conclusive evidence for a specific model of DNA replication. Which combination correctly identifies the **model proved** and the **experimental technique** used?

(A) Conservative replication; electron microscopy

(B) Dispersive replication; autoradiography with ^{32}P labelling

(C) Conservative replication; CsCl density-gradient centrifugation with $^{15}\mathrm{N}/^{14}\mathrm{N}$

(D) Semiconservative replication; CsCl density-gradient centrifugation with $^{15}\mathrm{N}/^{14}\mathrm{N}$

Q3. In the linear biosynthetic pathway $A \xrightarrow{E_1} B \xrightarrow{E_2} C \xrightarrow{E_3} D \xrightarrow{E_4} E$, accumulation of the end-product E slows the entire pathway. Which statement **best** describes this regulatory mechanism?

(A) End-product E activates enzyme E_4 (the last step) to accelerate consumption of D

(B) End-product E competitively inhibits enzyme E_4 at its active site

(C) End-product E allosterically inhibits enzyme E_1 (the **first committed step**), an example of feedback inhibition

(D) End-product E covalently phosphorylates enzyme E_3, rendering it inactive

Q4. Carbonic acid ($\mathrm{H_2CO_3}$) has $\mathrm{p}K_{a1} = 6.35$ and $\mathrm{p}K_{a2} = 10.33$. At blood pH of **7.4**, which species **predominates**?

(A) $\mathrm{H_2CO_3}$

(B) $\mathrm{HCO_3^-}$ (bicarbonate)

(C) $\mathrm{CO_3^{2-}}$ (carbonate)

(D) Equal amounts of $\mathrm{H_2CO_3}$ and $\mathrm{CO_3^{2-}}$

Q5. Which of the following statements about the ionic product of water ($K_w = [\mathrm{H^+}][\mathrm{OH^-}]$) is **correct**?

(A) K_w increases with temperature because the autoionisation of water is endothermic; consequently, the neutral pH falls *below* 7 at temperatures above 25 °C

(B) K_w is independent of temperature because water is a pure liquid with activity = 1

(C) K_w decreases with temperature; therefore the neutral pH rises above 7 at higher temperatures

(D) K_w increases with temperature, but the neutral pH remains exactly 7 regardless of temperature

Q6. Consider the following three statements regarding thermodynamic equilibrium and the Second Law:

(I) At equilibrium, $\Delta G_{\text{system}} = 0$ (at constant T and P).

(II) For any spontaneous process at constant T and P, $\Delta G_{\text{system}} < 0$.

(III) The Second Law of Thermodynamics requires $\Delta S_{\text{universe}} > 0$ for any spontaneous process.

Which combination is **correct**?

(A) Only statement (I) is correct

(B) Statements (I) and (II) only

(C) Statements (I) and (III) only

(D) Statements (I), (II), and (III) are all correct

Q7. The correct order of **lattice energy** for the series of alkali metal fluorides is:

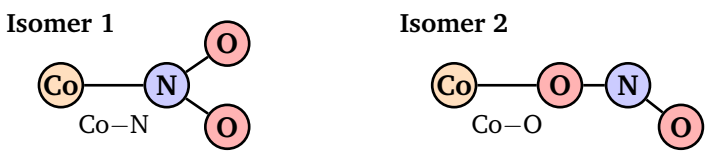
(A) $\mathrm{RbF} > \mathrm{KF} > \mathrm{NaF} > \mathrm{LiF}$

(B) $\mathrm{NaF} > \mathrm{LiF} > \mathrm{KF} > \mathrm{RbF}$

(C) $\mathrm{LiF} > \mathrm{NaF} > \mathrm{KF} > \mathrm{RbF}$

(D) $\mathrm{KF} > \mathrm{LiF} > \mathrm{NaF} > \mathrm{RbF}$

Q8. The two coordination species shown below are **linkage isomers** of the formula $[\mathrm{Co(NH_3)_5(NO_2/ONO)}]^{2+}$. Identify the correct names for Isomer 1 and Isomer 2.



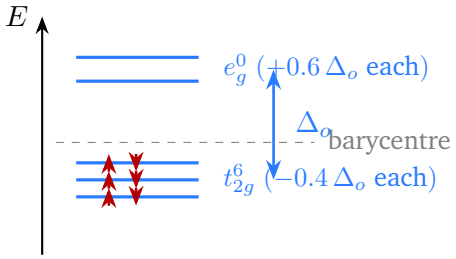
(A) Isomer 1 is *nitrito* (O-bonded); Isomer 2 is *nitro* (N-bonded)

(B) Isomer 1 is *nitro* (N-bonded); Isomer 2 is *nitrito* (O-bonded)

(C) Both Isomer 1 and Isomer 2 are *nitro* (N-bonded) forms

(D) Both Isomer 1 and Isomer 2 are *nitrito* (O-bonded) forms

Q9. The energy-level diagram below shows the d-orbital splitting for a **low-spin** d^6 ion in an octahedral crystal field (paired electrons shown on t_{2g}). What is the **crystal field stabilization energy (CFSE)**, ignoring the pairing-energy correction?



(A) $-2.4\,\Delta_o$

(B) $-1.6\,\Delta_o$

(C) $-0.4\,\Delta_o$

(D) $-2.0\,\Delta_o$

Q10. In a **Michael addition**, a soft nucleophile (Michael donor) reacts with an α,β-unsaturated carbonyl compound (Michael acceptor). At which carbon does the nucleophile attack, and how is this addition classified?

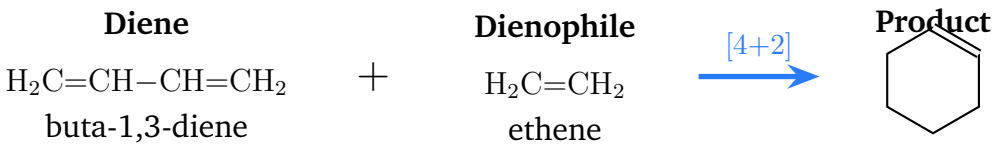
(A) The **carbonyl carbon** (*1,2-addition*); the product is a direct alkoxide

(B) The **carbonyl oxygen**; the product is an enol ether

(C) The α**-carbon** adjacent to the carbonyl; the product is a β-substituted carbonyl

(D) The β**-carbon** of the unsaturated system (*1,4-conjugate addition*); the enolate intermediate is then protonated

Q11. Identify the **product** of the Diels–Alder reaction shown below.



(A) Benzene (aromatic ring)

(B) Cyclohexane (fully saturated ring)

(C) Cyclohexene (six-membered ring with one double bond)

(D) Cyclohexa-1,3-diene (six-membered ring with two conjugated double bonds)

Q12. Using **Kohlrausch's law** of independent migration of ions, calculate the molar conductivity at infinite dilution (Λ_m°) of acetic acid (CH_3COOH) from the following data:

$$\Lambda_m^\circ(\mathrm{HCl}) = 426\ \mathrm{S\,cm^2\,mol^{-1}}, \quad \Lambda_m^\circ(\mathrm{CH_3COONa}) = 91\ \mathrm{S\,cm^2\,mol^{-1}}, \quad \Lambda_m^\circ(\mathrm{NaCl}) =$$

(A) $517\ \mathrm{S\,cm^2\,mol^{-1}}$

(B) $391\ \mathrm{S\,cm^2\,mol^{-1}}$

(C) $643\ \mathrm{S\,cm^2\,mol^{-1}}$

(D) $217\ \mathrm{S\,cm^2\,mol^{-1}}$

Q13. For a **second-order** reaction $\mathrm{A} \rightarrow \mathrm{Products}$ (rate $= k[\mathrm{A}]^2$), which expression gives the **half-life** $t_{1/2}$, and how does $t_{1/2}$ depend on the initial concentration $[\mathrm{A}]_0$?

(A) $t_{1/2} = \dfrac{1}{k[\mathrm{A}]_0}$; $t_{1/2}$ **decreases** as $[\mathrm{A}]_0$ increases

(B) $t_{1/2} = \dfrac{0.693}{k}$; $t_{1/2}$ is **independent** of $[\mathrm{A}]_0$

(C) $t_{1/2} = k[\mathrm{A}]_0$; $t_{1/2}$ **increases** as $[\mathrm{A}]_0$ increases

(D) $t_{1/2} = \dfrac{1}{2k[\mathrm{A}]_0}$; $t_{1/2}$ is **independent** of $[\mathrm{A}]_0$

Q14. Calculate the **spin-only magnetic moment** (μ_s) for Fe^{3+} in a high-spin complex. Use the formula $\mu_s = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons.

(A) $\sqrt{8}$ BM ≈ 2.83 BM $\quad (n = 2)$

(B) $\sqrt{24}$ BM ≈ 4.90 BM $\quad (n = 4)$

(C) $\sqrt{15}$ BM ≈ 3.87 BM $\quad (n = 3)$

(D) $\sqrt{35}$ BM ≈ 5.92 BM $\quad (n = 5)$

Q15. Polyacetylene, $[-CH = CH-]_n$, is the prototype conducting polymer. Which statement **correctly** explains the origin of its electrical conductivity?

(A) Polyacetylene is inherently metallic because all C–C bonds along the backbone are equivalent (delocalisation removes bond alternation completely in the undoped state)

(B) Conductivity arises from proton hopping along the $-CH = CH-$ backbone via Grotthuss-type mechanism

(C) Doping (oxidation or reduction) introduces charge carriers — **polarons** and **solitons** — into the conjugated π-system, dramatically increasing conductivity

(D) Conductivity results from ionic transport through water molecules absorbed in the amorphous regions of the polymer

Detailed Solutions

Q1.

Solution

Concept — Chirality and Amino Acids: A carbon atom is a chiral centre (stereogenic centre) only if it bears *four different* substituents. Among the standard α-amino acids, the α-carbon carries $-NH_2$, $-COOH$, $-H$, and the side chain $-R$. Glycine has $-R = -H$, so the α-carbon carries *two* hydrogen atoms — not four different groups — and is therefore **achiral**.

Step 1 — Examine the α-carbon of each option:

- **Glycine**: α-C carries $-NH_2$, $-COOH$, $-H$, $-H \Rightarrow$ two identical substituents

$\Rightarrow$ no stereogenic centre $\Rightarrow$ **achiral**.

- **Alanine**: $-\mathrm{R} = -\mathrm{CH_3}$; four different groups $\Rightarrow$ chiral.
- **Valine**: $-\mathrm{R} = -\mathrm{CH(CH_3)_2}$; four different groups $\Rightarrow$ chiral.
- **Leucine**: $-\mathrm{R} = -\mathrm{CH_2CH(CH_3)_2}$; four different groups $\Rightarrow$ chiral.

Step 2 — Conclusion: Only glycine has a symmetric α-carbon. All other listed amino acids are chiral (exist as L and D enantiomers in principle; only the L-form occurs naturally).

Why other options are wrong:

- Option A: Glycine — **correct**; it is the only achiral standard amino acid.
- Option B: Alanine has $-\mathrm{CH_3}$ as side chain; four distinct groups on α-C $\Rightarrow$ chiral.
- Option C: Valine has isopropyl side chain; chiral.
- Option D: Leucine has isobutyl side chain; chiral.

Final Answer: Glycine is the only achiral amino acid listed $\Rightarrow$ $\boxed{\text{A}}$

Answer: (A) Go Back to Q 1

Q2.

Solution

Concept — Meselson–Stahl Experiment: Three models of DNA replication were proposed: (1) *conservative* — the original double helix remains intact while a completely new copy is synthesised; (2) *semiconservative* — each parental strand serves as a template for a new strand, giving two hybrid duplexes; (3) *dispersive* — both strands of both daughter duplexes contain mixtures of old and new DNA. Meselson and Stahl (1958) used **CsCl density-gradient ultracentrifugation** with the heavy isotope $^{15}\mathrm{N}$ to distinguish these models.

Step 1 — Experimental design: *E. coli* cells were grown for many generations in $^{15}\mathrm{N}$-labelled medium (heavy DNA), then transferred to normal $^{14}\mathrm{N}$ medium. DNA was extracted after 0, 1, and 2 generations and centrifuged in a CsCl gradient to separate by density.

Step 2 — Observed result and interpretation:

- After **1 generation**: *one* band at intermediate density (hybrid $^{15}\mathrm{N}/^{14}\mathrm{N}$).
- After **2 generations**: *two* bands — one hybrid, one fully light ($^{14}\mathrm{N}$ only), in equal amounts.

Only the semiconservative model predicts this pattern: conservative would show two distinct bands (heavy + light) after 1 generation; dispersive would show a single gradually-lightening band at all generations.

Why other options are wrong:

- Option A: Conservative model was ruled out; electron microscopy was not the technique.
- Option B: Dispersive model was ruled out by the 2-generation data; ^{32}P autoradiography is a different experiment.
- Option C: Density-gradient centrifugation was used correctly, but the conclusion was semiconservative, not conservative.
- Option D: **Correct.**

Final Answer: Semiconservative replication; CsCl density-gradient with ^{15}N/^{14}N $\Rightarrow$ D

Answer: (D) Go Back to Q 2

Q3.

Solution

Concept — Feedback Inhibition (End-Product Inhibition): In a linear biosynthetic pathway, when the end-product accumulates beyond the cell's requirement, it inhibits the **first committed enzyme** of the pathway. This is called *feedback* or *end-product inhibition*. The inhibition is *allosteric*: the end-product binds a regulatory (allosteric) site on the first enzyme — not the active site — inducing a conformational change that reduces catalytic activity.

Step 1 — Why the first enzyme? Inhibiting enzyme E_1 ($A \rightarrow B$) conserves metabolic resources by preventing accumulation of intermediates B, C, D. Substrate A remains available for other pathways. This is far more efficient than inhibiting the last step.

Step 2 — Allosteric vs. competitive: Allosteric inhibition is non-competitive; the inhibitor binds a site geometrically distinct from the active site. It does not compete with substrate A. In contrast, competitive inhibition would require structural similarity between E and A, which is unlikely for the end-product of a multi-step pathway.

Why other options are wrong:

- Option A: Activation of E_4 would speed up the pathway, not slow it — the

opposite of what is described.

- Option B: Competitive inhibition at E_4 (last step) is not feedback inhibition; it would not prevent synthesis of all intermediates.
- Option C: **Correct** — feedback inhibition of E_1 is the hallmark of allosteric regulation in biosynthetic pathways.
- Option D: Covalent phosphorylation (of E_3) is a separate regulatory mechanism (covalent modification), not described in the question.

Final Answer: E allosterically inhibits E_1, the first committed step (feedback inhibition) $\Rightarrow$ C

Answer: (C) Go Back to Q 3

Q4.

Solution

Concept — Predominant Species of a Diprotic Acid: For a diprotic acid H_2A with pK_{a1} and pK_{a2}, the species diagram (speciation curve) shows:

$\text{pH} < pK_{a1}$: H_2A dominates; $pK_{a1} < \text{pH} < pK_{a2}$: HA^- dominates; $\text{pH} > pK_{a2}$: A^{2-} domina

Step 1 — Apply to carbonic acid at pH 7.4:

$$pK_{a1} = 6.35, \quad pK_{a2} = 10.33, \quad \text{pH} = 7.4$$

Since $6.35 < 7.4 < 10.33$, the monoprotonated species HCO_3^- (bicarbonate) **predominates**.

Step 2 — Quantitative ratio (Henderson–Hasselbalch for first equilibrium):

$$\text{pH} = pK_{a1} + \log \frac{[HCO_3^-]}{[H_2CO_3]} \quad \Rightarrow \quad \frac{[HCO_3^-]}{[H_2CO_3]} = 10^{(7.4-6.35)} = 10^{1.05} \approx 11$$

HCO_3^- is about 11-fold more concentrated than H_2CO_3 at pH 7.4, confirming its predominance.

Why other options are wrong:

- Option A: H_2CO_3 dominates only when $\text{pH} < 6.35$.
- Option B: **Correct** — HCO_3^- predominates between pK_{a1} and pK_{a2}.
- Option C: CO_3^{2-} dominates only when $\text{pH} > 10.33$.
- Option D: The two extreme species (H_2CO_3 and CO_3^{2-}) are both minor at pH 7.4.

Final Answer: HCO_3^- (bicarbonate) predominates at blood pH 7.4 $\Rightarrow$ B

Answer: (B) Go Back to Q 4

Q5.

Solution

Concept — K_w and Temperature: The autoionisation of water, $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, is **endothermic** ($\Delta H \approx +55.8$ kJ mol^{-1}). By Le Chatelier's principle, raising temperature shifts the equilibrium to the right, increasing both $[H^+]$ and $[OH^-]$ equally, so $K_w = [H^+][OH^-]$ **increases**.

Step 1 — Effect on neutral pH: At neutrality, $[H^+] = [OH^-]$, so $K_w = [H^+]^2$ and the neutral pH $= \frac{1}{2}\,pK_w$.

Temperature	K_w	Neutral pH
25 °C	1.0×10^{-14}	7.00
37 °C	$\approx 2.4 \times 10^{-14}$	≈ 6.81
60 °C	$\approx 9.6 \times 10^{-14}$	≈ 6.51

Step 2 — Key distinction: At 37 °C, a solution with pH $= 6.8$ is *neutral* (not acidic!), because $[H^+] = [OH^-]$ at that temperature. Acidity/neutrality/basicity depends on whether pH is below/equal/above $\frac{1}{2}\,pK_w$ at the given temperature.

Why other options are wrong:

- Option A: **Correct.**
- Option B: K_w definitely depends on temperature; this statement is false.
- Option C: K_w increases (not decreases) with temperature; neutral pH falls (not rises).
- Option D: Neutral pH does *not* remain at 7; it decreases as K_w increases with temperature.

Final Answer: K_w increases (endothermic autoionisation); neutral pH falls below 7 at $T > 25$ °C $\Rightarrow$ A

Answer: (A) Go Back to Q 5

Q6.

Solution

Concept — Gibbs Energy, Equilibrium, and the Second Law: At constant temperature and pressure, the Gibbs free energy G of the system decreases during a spontaneous process and reaches a *minimum* at equilibrium. The Second Law of Thermodynamics is stated in terms of the entropy of the *universe*.

Step 1 — Verify statement (I): At equilibrium, G is at its minimum: $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$, which is equivalent to $\Delta G = 0$ for an infinitesimal displacement. Statement (I) is **TRUE**.

Step 2 — Verify statement (II): For a spontaneous process at constant T and P:

$$\Delta G = \Delta H - T\Delta S_{\text{sys}} < 0$$

This is the criterion for spontaneity at constant T, P. Statement (II) is **TRUE**.

Step 3 — Verify statement (III): The Second Law: for any spontaneous process, $\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$. Note that $\Delta G_{\text{sys}} < 0 \Leftrightarrow \Delta S_{\text{universe}} > 0$ at constant T, P (they are equivalent formulations). Statement (III) is **TRUE**.

Why other options are wrong:

- Option A: Only (I) — omits (II) and (III), both of which are also correct.
- Option B: (I) and (II) — omits (III), the primary statement of the Second Law.
- Option C: (I) and (III) — omits (II), which is the Gibbs energy criterion for spontaneity.
- Option D: **Correct** — all three statements are valid thermodynamic principles.

Final Answer: Statements (I), (II), and (III) are all thermodynamically correct $\Rightarrow$ $\boxed{\text{D}}$

Answer: (D) Go Back to Q 6

Q7.

Solution

Concept — Lattice Energy and Ionic Radius: Lattice energy is the energy required to convert one mole of ionic crystal into its constituent gaseous ions. According to the Born–Landé equation:

$$U \propto \frac{|z^+||z^-|}{r_0}$$

where $r_0 = r_+ + r_-$ is the interionic distance. For alkali metal fluorides, the charge product ($|z^+||z^-| = 1$) is constant; therefore lattice energy **decreases as the cation size increases**.

Step 1 — Cation radii and interionic distances:

$$r(\mathrm{Li}^+) < r(\mathrm{Na}^+) < r(\mathrm{K}^+) < r(\mathrm{Rb}^+)$$

Adding the constant $r(\mathrm{F}^-)$ to each: $r_0(\mathrm{LiF}) < r_0(\mathrm{NaF}) < r_0(\mathrm{KF}) < r_0(\mathrm{RbF})$.

Step 2 — Lattice energy order (approximate values):

Salt	r_0 (pm)	U (kJ mol^{-1})
LiF	201	1037
NaF	231	923
KF	266	821
RbF	282	785

Smaller interionic distance $\Rightarrow$ stronger Coulombic attraction $\Rightarrow$ higher lattice energy: $\mathrm{LiF} > \mathrm{NaF} > \mathrm{KF} > \mathrm{RbF}$.

Why other options are wrong:

- Option A: Reverse order — incorrect; lattice energy *decreases* down the group.
- Option B: Puts NaF above LiF — incorrect; $r(\mathrm{Li}^+) < r(\mathrm{Na}^+)$ so LiF has smaller r_0.
- Option C: **Correct.**
- Option D: Places KF above both LiF and NaF — incorrect.

Final Answer: $\mathrm{LiF} > \mathrm{NaF} > \mathrm{KF} > \mathrm{RbF}$ (shorter bond $\Rightarrow$ stronger attraction) $\Rightarrow$ C

Answer: (C) Go Back to Q 7

Q8.

Solution

Concept — Linkage Isomerism: Linkage isomers arise when an **ambidentate ligand** — one capable of coordinating through two different donor atoms — bonds through different atoms in two otherwise identical complexes. NO_2^- (nitrite) is the classic ambidentate ligand: it can coordinate via **nitrogen** (giving a *nitro* complex, prefixed *nitro-*) or via **oxygen** (giving a *nitrito* complex, prefixed *nitrito-*).

Step 1 — IUPAC nomenclature:

- **Nitro** (κN-coordination): The nitrogen of NO_2^- bonds to the metal. Bond: $Co - NO_2$. Name prefix: *nitro*.
- **Nitrito** (κO-coordination): One oxygen of NO_2^- bonds to the metal. Bond: $Co - ONO$. Name prefix: *nitrito-*κO.

Step 2 — Reading the diagram: In **Isomer 1**: the bond drawn is **Co**$-$**N** (cobalt bonds directly to the nitrogen atom of NO_2) $\Rightarrow$ *nitro* form, $[Co(NH_3)_5(NO_2)]^{2+}$.
In **Isomer 2**: the bond drawn is **Co**$-$**O** (cobalt bonds to an oxygen, which connects to N) $\Rightarrow$ *nitrito* form, $[Co(NH_3)_5(ONO)]^{2+}$.

Why other options are wrong:

- Option A: Reverses the names; Isomer 1 shows Co$-$N (nitro), not nitrito.
- Option B: **Correct.**
- Option C: Isomer 2 clearly shows a Co$-$O bond, not Co$-$N; cannot both be nitro.
- Option D: Isomer 1 clearly shows a Co$-$N bond; cannot both be nitrito.

Final Answer: Isomer 1 = nitro (Co$-$N bond); Isomer 2 = nitrito (Co$-$O bond) $\Rightarrow$ $\boxed{B}$

Answer: (B) Go Back to Q 8

Q9.

Solution

Concept — Crystal Field Stabilization Energy (CFSE): In an octahedral crystal field the five d orbitals split into a lower-energy t_{2g} set (three orbitals, each at energy $-0.4\,\Delta_o$ relative to the barycentre) and an upper e_g set (two orbitals, each at $+0.6\,\Delta_o$). For a **strong-field** (low-spin) d^6 ion, the Aufbau principle fills the t_{2g} level first: all 6 electrons occupy t_{2g} ($t_{2g}^6\, e_g^0$).

Step 1 — Calculate CFSE for $t_{2g}^6\, e_g^0$:

$$\text{CFSE} = 6 \times (-0.4\,\Delta_o) + 0 \times (+0.6\,\Delta_o) = -2.4\,\Delta_o$$

Step 2 — Compare with high-spin d^6 ($t_{2g}^4\, e_g^2$):

$$\text{CFSE}_{\text{HS}} = 4(-0.4\,\Delta_o) + 2(+0.6\,\Delta_o) = -1.6 + 1.2 = -0.4\,\Delta_o$$

The low-spin configuration is far more stabilised (-2.4 vs. -0.4), reflecting the stronger field ligand that forces electron pairing.

Why other options are wrong:

- Option A: **Correct** — $-2.4\,\Delta_o$ for $t_{2g}^6\, e_g^0$.
- Option B: $-1.6\,\Delta_o$ — this is the partial CFSE of only the four t_{2g} electrons in high-spin d^6 (before the $+e_g$ contribution is added); not a standard result on its own.
- Option C: $-0.4\,\Delta_o$ — this is the CFSE for *high-spin* d^6 ($t_{2g}^4\, e_g^2$).
- Option D: $-2.0\,\Delta_o$ — this corresponds to d^5 low-spin ($t_{2g}^5\, e_g^0 = 5 \times (-0.4)$), not d^6.

Final Answer: CFSE for low-spin d^6 octahedral $= -2.4\,\Delta_o \Rightarrow$ A

Answer: (A) Go Back to Q 9

Q10.

Solution

Concept — Michael Addition (1,4-Conjugate Addition): An α,β-unsaturated carbonyl (enone/enal) has a conjugated π-system: $\text{C}_\beta{=}\text{C}_\alpha{-}\text{C}(=\text{O})$. The LUMO of this system has a large coefficient at the β**-carbon**. A soft nucleophile (controlled by orbital interactions) attacks the β-carbon in a *1,4-addition*:

$$\text{Nu}^- + \text{C}_\beta{=}\text{C}_\alpha{-}\text{C}(=\text{O}){-}\text{R} \longrightarrow \text{Nu}{-}\text{C}_\beta{-}\text{C}_\alpha{=}\text{C}(-\text{O}^-)\text{R} \xrightarrow{H^+} \text{Nu}{-}\text{C}_\beta{-}\text{C}_\alpha\text{H}{-}\text{C}(=\text{O})\text{R}$$

Step 1 — Why 1,4 and not 1,2?

- *Hard* nucleophiles (organolithium, Grignard in some cases) prefer *1,2-addition* (direct attack on carbonyl carbon).
- *Soft* nucleophiles (stabilised carbanions, cyanide, thiols) prefer *1,4-addition* (Michael conditions) because orbital energy matching favours the β-carbon.

Step 2 — Mechanism: (1) Soft nucleophile attacks C_β; (2) negative charge relays to oxygen via the enolate; (3) protonation of the enolate gives the β-substituted carbonyl product.

Why other options are wrong:

- Option A: 1,2-addition at the carbonyl carbon characterises hard nucleophiles, not the Michael reaction.
- Option B: Nucleophilic attack on oxygen does not occur in normal carbonyl chemistry.
- Option C: Attack at the α-carbon would break conjugation and is not mechanistically favoured.
- Option D: **Correct** — β-carbon attack, 1,4-conjugate addition.

Final Answer: Michael donor attacks the β-carbon (1,4-conjugate addition) $\Rightarrow$ $\boxed{\text{D}}$

Answer: (D) Go Back to Q 10

Q11.

Solution

Concept — Diels–Alder Reaction $[4+2]$ Cycloaddition: The Diels–Alder reaction is a concerted, thermally allowed $[4\pi_s + 2\pi_s]$ cycloaddition between a conjugated **diene** (4 π electrons, must adopt *s-cis* conformation) and a **dienophile** (2 π electrons). The product is always a **six-membered ring** with one new double bond derived from the central diene bonds.

Step 1 — Count atoms and bonds:

- Diene: buta-1,3-diene contributes 4 carbons with two terminal double bonds ($C_1{=}C_2{-}C_3{=}C_4$).
- Dienophile: ethene contributes 2 carbons with one double bond.
- Two new σ bonds form: between C_1 and one carbon of ethene, and between C_4 and the other carbon of ethene. The $C_1{=}C_2$ and $C_3{=}C_4$ double bonds break; the $C_2{-}C_3$ bond becomes the ring double bond at $C_2{=}C_3$.

Total ring: 6 carbons with **one** double bond (C2=C3) $\Rightarrow$ **cyclohexene**.

Step 2 — Confirm ring size: $4+2 = 6$ atoms in the ring; one double bond remains from the diene interior. Product is cyclohex-2-ene (= cyclohexene).

Why other options are wrong:

- Option A: Benzene requires three double bonds (aromatic); it is not the direct $[4+2]$ product of these reactants.
- Option B: Cyclohexane (fully saturated) would require a reduction step after the Diels–Alder reaction.
- Option C: **Correct** — cyclohexene with one remaining double bond.
- Option D: Cyclohexa-1,3-diene would require a dienophile with a triple bond (e.g., acetylene), not ethene.

Final Answer: Buta-1,3-diene + ethene $\xrightarrow{[4+2]}$ cyclohexene $\Rightarrow \boxed{\text{C}}$

Answer: (C) Go Back to Q 11

Q12.

Solution

Concept — Kohlrausch's Law for Weak Electrolytes: The molar conductivity at infinite dilution (Λ_m°) of a weak electrolyte cannot be measured directly by extrapolation (conductance rises steeply near infinite dilution). Instead, it is obtained by combining Λ_m° values of strong electrolytes sharing the same ions (Kohlrausch's law of independent ion migration):

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-)$$

Step 1 — Express ionic conductances from data:

$$\Lambda_m^\circ(\text{HCl}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-) = 426$$

$$\Lambda_m^\circ(\text{CH}_3\text{COONa}) = \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+) = 91$$

$$\Lambda_m^\circ(\text{NaCl}) = \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-) = 126$$

Step 2 — Combine (Hess's law for conductances):

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{CH}_3\text{COONa}) - \Lambda_m^\circ(\text{NaCl})$$

$$= 426 + 91 - 126 = \mathbf{391}\ \text{S}\,\text{cm}^2\,\text{mol}^{-1}$$

(This cancels $\lambda^\circ(\text{Na}^+)$ and $\lambda^\circ(\text{Cl}^-)$, leaving $\lambda^\circ(\text{H}^+) + \lambda^\circ(\text{CH}_3\text{COO}^-)$.)

Why other options are wrong:

- Option A: $517 = 426 + 91$ — forgets to subtract $\Lambda_m^\circ(\text{NaCl})$.
- Option B: **Correct** — $391\ \text{S}\,\text{cm}^2\,\text{mol}^{-1}$.

- Option C: $643 = 426+91+126$ — incorrectly *adds* NaCl instead of subtracting.
- Option D: 217 does not follow from any valid arithmetic on the given data.

Final Answer: $\Lambda_m^\circ(CH_3COOH) = 426 + 91 - 126 = 391\ \text{S cm}^2\,\text{mol}^{-1} \Rightarrow \boxed{\text{B}}$

Answer: (B) Go Back to Q 12

Q13.

Solution

Concept — Integrated Rate Law for Second-Order Reactions: For $\text{A} \rightarrow \text{P}$ with rate $= k[\text{A}]^2$, integrating the differential rate law gives:

$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + kt$$

Step 1 — Derive the half-life: At $t = t_{1/2}$, $[\text{A}]_t = [\text{A}]_0/2$:

$$\frac{2}{[\text{A}]_0} = \frac{1}{[\text{A}]_0} + k\,t_{1/2} \implies k\,t_{1/2} = \frac{1}{[\text{A}]_0} \implies \boxed{t_{1/2} = \frac{1}{k[\text{A}]_0}}$$

Step 2 — Concentration dependence: Since $t_{1/2} \propto 1/[\text{A}]_0$, doubling the initial concentration *halves* the half-life. Unlike the constant half-life of first-order reactions, for a second-order reaction each successive half-life is *twice* as long as the previous one (as $[\text{A}]$ falls, $t_{1/2}$ increases).

Why other options are wrong:

- Option A: **Correct** — $t_{1/2} = 1/(k[\text{A}]_0)$; inversely proportional to $[\text{A}]_0$.
- Option B: $t_{1/2} = 0.693/k$ is the *first-order* half-life; it is concentration-independent.
- Option C: $t_{1/2} = k[\text{A}]_0$ has wrong units (gives time $\times$ conc^{-1} $\times$ conc $=$ time units only if k has odd units) and the incorrect proportionality.
- Option D: $t_{1/2} = 1/(2k[\text{A}]_0)$ introduces a spurious factor of 2; the correct result has no factor of 2 in the denominator.

Final Answer: $t_{1/2} = 1/(k[\text{A}]_0)$; decreases as $[\text{A}]_0$ increases $\Rightarrow \boxed{\text{A}}$

Answer: (A) Go Back to Q 13

Q14.

Solution

Concept — Spin-Only Magnetic Moment: The spin-only formula gives the magnetic moment contributed by unpaired electron spins:

$$\mu_s = \sqrt{n(n+2)}\ \text{BM}$$

where n = number of unpaired electrons and BM = Bohr magneton. This formula is valid when orbital angular momentum is quenched (as in most first-row transition metal complexes).

Step 1 — Electronic configuration of Fe^{3+}:

$$\text{Fe}:\ [\text{Ar}]\,3d^6\,4s^2 \xrightarrow{-3e^-} \text{Fe}^{3+}:\ [\text{Ar}]\,3d^5$$

In a high-spin field (weak-field ligands, e.g. F^-, H_2O), the $3d^5$ configuration follows Hund's rule: $\uparrow\uparrow\uparrow\uparrow\uparrow$ (one electron in each d orbital) $\Rightarrow n = 5$ unpaired electrons.

Step 2 — Calculate μ_s:

$$\mu_s = \sqrt{5(5+2)} = \sqrt{5\times 7} = \sqrt{35} \approx 5.92\ \text{BM}$$

This is consistent with experimental measurements for high-spin Fe^{3+} complexes (≈ 5.9 BM).

Why other options are wrong:

- Option A: $\sqrt{8}$ ($n = 2$) corresponds to Ni^{2+} (d^8, 2 unpaired), not Fe^{3+}.
- Option B: $\sqrt{24}$ ($n = 4$) corresponds to Fe^{2+} high-spin (d^6, 4 unpaired in $t_{2g}^4\, e_g^2$).
- Option C: $\sqrt{15}$ ($n = 3$) corresponds to Co^{2+} low-spin (d^7, 3 unpaired) or Cr^{3+} (d^3).
- Option D: **Correct** — $\sqrt{35} \approx 5.92$ BM for Fe^{3+} (d^5, 5 unpaired, high-spin).

Final Answer: $\mu_s(\text{Fe}^{3+}) = \sqrt{35} \approx 5.92$ BM ($n = 5$ unpaired electrons) $\Rightarrow$ D

Answer: (D) Go Back to Q 14

Q15.

Solution

Concept — Conducting Polymers and Doping: Polyacetylene $[-\mathrm{CH}=\mathrm{CH}-]_n$ has a conjugated π-system with alternating single and double bonds. In the *undoped* state it is a *semiconductor* (band gap $\sim 1.5\ \mathrm{eV}$), not a metal. Its conductivity is dramatically increased by **doping**: chemical oxidation (p-doping, e.g. with $\mathrm{I_2}$, $\mathrm{AsF_5}$) or reduction (n-doping, e.g. with Na). This discovery by Shirakawa, MacDiarmid, and Heeger earned the 2000 Nobel Prize in Chemistry.

Step 1 — Mechanism of doping:

- *p-Doping* (oxidation): removes electrons from the π-band, creating positively charged defects called **solitons** or **polarons**.
- *n-Doping* (reduction): adds electrons to the π-band.

These charge carriers are mobile along the conjugated backbone, enabling electrical conduction. Conductivities can reach $10^5\ \mathrm{S\,cm^{-1}}$ — comparable to copper — upon heavy doping.

Step 2 — Why undoped polyacetylene is not metallic: The alternating bond-length structure (Peierls distortion) opens a band gap at the Fermi level, preventing metallic conductivity in the pristine material. Doping partially fills or empties this band, closing the effective gap.

Why other options are wrong:

- Option A: Bond alternation (Peierls distortion) means bonds are *not* equivalent; undoped polyacetylene is a semiconductor, not a metal.
- Option B: Conductivity is electronic (via π-band carriers), not protonic; proton hopping occurs in certain proton-exchange membranes, not conjugated polymers.
- Option C: **Correct** — doping introduces polarons/solitons into the π-system, generating conductivity.
- Option D: Ionic conduction through absorbed water is relevant to polyelectrolytes and fuel-cell membranes, not to the π-conjugated mechanism in polyacetylene.

Final Answer: Doping (oxidation/reduction) creates mobile charge carriers in the conjugated π-system $\Rightarrow$ C

Answer: (C) Go Back to Q 15

Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	A	2	D	3	C	4	B	5	A
6	D	7	C	8	B	9	A	10	D
11	C	12	B	13	A	14	D	15	C