TIFR GS Chemistry

Sample Paper – 7

Duration: 180 Minutes **Maximum Marks: 120**

Instructions

- This paper contains **40** Multiple Choice Questions (Single Correct Answer), modelled on the **TIFR Graduate School (GS) Chemistry** entrance examination.
- Each correct answer carries **+3 marks**. **1 mark** is deducted for each incorrect answer. Unattempted questions carry **zero** marks.
- Only **one** option is correct. Choose carefully before marking.
- Syllabus level: B.Sc./M.Sc. Chemistry — Physical, Organic, Inorganic, Analytical, Quantum Chemistry, Spectroscopy (NMR, IR, UV-Vis, MS), Electrochemistry, Biophysics, and Mathematical Methods.
- Personal calculators, mobile phones, and electronic gadgets are strictly prohibited. Rough sheets will be provided at the examination centre.

Q1. For a real gas with a positive second virial coefficient $B > 0$, the fugacity f compared to pressure P at moderate pressures obeys:

(A) $f < P$

(B) $f = P$

(C) $f = RT/P$

(D) $f > P$

Q2. For an irreversible isothermal free expansion of an ideal gas against zero external pressure (Joule expansion), which statement correctly applies the Clausius inequality?

(A) $\Delta S_{\text{total}} = 0$

(B) $\Delta S_{\text{system}} = 0$

(C) $\Delta S_{\text{total}} > 0$ (entropy of the universe increases)

(D) $\Delta S_{\text{surroundings}} > 0$

Q3. For consecutive first-order reactions $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$ with $k_1 = 0.10\ \text{s}^{-1}$ and $k_2 = 0.010\ \text{s}^{-1}$, starting from pure A, the time $t_{\max}$ at which the concentration of B is maximum is approximately:

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

(B) $26\ \text{s}$

(C) $100\ \text{s}$

(D) $0.9\ \text{s}$

Q4. In the Lindemann–Hinshelwood mechanism for unimolecular reactions, at HIGH pressure the apparent rate constant k_{eff} approaches:

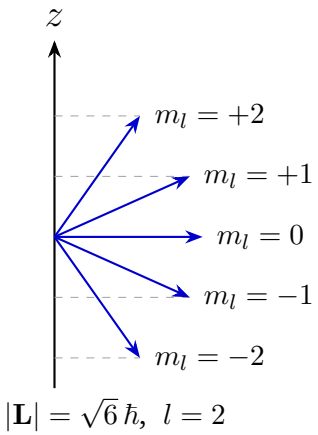
(A) $k_1 k_2 / k_{-1}$ (first-order, pressure-independent)

(B) $k_1[\text{M}]$ (second-order in reactant)

(C) k_2 (rate-limiting isomerisation only)

(D) k_1 (rate-limiting activation only)

Q5. For an electron in an orbital with azimuthal quantum number $l = 2$ (a d orbital), the possible values of the magnetic quantum number m_l are shown in the vector model below. Which set is correct?



(A) $0, +1, +2$ only

(B) $-2, -1, 0$ only

(C) $-1, 0, +1$ only

(D) $-2, -1, 0, +1, +2$

Q6. For the electron configuration d^1 giving term symbol ${}^2D$ ($L = 2$, $S = \frac{1}{2}$), which J value corresponds to the ground state according to Hund's third rule (less-than-half-filled shell)?

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

(B) ${}^2D_2$

(C) ${}^2D_{3/2}$

(D) ${}^2D_{5/2}$

Q7. In a homonuclear ${}^1\mathrm{H}$–${}^1\mathrm{H}$ decoupling experiment, the resonance frequency of proton $\mathrm{H_A}$ is irradiated while the signal of proton $\mathrm{H_X}$ (which is J-coupled to $\mathrm{H_A}$) is observed. The result is:

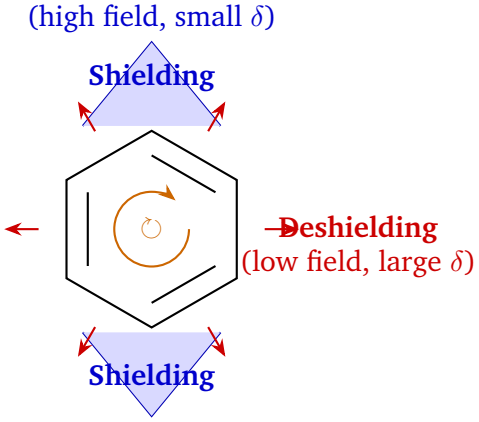
(A) The $\mathrm{H_X}$ signal disappears entirely

(B) The $\mathrm{H_X}$ multiplet collapses to a singlet

(C) The chemical shift of $\mathrm{H_X}$ changes significantly

(D) The $\mathrm{H_A}$ and $\mathrm{H_X}$ peaks merge into one signal

Q8. Protons located above or below the plane of a benzene ring (inside the shielding cone of the ring current, as shown) are expected to resonate at:



(A) Unusually high field (small δ, upfield)

(B) Unusually low field (large δ, downfield)

(C) The same chemical shift as a CH_3 group

(D) The same chemical shift as an OH group

Q9. The McLafferty rearrangement requires a carbonyl group, a γ-hydrogen, and a six-membered cyclic transition state. Which compound **cannot** undergo a McLafferty rearrangement?

(A) Pentan-2-one ($CH_3COCH_2CH_2CH_3$)

(B) 4-Methylpentan-2-one

(C) Hexan-2-one

(D) Propan-2-one (acetone, CH_3COCH_3)

Q10. Using Hooke's law ($\tilde{\nu} \propto \sqrt{k/\mu}$), arrange the following bonds in order of **increasing** stretching frequency:

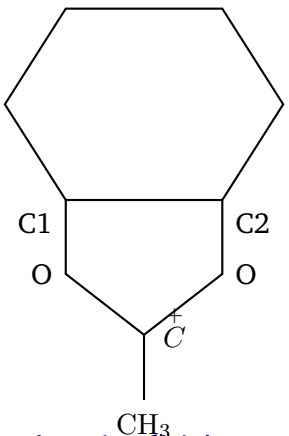
(A) $C{\equiv}C < C{=}C < C{-}C$

(B) $C{=}C < C{-}C < C{\equiv}C$

(C) $C{-}C < C{=}C < C{\equiv}C$

(D) $C{-}C < C{\equiv}C < C{=}C$

Q11. Acetolysis of *trans*-2-acetoxycyclohexyl brosylate proceeds with overall **retention** of configuration at both stereocentres. The key intermediate responsible for this outcome is shown below. This mechanism proceeds via:



Acyloxonium (cyclic) intermediate
(1,3-dioxolan-2-ylium fused to cyclohexane)

(A) Direct S_N1 with carbenium ion racemisation

(B) Neighboring group participation via cyclic acyloxonium ion giving double inversion (net retention)

(C) E2 elimination followed by electrophilic addition

(D) Direct S_N2 with inversion at C1 only

Q12. Treatment of 2,3-dimethyl-2,3-butanediol (pinacol) with dilute H_2SO_4 gives primarily:

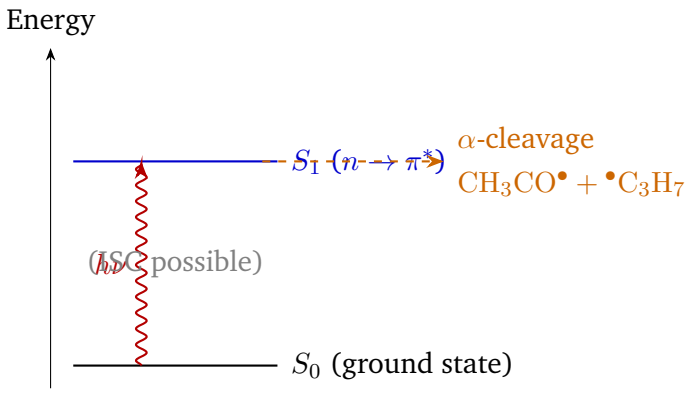
(A) 3,3-Dimethylbutan-2-one (pinacolone)

(B) 2,3-Dimethylbut-2-ene

(C) 2-Methylpropan-1-ol

(D) 2,3-Dimethylbutanal

Q13. Irradiation of pentan-2-one ($CH_3COCH_2CH_2CH_3$) with UV light leads to Norrish Type I α-cleavage (see energy diagram). Which pair of radical fragments is formed in the **primary** step?



(A) $CH_3^\bullet$ and $^\bullet COCH_2CH_2CH_3$

(B) CO and pentane-derived radicals

(C) $CH_3CH_2^\bullet$ and $CH_3CO-CH_2^\bullet$

(D) $CH_3CO^\bullet$ (acetyl radical) and $^\bullet CH_2CH_2CH_3$ (propyl radical)

Q14. Photochemical [2+2] cycloaddition of two alkene molecules is thermally forbidden but photochemically allowed because:

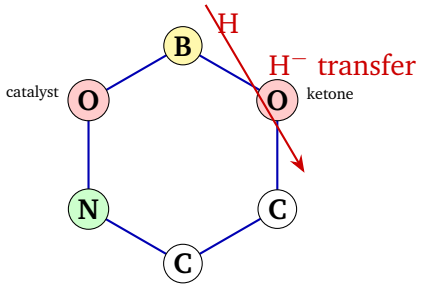
(A) Light provides the thermal activation energy required to overcome the barrier

(B) The reaction is thermally allowed at sufficiently elevated temperatures

(C) In the excited state, the HOMO symmetry is reversed so it can overlap constructively with the ground-state LUMO

(D) It proceeds through a triplet state with no orbital-symmetry constraints at all

Q15. In the Corey–Bakshi–Shibata (CBS) reduction, the oxazaborolidine catalyst activates BH_3 and the ketone coordinates to boron. The key six-membered transition state (schematic shown below) delivers the hydride from:



CBS six-membered TS

(A) The nitrogen atom of the oxazolidine ring

(B) The boron atom of the activated BH_3 within the chiral transition state

(C) External $NaBH_4$ in solution

(D) A proton from the chiral auxiliary

Q16. Base-catalysed ester hydrolysis ($B_{AC}2$ mechanism) proceeds by:

(A) Nucleophilic addition of OH^- to the acyl carbon forming a tetrahedral intermediate (rate-limiting step)

(B) E1cb elimination at the ester linkage

(C) Protonation of the acyl oxygen followed by S_N2 at the alkyl carbon

(D) Carbenium ion formation at the alkyl carbon

Q17. Which of the following is a **meso** compound (achiral despite having two stereocentres)?

(A) (R, R)-Tartaric acid

(B) (S, S)-Tartaric acid

(C) (R, S)-Lactic acid (has only one stereocentre)

(D) $(2R, 3S)$-Tartaric acid

Q18. In the Stork enamine synthesis, cyclohexanone is converted to its pyrrolidine enamine, which is then reacted with allyl bromide. After aqueous hydrolysis, the major product is:

(A) 3-Allylcyclohexan-1-one

(B) 1-Allylcyclohexanol

(C) 2-Allylcyclohexan-1-one

(D) Cyclohexyl allyl ether

Q19. Singlet methylene ($:CH_2$, singlet state) adds to *cis*-but-2-ene. The stereochemical outcome is:

(A) *trans*-1,2-Dimethylcyclopropane

(B) *cis*-1,2-Dimethylcyclopropane

(C) Racemic mixture of *cis* and *trans* isomers

(D) 1-Methylcyclopropane

Q20. In a Lewis acid-catalysed Diels–Alder reaction using an Evans oxazolidinone dienophile, the chiral auxiliary controls facial selectivity. The major product forms via diene attack on which face of the dienophile?

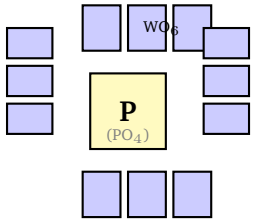
(A) Re face (away from the bulky group of the chiral auxiliary)

(B) Si face (same side as the chiral auxiliary)

(C) Both faces equally – no selectivity without Lewis acid

(D) Top face always, regardless of auxiliary configuration

Q21. The Keggin anion $[PW_{12}O_{40}]^{3-}$ has which structural type? (Schematic diagram shown below.)



Keggin structure: $[PW_{12}O_{40}]^{3-}$

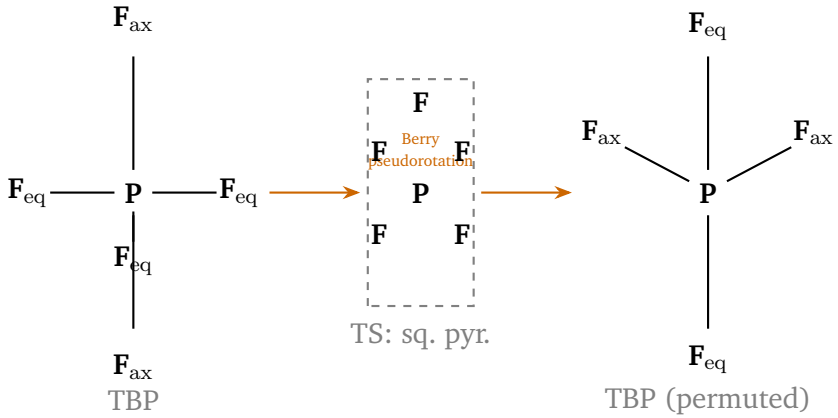
(A) Linear chain of WO_6 octahedra

(B) Corner-sharing WO_4 tetrahedra only

(C) Ring of 12 WO_6 octahedra with no central heteroatom

(D) Central PO_4 tetrahedron surrounded by 12 corner- and edge-sharing WO_6 octahedra

Q22. Berry pseudorotation is a fluxional process in trigonal bipyramidal molecules. The diagram below shows the process for PF_5. This process:



(A) Exchanges only the equatorial F atoms

(B) Requires breaking and re-forming P–F bonds

(C) Interconverts axial and equatorial F atoms via a square pyramidal transition state

(D) Occurs only at temperatures above 200 °C

Q23. The complex $[Re_2Cl_8]^{2-}$ features a quadruple Re–Re bond. This bond consists of:

(A) One σ and two π bonds (triple bond)

(B) One σ, two π, and one δ bond (quadruple bond)

(C) Four σ bonds

(D) Two σ and two π bonds

Q24. In Ziegler–Natta polymerisation of propylene using $TiCl_4/Al(C_2H_5)_3$, propylene insertion occurs by:

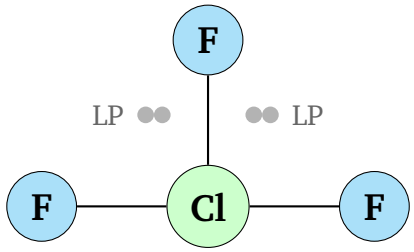
(A) 1,2-Insertion of the alkene into the Ti–C bond via a four-centre transition state (Cossée–Arlman mechanism)

(B) Radical addition to $TiCl_4$

(C) Olefin metathesis of the propylene C=C bond

(D) Anionic polymerisation initiated by the alkylaluminium

Q25. The molecular geometry of ClF_3 (3 bonding pairs + 2 lone pairs on Cl, VSEPR) is shown below. The correct name for this geometry is:



ClF_3: 3 bonding + 2 lone pairs

(A) Trigonal planar

(B) Pyramidal (trigonal pyramidal)

(C) Trigonal bipyramidal

(D) T-shaped

Q26. In diborane (B_2H_6), the two bridging B–H–B bonds are best described as:

(A) Conventional 2-centre 2-electron covalent bonds

(B) Ionic bonds (H^- bridging B^+)

(C) Three-centre two-electron (3c-2e) banana bonds

(D) Hydrogen bonds

Q27. In the ideal cubic perovskite structure (ABX_3, e.g. $CaTiO_3$), the coordination number of the large A cation (e.g. Ca^{2+}) is:

(A) 6 (octahedral)

(B) 12 (cuboctahedral)

(C) 4 (tetrahedral)

(D) 8 (cubic)

Q28. The $[2Fe{-}2S]$ ferredoxin cluster contains:

(A) 2 Fe bridged by 2 S^{2-} ions, each Fe also ligated by 2 cysteinyl sulfur atoms; one-electron redox (Fe^{3+}/Fe^{2+})

(B) 2 Fe in high-spin tetrahedral sites, two-electron redox

(C) 2 Fe bridged by 2 oxo (O^{2-}) ions

(D) Equal numbers of Fe^{2+} and Fe^{3+} in separate sites with no bridging ligand

Q29. In the Mohr method for determining Cl^- by titration with $AgNO_3$, the indicator used to detect the endpoint is:

(A) Eriochrome Black T

(B) Phenolphthalein

(C) Starch solution

(D) Potassium chromate (K_2CrO_4)

Q30. In potentiometric titration, the equivalence point is most accurately located by:

(A) The point where the cell potential $E = 0.0$ V

(B) The point where the potential changes most slowly (minimum $\mathrm{d}E/\mathrm{d}V$)

(C) The maximum in $\mathrm{d}E/\mathrm{d}V$ (or the zero-crossing in $\mathrm{d}^2E/\mathrm{d}V^2$)

(D) The point where the total titrant volume equals half the equivalence volume

Q31. In thin-layer chromatography (TLC) on silica gel (polar stationary phase) with a non-polar eluent, which compound has the **higher** R_f value (travels further)?

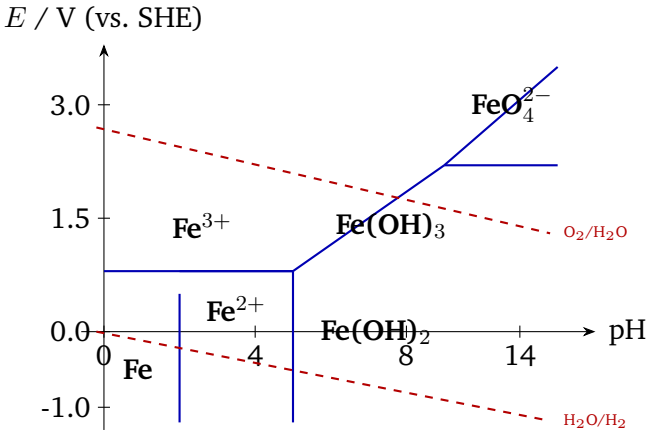
(A) Benzoic acid

(B) Hexane

(C) Phenol

(D) Ethanol

Q32. In the Pourbaix (E–pH) diagram for iron (schematic below), the region of **metallic Fe** stability is found at:



(A) Low potential (negative E, strongly reducing conditions)

(B) High potential and low pH

(C) High potential and high pH

(D) Any potential at pH 7

Q33. For an electrode reaction with transfer coefficient $\alpha = 0.50$ at $T = 298$ K, the Tafel slope $b = 2.303RT/(\alpha F)$ for the anodic branch is approximately:

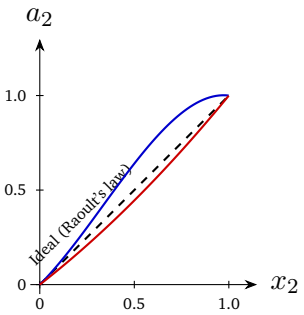
(A) 59 mV/decade

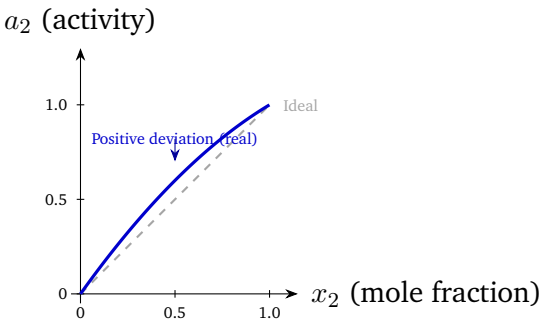
(B) 30 mV/decade

(C) 240 mV/decade

(D) 118 mV/decade

Q34. A solution shows **positive** deviation from Raoult's law (activity curve shown below). This occurs when:





(A) A–B interactions are stronger than A–A and B–B interactions

(B) The solution is ideal (Raoult's law holds exactly)

(C) A–B interactions are weaker than A–A and B–B interactions

(D) The boiling point of the mixture is higher than either pure component

Q35. Blood is a non-Newtonian fluid exhibiting shear-thinning (pseudoplastic) behaviour. This means its apparent viscosity:

(A) Increases as the shear rate increases (shear-thickening)

(B) Decreases as the shear rate increases (shear-thinning)

(C) Is constant regardless of shear rate (Newtonian)

(D) Is zero at all shear rates

Q36. At very low temperatures ($T \ll \theta_D$), which model correctly predicts that the molar heat capacity $C_V \propto T^3$?

(A) Debye model

(B) Einstein model

(C) Classical Dulong–Petit model ($C_V = 3R$)

(D) Ideal gas model ($C_V = \frac{3}{2}R$)

Q37. In a lipid bilayer, increasing the proportion of cholesterol:

(A) Significantly lowers the melting temperature T_m of saturated lipids

(B) Increases the phase-transition enthalpy ΔH_{trans}

(C) Has no effect on the phase behaviour of the bilayer

(D) Abolishes the sharp gel$\leftrightarrow$liquid-crystalline phase transition

Q38. For a long double-stranded DNA in 1 M NaCl, using the approximation $T_m\,(^\circ\text{C}) = 69.3 + 0.41 \times (\%\text{GC})$, a fragment with 60% GC content has T_m approximately equal to:

(A) $79\ ^\circ\text{C}$

(B) $87\ ^\circ\text{C}$

(C) $94\ ^\circ\text{C}$

(D) $100\ ^\circ\text{C}$

Q39. The Laplace transform of the function $f(t) = e^{-at}$ (with $a > 0$, $t \geq 0$) is:

(A) $\dfrac{1}{s-a}$

(B) $\dfrac{1}{s+a}$

(C) $\dfrac{a}{s^2+a^2}$

(D) $\dfrac{s}{s^2+a^2}$

Q40. The Mark–Houwink equation is $[\eta] = KM^a$, where $[\eta]$ is intrinsic viscosity and M is molar mass. For a polymer in a **good solvent** forming a random-coil conformation, the exponent a is approximately:

(A) 0.6–0.8 (random coil in good solvent)

(B) ≈ 0 (compact sphere)

(C) ≈ 1.8 (rigid rod)

(D) ≈ 3

Detailed Solutions

Q1.

Solution

Concept — Fugacity of Real Gases:
Fugacity f is defined via $\mu = \mu^\circ + RT\ln(f/P^\circ)$. At moderate pressures, the virial equation gives $\ln(f/P) = BP/RT$, where B is the second virial coefficient.

Step 1 — Apply the virial expression for fugacity:
For $B > 0$ and $P > 0$, we have $BP/RT > 0$. Therefore $\ln(f/P) > 0$, which means $f/P > 1$, i.e. $f > P$.

Physical interpretation:
A positive B indicates repulsive intermolecular interactions dominate. Molecules escape the gas more easily than in an ideal gas, so the effective pressure (fugacity) exceeds the measured pressure.

Why other options are wrong:
Option A: $f < P$ holds only when $B < 0$ (attractive interactions, as in van der Waals gases below the Boyle temperature).
Option B: $f = P$ is the ideal-gas limit ($B = 0$).
Option C: $f = RT/P$ has incorrect dimensions and is not a valid fugacity expression.

Final Answer: For $B > 0$, $\ln(f/P) = BP/RT > 0 \Rightarrow f > P \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#1

Q2.

Solution

Concept — Clausius Inequality and Free Expansion:
In a free (Joule) expansion against zero external pressure, $w = 0$ and for an ideal gas $\Delta U = 0$, so by the first law $q = 0$.

Step 1 — Entropy of the system:
Although no heat is exchanged with surroundings, the gas expands irreversibly into a larger volume. The entropy change is calculated reversibly: $\Delta S_{\text{sys}} = nR\ln(V_2/V_1) > 0$ (since $V_2 > V_1$).

Step 2 — Entropy of the surroundings:
Since $q_{\text{surr}} = 0$ (no heat exchanged), $\Delta S_{\text{surr}} = q_{\text{surr}}/T = 0$.

Step 3 — Total entropy:
$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + 0 > 0$. This satisfies the Clausius inequality for an irreversible process.

Why other options are wrong:

Option A: $\Delta S_{\text{total}} = 0$ is only true for a reversible process.
Option B: $\Delta S_{\text{system}} = 0$ contradicts the irreversible expansion.
Option D: $\Delta S_{\text{surr}} > 0$ is incorrect since no heat flows to the surroundings.

Final Answer: $\Delta S_{\text{total}} > 0$ (entropy of the universe increases) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#2

Q3.

Solution

Concept — Consecutive First-Order Reactions:
For $\text{A} \to \text{B} \to \text{C}$, the time of maximum $[\text{B}]$ is given by:

$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2}$$

Step 1 — Substitute values:
$k_1 = 0.10\ \text{s}^{-1}$, $k_2 = 0.010\ \text{s}^{-1}$, so $k_1/k_2 = 10$ and $k_1 - k_2 = 0.090\ \text{s}^{-1}$.

Step 2 — Calculate:

$$t_{\max} = \frac{\ln(10)}{0.090} = \frac{2.303}{0.090} \approx 25.6\ \text{s} \approx 26\ \text{s}$$

Why other options are wrong:
Option A: 10 s would arise from $1/k_1 = 10$ s – this is the half-life of A, not $t_{\max}$ of B.
Option C: 100 s would result if k_2 were used as $1/k_2$, which is incorrect.
Option D: 0.9 s is far too short – it approximates $k_1 - k_2$, not $t_{\max}$.

Final Answer: $t_{\max} = \ln(10)/0.090 \approx 26$ s $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#3

Q4.

Solution

Concept — Lindemann–Hinshelwood Mechanism (high-pressure limit):
In this mechanism: $\text{A} + \text{M} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{A}^* + \text{M}$, then $\text{A}^* \xrightarrow{k_2} \text{Products}$.

Step 1 — Steady-state on A*:

$$[\text{A}^*]_{\text{ss}} = \frac{k_1[\text{A}][\text{M}]}{k_{-1}[\text{M}] + k_2}$$

Step 2 — Rate expression:

$$\text{rate} = k_2[\text{A}^*]_{\text{ss}} = \frac{k_1 k_2[\text{A}][\text{M}]}{k_{-1}[\text{M}] + k_2}$$

Step 3 — High-pressure limit ([M] large, $k_{-1}[\mathrm{M}] \gg k_2$):

$$k_{\text{eff}} = \frac{k_1 k_2}{k_{-1}}$$

This is a constant, giving true first-order kinetics independent of pressure.

Why other options are wrong:
Option B: $k_1[\mathrm{M}]$ is the *low*-pressure limit where $k_2 \gg k_{-1}[\mathrm{M}]$.
Option C: k_2 alone is the rate constant for isomerisation but is not the observed k_{eff}.
Option D: k_1 alone would apply if activation were rate-limiting with no back-reaction.

Final Answer: High-pressure limit $\Rightarrow k_{\text{eff}} = k_1 k_2 / k_{-1} \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#4

Q5.

Solution

Concept — Magnetic Quantum Number for $l = 2$:
For a given azimuthal quantum number l, the magnetic quantum number m_l takes all integer values from $-l$ to $+l$, giving $2l + 1$ values total.

Step 1 — Apply the rule for $l = 2$:
$m_l = -2, -1, 0, +1, +2$ – a total of $2(2) + 1 = 5$ values, corresponding to the 5 spatial orientations of d orbitals (d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}).

Step 2 — Vector model context:
The total angular momentum magnitude is $|\mathbf{L}| = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar$. Each m_l value gives the z-component $L_z = m_l \hbar$, as shown in the vector diagram.

Why other options are wrong:
Option A: $0, +1, +2$ omits the negative m_l values.
Option B: $-2, -1, 0$ omits the positive values.
Option C: $-1, 0, +1$ is valid only for $l = 1$ (p orbitals).

Final Answer: For $l = 2$, $m_l \in \{-2, -1, 0, +1, +2\} \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#5

Q6.

Solution

Concept — Hund's Third Rule (Spin–Orbit Coupling):
For a term ${}^{2S+1}L_J$ with given L and S:
– **Less than half-filled**: $J_{\text{min}} = |L - S|$ (lowest energy).

– **More than half-filled**: $J_{\max} = L + S$ (lowest energy).

Step 1 — Identify L, S, and filling:
d^1 configuration: $L = 2$, $S = 1/2$, less than half-filled (half-filled needs d^5).

Step 2 — Find J values and select the ground state:
$J = |L - S|$ to $L + S$, so $J = |2 - 1/2| = 3/2$ or $J = 2 + 1/2 = 5/2$.
For less-than-half-filled: ground state has $J_{\min} = 3/2$, giving ${}^2D_{3/2}$.

Why other options are wrong:
Option A: $J = 1/2$ is not valid for $L = 2$, $S = 1/2$ (minimum J is $3/2$).
Option B: $J = 2$ is not a half-integer and is not valid for this term.
Option D: ${}^2D_{5/2}$ would be the ground state for d^9 (more than half-filled), not d^1.

Final Answer: d^1 ground state $= {}^2D_{3/2} \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#6

Q7.

Solution

Concept — Homonuclear Spin Decoupling in NMR:
When proton H_A is irradiated at its resonance frequency, its spin state is rapidly averaged. Any coupling between H_A and H_X that produced splitting of the H_X signal is therefore removed.

Step 1 — Effect on H_X multiplicity:
The J-coupling arises from spin–spin interaction transmitted through bonds. Saturating H_A eliminates its spin states, so H_X no longer "sees" H_A and its multiplet (doublet, triplet, etc.) collapses to a singlet.

Step 2 — No effect on chemical shift:
Decoupling only removes J-coupling; the chemical shift (Larmor frequency) of H_X is determined by its electronic environment and is unchanged.

Why other options are wrong:
Option A: H_X does not disappear; only its coupling pattern is removed.
Option C: Chemical shift of H_X is not changed by decoupling.
Option D: H_A and H_X signals remain at their own frequencies and do not merge.

Final Answer: H_X multiplet collapses to a singlet $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#7

Q8.

Solution

Concept — Aromatic Ring Current and NMR Shielding:
The π electrons of benzene circulate in an induced ring current when placed in

an external magnetic field B_0. This current generates a local magnetic field that opposes B_0 above/below the ring (shielding) and reinforces B_0 at the periphery (deshielding).

Step 1 — Effect on protons in the shielding cone:
Protons above or below the ring plane experience a reduced effective field $B_{\text{eff}} < B_0$. They therefore resonate at a lower frequency (smaller δ, upfield) compared to a proton with no ring current effect.

Step 2 — Quantitative context:
Protons inside [18]annulene inner cavity resonate near $\delta \approx -3$ ppm (highly upfield). Aromatic ring protons on the periphery resonate at $\delta \approx 7$–8 ppm (downfield) due to deshielding.

Why other options are wrong:
Option B: Downfield (large δ) applies to protons at the *periphery* (deshielding zone), not above/below the ring.
Option C: CH_3 resonates near $\delta \approx 0.9$ ppm, not where ring-current effects dominate.
Option D: OH groups resonate at $\delta \approx 2$–5 ppm, unrelated to ring current position.

Final Answer: Shielding cone protons $\rightarrow$ unusually high field (small δ) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#8

Q9.

Solution

Concept — McLafferty Rearrangement Requirements:
The McLafferty rearrangement requires: (i) a carbonyl group, (ii) a γ-hydrogen (on the carbon three bonds away from C=O), and (iii) a six-membered cyclic transition state.

Step 1 — Check each compound for γ-hydrogens:
Pentan-2-one ($CH_3COCH_2CH_2CH_3$): α-C is C3, β-C is C4, γ-C is C5 (CH_3) – **has** γ-H.
Propan-2-one (CH_3COCH_3): α-carbons are both CH_3 groups. There is no β or γ carbon – **no** γ-H possible.

Step 2 — Confirm acetone cannot rearrange:
With only α-CH_3 groups and no chain extension, the six-membered TS cannot form. Acetone therefore does not undergo McLafferty rearrangement in mass spectrometry.

Why other options are wrong:
Options A, B, C: All have a chain of at least 4 carbons from the carbonyl carbon, providing a γ-hydrogen and enabling the rearrangement.

Final Answer: Acetone (propan-2-one) has no γ-H $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#9

Solution

Concept — IR Stretching Frequencies and Bond Order:
By Hooke's law, $\tilde{\nu} \propto \sqrt{k/\mu}$, where k is the force constant (bond stiffness) and μ is the reduced mass. Higher bond order $\Rightarrow$ larger k $\Rightarrow$ higher $\tilde{\nu}$.

Step 1 — Compare bond orders and typical frequencies:

Q10.

- C–C single bond ($k \approx 500\ \mathrm{N\,m^{-1}}$): $\tilde{\nu} \approx 1000\ \mathrm{cm^{-1}}$
- C=C double bond ($k \approx 1000\ \mathrm{N\,m^{-1}}$): $\tilde{\nu} \approx 1650\ \mathrm{cm^{-1}}$
- C≡C triple bond ($k \approx 1500\ \mathrm{N\,m^{-1}}$): $\tilde{\nu} \approx 2100\ \mathrm{cm^{-1}}$

Step 2 — Order:
$\mathrm{C{-}C}$ (lowest) $<$ $\mathrm{C{=}C}$ $<$ $\mathrm{C{\equiv}C}$ (highest)

Why other options are wrong:
Options A, B, D: All incorrectly place C≡C below C=C or C–C, which contradicts the bond-order vs. force-constant relationship.

Final Answer: C–C $<$ C=C $<$ C≡C $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#10

Q11.

Solution

Concept — Neighboring Group Participation (NGP):
When a nucleophilic group (here the acetate OAc at C2) is *trans* to a leaving group at C1, it can participate intramolecularly to form a cyclic intermediate before external nucleophile attack.

Step 1 — Formation of the cyclic acyloxonium ion:
The carbonyl oxygen (or ester oxygen) of the OAc at C2 attacks C1 as the brosylate departs. This gives a bicyclic 1,3-dioxolan-2-ylium (acyloxonium) cation fused to the cyclohexane ring – the first inversion at C1.

Step 2 — Attack by external nucleophile (acetate):
The acyloxonium ion is attacked by $\mathrm{AcO^-}$ (or AcOH) at C1 (or symmetrically at C2). This second inversion at C1 returns configuration. Net result: double inversion = overall retention at both C1 and C2.

Why other options are wrong:
Option A: An $\mathrm{S_N1}$ carbenium ion would give racemisation, not retention.

Option C: No elimination is observed; substrate geometry is preserved.
Option D: Direct S_N2 would give net inversion, not retention.

Final Answer: NGP via cyclic acyloxonium $\rightarrow$ double inversion $\rightarrow$ net retention $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#11

Q12.

Solution

Concept — Pinacol Rearrangement:
Pinacol (2,3-dimethyl-2,3-butanediol) undergoes acid-catalysed 1,2-shift to give a ketone (pinacolone).

Step 1 — Protonation and departure:
H^+ protonates one OH group. Loss of water generates a tertiary carbocation.

Step 2 — 1,2-Methyl shift:
An adjacent methyl group migrates to the electron-deficient carbon, forming a more stable tertiary oxocarbenium ion (or tertiary carbocation stabilised by the adjacent oxygen).

Step 3 — Loss of proton:
Deprotonation of the oxocarbenium ion gives the ketone: $(CH_3)_3C{-}CO{-}CH_3$ = 3,3-dimethylbutan-2-one (pinacolone).

Why other options are wrong:
Option B: Alkene formation would require dehydration with no rearrangement – minor pathway.
Option C: 2-Methylpropan-1-ol would require fragmentation, not a 1,2-shift.
Option D: Aldehyde formation requires a terminal primary carbon, which is absent here.

Final Answer: Pinacol $\xrightarrow{H^+}$ pinacolone (3,3-dimethylbutan-2-one) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#12

Q13.

Solution

Concept — Norrish Type I Photochemical α-Cleavage:
Upon UV absorption, the carbonyl compound is promoted to S_1 (n$\rightarrow \pi^*$ excited state). Norrish Type I involves homolytic cleavage of the C$-$C bond α to the carbonyl carbon.

Step 1 — Identify the α-C$-$C bonds in pentan-2-one:

$CH_3-\underbrace{CO}_{C=O}-CH_2CH_2CH_3$. The α-bonds are:
(i) CH_3–CO (gives $CH_3CO^\bullet$ + $^\bullet CH_2CH_2CH_3$)
(ii) CO–CH_2 (gives $^\bullet CH_3$ + $^\bullet COCH_2CH_2CH_3$)

Step 2 — Primary cleavage (most common):
Cleavage of the C_2-C_3 bond gives **acetyl radical** $CH_3CO^\bullet$ and **propyl radical** $^\bullet CH_2CH_2CH_3$. The acetyl radical may subsequently lose CO to give $CH_3^\bullet$.

Why other options are wrong:
Option A: $CH_3^\bullet$ is a secondary fragment from decarbonylation of $CH_3CO^\bullet$, not the primary cleavage product.
Option B: CO and pentane radicals do not arise directly from α-cleavage.
Option C: $CH_3CH_2^\bullet$ is not formed; this describes an incorrect bond position.

Final Answer: Primary α-cleavage $\rightarrow CH_3CO^\bullet + {}^\bullet C_3H_7 \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#13

Q14.

Solution

Concept — Woodward–Hoffmann Rules for [2+2] Cycloaddition:
Orbital symmetry (frontier molecular orbital theory) governs whether concerted cycloadditions are thermally or photochemically allowed.

Step 1 — Thermal [2+2] (forbidden):
Ground state HOMO of alkene (ψ_1) has symmetric symmetry with respect to the forming σ bonds. The HOMO of one alkene and LUMO of the other have the wrong symmetry for constructive overlap in the thermal suprafacial–suprafacial pathway – **forbidden**.

Step 2 — Photochemical [2+2] (allowed):
One alkene absorbs $h\nu$ and is promoted to its first excited state. Its HOMO is now ψ_2^* (the former LUMO), whose symmetry is *antisymmetric*. This reversed HOMO symmetry matches the LUMO of the ground-state alkene, allowing constructive orbital overlap $\rightarrow$ **photochemically allowed**.

Why other options are wrong:
Option A: Light does not simply lower a thermal barrier; it changes orbital symmetry.
Option B: Thermal [2+2] remains forbidden at all temperatures (symmetry-forbidden).
Option D: Triplet-state reactions are non-concerted (stepwise diradical) and bypass symmetry, but the question asks about the reason for photochemical allowedness.

Final Answer: Excited-state HOMO symmetry reversal enables constructive overlap ⇒ **(C)**

Answer: (C) ← Go Back to Q#14

Q15.

Solution

Concept — CBS Reduction Mechanism:
The Corey–Bakshi–Shibata (CBS) reduction uses a chiral oxazaborolidine (B–N containing 5-membered ring) with BH_3 to reduce ketones enantioselectively.

Step 1 — Activation:
BH_3 coordinates to the nitrogen of the oxazaborolidine. This activates the boron, which then coordinates the ketone oxygen. The ketone is thus tethered within a six-membered cyclic transition state.

Step 2 — Hydride delivery:
The hydride on the *boron of the activated* BH_3 is delivered intramolecularly to the si or re face of the ketone carbonyl carbon. The chiral environment determines which face is preferentially attacked, giving high enantioselectivity.

Step 3 — Stereochemical outcome:
The bulky substituent on the oxazaborolidine blocks one face, directing hydride from the boron to the exposed face (Re or Si, depending on the CBS catalyst enantiomer used).

Why other options are wrong:
Option A: Nitrogen does not deliver the hydride; it coordinates BH_3 to enhance Lewis acidity of B.
Option C: External $NaBH_4$ is not involved; the reduction uses BH_3 within the catalyst complex.
Option D: The chiral auxiliary provides a stereochemical environment, not a proton.

Final Answer: Hydride from the B of activated BH_3 within the chiral TS ⇒ **(B)**

Answer: (B) ← Go Back to Q#15

Q16.

Solution

Concept — $B_{AC}2$ Ester Hydrolysis Mechanism:
$B_{AC}2$ = Base-catalysed, Acyl-bond cleavage, bimolecular. The hydroxide acts as a nucleophile at the acyl carbon.

Step 1 — Nucleophilic addition:

OH^- attacks the electrophilic acyl carbon of the ester (RCOOR'), forming a high-energy tetrahedral intermediate (alkoxide–acid–OH group). This is the **rate-determining step**.

Step 2 — Collapse of tetrahedral intermediate:
The tetrahedral intermediate collapses by expelling the alkoxide $R'O^-$, giving the carboxylate $RCOO^-$ (and ultimately the carboxylic acid on workup). The reaction is irreversible under basic conditions ("saponification").

Why other options are wrong:
Option B: E1cb would require a β-elimination – not applicable to ester hydrolysis.
Option C: Acid-catalysed hydrolysis ($A_{AC}2$) involves protonation of C=O oxygen then nucleophilic attack by water at the acyl C – different from $B_{AC}2$.
Option D: Carbenium ion at the alkyl carbon is the $B_{AL}1$ pathway – not $B_{AC}2$.

Final Answer: OH^- addition to acyl C forming tetrahedral intermediate (RDS) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#16

Q17.

Solution

Concept — Meso Compounds:
A meso compound has two or more stereocentres with an internal plane of symmetry, making the molecule achiral (superimposable on its mirror image) despite the presence of stereocentres.

Step 1 — Check tartaric acid isomers:
Tartaric acid ($HOOC-CHOH-CHOH-COOH$) has two stereocentres.
(R, R): chiral (enantiomer of (S, S)).
(S, S): chiral (enantiomer of (R, R)).
$(2R, 3S)$: the R and S configurations are mirror images of each other within the same molecule. An internal mirror plane bisects the central C–C bond $\Rightarrow$ **meso compound**.

Step 2 — Confirm internal plane:
In $(2R, 3S)$-tartaric acid, the top half ($2R$) is the mirror image of the bottom half ($3S$), so the molecule is achiral overall.

Why other options are wrong:
Options A and B: (R, R) and (S, S) are enantiomers of each other – both are chiral.
Option C: Lactic acid has only one stereocentre – it cannot be a meso compound.

Final Answer: $(2R, 3S)$-tartaric acid is the meso form $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#17

Q18.

Solution

Concept — Stork Enamine Synthesis:
Enamines are formed from secondary amines + ketones. They act as nucleophilic equivalents of enolates, alkylating at the α-carbon. Hydrolysis then regenerates the carbonyl.

Step 1 — Enamine formation:
Cyclohexanone + pyrrolidine (with acid catalyst, Dean–Stark) gives the enamine, with the C=C double bond between C1 and C2 of the ring (the former C1=O becomes C1=C2–N).

Step 2 — Alkylation:
The nucleophilic β-carbon (C2, the α-carbon of the original ketone) attacks allyl bromide. The allyl group attaches to the α-carbon (C2 of cyclohexanone, i.e. position 2).

Step 3 — Hydrolysis:
Aqueous acid hydrolyses the iminium ion to restore the ketone: product is **2-allylcyclohexan-1-one**.

Why other options are wrong:
Option A: 3-Allylcyclohexan-1-one would require β-alkylation, which does not occur.
Option B: 1-Allylcyclohexanol would imply allylation of the carbonyl carbon rather than the α-carbon.
Option D: Ether formation is not the reaction pathway; no O-alkylation occurs under these conditions.

Final Answer: α-alkylation gives 2-allylcyclohexan-1-one $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#18

Q19.

Solution

Concept — Singlet Carbene Stereochemistry:
Singlet carbene has two electrons in the same orbital (paired) and adds to alkenes in a *concerted, stereospecific* manner (like an S_N2 reaction – both bonds form simultaneously from the same face).

Step 1 — Singlet :CH_2 + *cis*-but-2-ene:
In *cis*-but-2-ene, the two methyl groups are on the same side of the double bond. The concerted addition of singlet carbene preserves this relationship. Both C–C bonds to the carbene carbon form simultaneously from the same face.

Step 2 — Product:
The two methyl groups remain *cis* in the cyclopropane product: ***cis*-1,2-dimethylcyclopropane**.

Contrast with triplet carbene:
Triplet :CH_2 adds stepwise (diradical intermediate), losing stereospecificity and giving a mixture of *cis* and *trans* products.

Why other options are wrong:
Option A: *trans*-product would arise from a triplet carbene or from *trans*-but-2-ene with singlet carbene.
Option C: Racemic mixture is the result of triplet carbene addition, not singlet.
Option D: 1-Methylcyclopropane would require loss of a methyl group – not possible here.

Final Answer: Singlet carbene adds concertedly $\rightarrow$ *cis*-1,2-dimethylcyclopropane $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#19

Q20.

Solution

Concept — Evans Oxazolidinone Chiral Auxiliary in Diels–Alder:
The Evans auxiliary controls the geometry of the dienophile and, after chelation with a Lewis acid (e.g. Et_2AlCl or $MgBr_2$), locks the s-cis conformation of the enone dienophile. The bulky oxazolidinone substituent blocks one π-face.

Step 1 — Lewis acid chelation:
The Lewis acid chelates both the oxazolidinone carbonyl and the dienophile carbonyl, creating a rigid bicyclic arrangement. The oxazolidinone's C4 substituent (benzyl or isopropyl) occupies axial or pseudo-axial space.

Step 2 — Facial selectivity:
The bulky group (e.g. benzyl) projects over the Si face of the dienophile. The diene therefore attacks from the **Re face** (opposite to the blocking group), giving high diastereoselectivity.

Why other options are wrong:
Option B: Si-face attack would be blocked by the auxiliary substituent.
Option C: Lewis acid is essential for both s-cis lock and facial differentiation.
Option D: The facial preference depends on the auxiliary configuration; it is not universally "top face."

Final Answer: Diene attacks the Re face (away from the chiral auxiliary's bulky group) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#20

Q21.

Solution

Concept — Keggin Structure of Polyoxometalates:
The Keggin anion $[XM_{12}O_{40}]^{n-}$ (X = heteroatom, M = addenda metal) is the most important polyoxometalate structural type.

Step 1 — Structural description:
A central XO_4 tetrahedron (here X = P, so PO_4^{3-}) is surrounded by **12 MO_6 octahedra** (M = W^{6+}). The 12 octahedra are arranged as four groups of three edge-sharing octahedra (M_3O_{13} units), each group corner-sharing with the central tetrahedron.

Step 2 — Symmetry:
The Keggin structure has T_d symmetry. The overall charge of $[PW_{12}O_{40}]^{3-}$ arises from the PO_4^{3-} core enclosed within 12 d^0 W^{6+} octahedra.

Why other options are wrong:
Option A: Linear chains would not enclose the central P.
Option B: WO_4 tetrahedra are not the building blocks; octahedra are.
Option C: There is a central heteroatom (P) in all Keggin anions by definition.

Final Answer: Central PO_4 tetrahedron + 12 WO_6 octahedra (edge/corner-sharing) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#21

Q22.

Solution

Concept — Berry Pseudorotation in PF_5:
Trigonal bipyramidal PF_5 is fluxional: all five F environments are equivalent on the ^{19}F NMR timescale at room temperature, even though two are axial and three are equatorial in the static structure.

Step 1 — Mechanism:
Two equatorial F atoms and the two axial F atoms move toward a square pyramidal (SP) geometry (the transition state). From the SP TS, the motion continues to a new TBP where the original axial positions have become equatorial and two of the original equatorial positions have become axial. No bonds are broken.

Step 2 — NMR consequence:
The exchange is fast on the NMR timescale, so only one ^{19}F signal is observed (all five F atoms appear equivalent) at room temperature.

Why other options are wrong:
Option A: Exchange involves *both* axial and equatorial positions, not only equa-

torial.
Option B: Berry pseudorotation is an intramolecular motion; no P–F bonds break.
Option D: It occurs well below 200 °C; PF_5 shows fluxional NMR at room temperature.

Final Answer: Axial $\leftrightarrow$ equatorial exchange via SP transition state $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#22

Q23.

Solution

Concept — Quadruple Metal–Metal Bond in $[Re_2Cl_8]^{2-}$:
This landmark complex (Cotton, 1964) was the first recognised example of a quadruple metal–metal bond.

Step 1 — Identify the bond components:
Each Re has formal d^4 configuration in Re(III). Using the D_{4h} metal–metal axis (z-axis):
– d_{z^2}–d_{z^2}: $\boldsymbol{\sigma}$ bond (head-on overlap)
– d_{xz}–d_{xz} and d_{yz}–d_{yz}: two $\boldsymbol{\pi}$ bonds
– d_{xy}–d_{xy}: $\boldsymbol{\delta}$ bond (face-to-face overlap, requires eclipsed conformation)

Step 2 — Total bond order:
$\sigma+\pi+\pi+\delta = 1+1+1+1 = 4$ (quadruple bond). The eclipsed (D_{4h}) conformation of the Cl atoms is a key consequence of maximising the δ overlap.

Why other options are wrong:
Option A: Triple bond ($\sigma + 2\pi$) is seen in Mo_2 and some other systems but not in $[Re_2Cl_8]^{2-}$.
Option C: Four σ bonds would require four collinear orbitals, which is geometrically impossible.
Option D: Two σ and two π bonds would give bond order 4 only if both σ bonds are counted separately, which is not the standard analysis.

Final Answer: $\sigma + 2\pi + \delta$ = quadruple bond $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#23

Q24.

Solution

Concept — Ziegler–Natta Cossée–Arlman Mechanism:
Polymerisation occurs at the surface of $TiCl_4$ activated by $Al(C_2H_5)_3$. The active site is a Ti–C bond at a surface vacancy.

Step 1 — Coordination of propylene:

Propylene coordinates to the Ti centre (Lewis acid) at the vacant coordination site adjacent to the Ti–C bond.

Step 2 — Insertion:
Propylene inserts into the Ti–C bond via a four-centre, four-electron transition state:

$$\mathrm{Ti{-}C_n} + \underset{\pi}{\mathrm{CH_2{=}CHCH_3}} \rightarrow \mathrm{Ti{-}CH(CH_3){-}C_n}$$

This is **1,2-insertion** (Markovnikov with respect to Ti). The stereoregularity (isotactic/syndiotactic) arises from the chiral surface environment of the catalyst.

Why other options are wrong:
Option B: Radical mechanisms do not operate under Ziegler–Natta conditions.
Option C: Metathesis involves ROMP/ADMET chemistry with different catalysts (Mo, W, Ru).
Option D: Anionic polymerisation uses pure alkyllithium or Ziegler-type but is distinct from the Cossée–Arlman surface mechanism.

Final Answer: 1,2-Insertion into Ti–C bond (Cossée–Arlman) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#24

Q25.

Solution

Concept — VSEPR and Molecular Geometry of ClF_3:
VSEPR analysis: Cl has 7 valence electrons. Three bonds to F use 3 electrons; remaining 4 form 2 lone pairs. Electron geometry = trigonal bipyramidal (5 electron domains); molecular geometry based on 3 F positions.

Step 1 — Lone pair placement:
Lone pairs prefer equatorial positions in TBP geometry (more space, less repulsion). With 2 lone pairs both equatorial, the three F atoms occupy: both axial positions and *one* equatorial position.

Step 2 — Resulting shape:
The arrangement: F(axial)–Cl–F(axial) vertically, plus F(equatorial) horizontally. The three F atoms form a letter "T" shape. The molecule is therefore **T-shaped** with bond angles $< 90°$ (axial) and $< 120°$ (equatorial) due to lone pair repulsion.

Why other options are wrong:
Option A: Trigonal planar requires 3 bonding pairs + 0 lone pairs (sp^2, e.g. BF_3).
Option B: Trigonal pyramidal has 3 bonds + 1 lone pair (e.g. NH_3); ClF_3 has 2 lone pairs.
Option C: Trigonal bipyramidal describes the *electron* geometry, not the molecular (bond) geometry.

Final Answer: 3 bonds + 2 lone pairs (equatorial) $\rightarrow$ T-shaped $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#25

Q26.

Solution

Concept — Electron-Deficient Bridged Bonding in Diborane:
B_2H_6 has only 12 valence electrons but 8 bonds to accommodate. Classical 2c-2e bonds are insufficient.

Step 1 — Count electrons for bridging B–H–B:
Each B has 3 valence electrons; each H contributes 1. In B_2H_6 with two B–H–B bridges, there are $2 \times 3 + 6 \times 1 = 12$ electrons total. Four terminal B–H bonds use 8 electrons, leaving only 4 electrons (2 pairs) for the two bridging bonds.

Step 2 — 3c-2e (banana) bonds:
Each bridging B–H–B bond involves 3 atoms sharing 2 electrons – a *three-centre two-electron* (3c-2e) bond. The MO picture: the bonding MO spreads over both B and the bridging H; only this one MO is occupied per bridge.

Why other options are wrong:
Option A: Conventional 2c-2e bonds would require 16 electrons for 8 bonds – diborane only has 12.
Option B: Ionic model (H^- bridging B^+) is inconsistent with the observed structure and thermochemistry.
Option D: Hydrogen bonds are weak electrostatic interactions (not covalent bond type), inappropriate here.

Final Answer: Bridging B–H–B bonds are 3c-2e (banana) bonds $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#26

Q27.

Solution

Concept — Perovskite Structure (ABX_3):
In cubic perovskite (e.g. $CaTiO_3$, $BaTiO_3$), the unit cell has:
– A cation (large, e.g. Ca^{2+}, Ba^{2+}) at the *corner* (or equivalently at the centre of the pseudo-fcc X sublattice).
– B cation (small, e.g. Ti^{4+}) at the body centre, octahedrally coordinated by 6 X anions.
– X anions (O^{2-}) at the face centres.

Step 1 — Coordination of A cation:
The A cation sits at the corner of the cube. In terms of X-anion nearest neighbours: each corner A is surrounded by 12 nearest X (O^{2-}) anions from 4 adjacent unit

cells, giving cuboctahedral (12-fold) coordination.

Step 2 — Confirm with ionic radii tolerance:
Goldschmidt tolerance factor $t = (r_A + r_X)/(\sqrt{2}(r_B + r_X))$. For ideal perovskite $t \approx 1$, consistent with 12-coordinate A cations.

Why other options are wrong:
Option A: 6-coordinate (octahedral) is the coordination of the *B* cation (Ti^{4+}), not A.
Option C: 4-coordinate (tetrahedral) is too small for the large A cation in this structure.
Option D: 8-coordinate (cubic) describes the A site in fluorite (CaF_2) or simple CsCl, not perovskite.

Final Answer: A cation in perovskite is 12-coordinate (cuboctahedral) $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#27

Q28.

Solution

Concept — Iron–Sulfur Cluster [2Fe–2S]:
These are ancient redox-active prosthetic groups found in ferredoxins and other electron-transport proteins.

Step 1 — Structure:
Two Fe atoms are bridged by two inorganic S^{2-} ions, forming a planar rhombic Fe_2S_2 core. Each Fe is additionally coordinated by two cysteinyl sulfur atoms from the protein, giving pseudo-tetrahedral coordination overall (four sulfur ligands per Fe).

Step 2 — Redox chemistry:
The cluster undergoes one-electron oxidation/reduction: $[2Fe^{3+}/2Fe^{3+}] \leftrightarrow [Fe^{3+}/Fe^{2+}]$ (net Fe^{3+}/Fe^{2+} couple). This is a *one-electron* process. The reduction potential is typically in the range -0.4 to $+0.35$ V vs. NHE depending on the protein.

Why other options are wrong:
Option B: Two-electron redox is not observed; [2Fe-2S] clusters perform one-electron chemistry.
Option C: The bridging ligands are sulfide S^{2-}, not oxo O^{2-}.
Option D: Both Fe atoms share the same rhombic core and are bridged; they are not in separate non-bridged sites.

Final Answer: 2 Fe + 2 S^{2-} bridges + cysteinyl ligation + one-electron redox $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#28

Q29.

Solution

Concept — Mohr Method (Precipitation Titration):
In the Mohr method, Cl^- is titrated with standard $AgNO_3$. The endpoint is signalled by a colour change when excess Ag^+ precipitates with the chromate indicator.

Step 1 — Indicator reaction:
K_2CrO_4 (potassium chromate) is the indicator. During the titration, $AgCl$ ($K_{sp} = 1.8 \times 10^{-10}$) precipitates first (white). At the endpoint, all Cl^- has precipitated, and excess Ag^+ precipitates with CrO_4^{2-} as brick-red Ag_2CrO_4 ($K_{sp} = 1.1 \times 10^{-12}$).

Step 2 — pH requirement:
The Mohr method requires neutral to slightly alkaline conditions (pH 6.5–10). At acidic pH, Ag_2CrO_4 dissolves; at high pH, Ag_2O precipitates.

Why other options are wrong:
Option A: Eriochrome Black T is a metallochromic indicator used in EDTA complexometric titrations (e.g. Ca^{2+}, Mg^{2+}), not precipitation.
Option B: Phenolphthalein is an acid–base indicator, not used for Ag^+/Cl^- systems.
Option C: Starch is used as an indicator in iodometric titrations (detects I_2), not $AgNO_3$ titrations.

Final Answer: K_2CrO_4 (potassium chromate) is the Mohr indicator $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#29

Q30.

Solution

Concept — Equivalence Point in Potentiometric Titration:
During a potentiometric titration, the cell potential E changes as titrant is added. Near the equivalence point, E changes sharply.

Step 1 — First derivative:
Plotting $\mathrm{d}E/\mathrm{d}V$ vs. volume V gives a peak (*maximum*) at the equivalence point, because E changes most rapidly there.

Step 2 — Second derivative:
Plotting $\mathrm{d}^2E/\mathrm{d}V^2$ vs. V gives a *zero crossing* (sign change from positive to negative) exactly at the equivalence point. This is the most precise method for locating the endpoint.

Why other options are wrong:
Option A: $E = 0.0$ V has no special significance at the equivalence point (depends

on reference electrode and ion concentrations).
Option B: Minimum $\mathrm{d}E/\mathrm{d}V$ occurs far from the equivalence point, in the buffer/plateau region.
Option D: Half-volume is used to estimate $\mathrm{p}K_a$ (at half-equivalence point), not to locate the equivalence point itself.

Final Answer: Equivalence point $\equiv$ maximum in $\mathrm{d}E/\mathrm{d}V$ or zero in $\mathrm{d}^2E/\mathrm{d}V^2 \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#30

Q31.

Solution

Concept — TLC on Silica Gel (Polarity and Retention):
Silica gel is a *polar* stationary phase. Polar compounds interact more strongly with silica (larger k'), travel less, and have *lower* R_f. Non-polar compounds interact weakly, travel further, and have *higher* R_f.

Step 1 — Compare polarity of compounds:
Benzoic acid: carboxylic acid – very polar (H-bond donor and acceptor). R_f low.
Phenol: phenol – moderately polar (H-bond donor). R_f medium-low.
Ethanol: alcohol – moderately polar. R_f medium.
Hexane: pure hydrocarbon – **non-polar**. Very weak interaction with silica. R_f **highest**.

Step 2 — Confirm:
With a non-polar eluent (e.g. hexane as both compound and mobile phase), hexane itself would barely be retained, giving $R_f \approx 1$. In practice, hexane as a *compound* on TLC always travels near the solvent front.

Why other options are wrong:
Options A, C, D: Benzoic acid, phenol, and ethanol are all polar and will be more strongly retained by the silica stationary phase.

Final Answer: Hexane (non-polar) has the highest R_f on silica gel TLC $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#31

Q32.

Solution

Concept — Pourbaix (E–pH) Diagram for Iron:
A Pourbaix diagram shows the thermodynamically stable phase of an element as a function of electrode potential E and pH.

Step 1 — Stability region of metallic Fe:

Metallic iron is stable only when the electrode potential is sufficiently *negative* (strongly reducing conditions), so that Fe^{2+} cannot be formed. This region appears at the bottom-left of the diagram – **low (negative)** E at any pH.

Step 2 — Other regions:
Fe^{2+} (aq): low-medium E, low-medium pH (acidic, moderately reducing).
Fe^{3+} (aq): high E, low pH (acidic, oxidising).
$Fe(OH)_2$ / FeO: low E, high pH (alkaline, reducing).
$Fe(OH)_3$ / Fe_2O_3: medium E, high pH (alkaline, mildly oxidising).

Why other options are wrong:
Option B: High potential + low pH is the Fe^{3+}(aq) region – metallic Fe is oxidised.
Option C: High potential + high pH is the region of $Fe(OH)_3$ or Fe_2O_3 – Fe is oxidised.
Option D: At E = intermediate, pH 7, iron is in the Fe^{2+} or $Fe(OH)_2$ region depending on E, not metallic Fe.

Final Answer: Metallic Fe stable at low (negative) E / strongly reducing conditions $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#32

Q33.

Solution

Concept — Tafel Slope Calculation:
For the Butler–Volmer equation, the anodic Tafel slope is:

$$b = \frac{2.303\,RT}{\alpha F}$$

Step 1 — Substitute values:
$R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$, $T = 298\ \text{K}$, $\alpha = 0.50$, $F = 96485\ \text{C mol}^{-1}$:

$$b = \frac{2.303 \times 8.314 \times 298}{0.50 \times 96485} = \frac{5706.7}{48242.5} = 0.1183\ \text{V/decade} \approx 118\ \text{mV/decade}$$

Physical meaning:
The Tafel slope represents how much overpotential η must be applied to increase the anodic current by one decade (factor of 10). A larger α (faster electron transfer response) gives a smaller Tafel slope.

Why other options are wrong:
Option A: $59\ \text{mV/decade} = 2.303RT/F$ (valid for $\alpha = 1.0$ or for the Nernst factor at 25 °C).
Option B: $30\ \text{mV/decade}$ would require $\alpha \approx 2$, which is unphysical for a single-

electron step.
Option C: 240 mV/decade would require $\alpha \approx 0.25$, and is unusually large.

Final Answer: $b = 2.303RT/(\alpha F) \approx 118$ mV/decade for $\alpha = 0.50 \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#33

Q34.

Solution

Concept — Positive Deviation from Raoult's Law:
Raoult's law: $p_i = x_i\, p_i^*$ assumes ideal behaviour (all intermolecular interactions equal). Deviations arise from differences in A–A, B–B, and A–B interactions.

Step 1 — Positive deviation:
When A–B interactions are *weaker* than A–A and B–B interactions, molecules of A (or B) find it *easier* to escape the mixture than from the pure liquid. Vapour pressure is therefore *higher* than ideal ($p_{\text{real}} > x_i p_i^*$), and the activity $a_i > x_i$ – the curve lies *above* the ideal Raoult line.

Step 2 — Examples:
Ethanol–hexane, acetone–carbon disulfide, ethanol–benzene – all show positive deviations because unlike-molecule interactions are weaker. These systems may exhibit a minimum boiling azeotrope.

Why other options are wrong:
Option A: Stronger A–B interactions $\Rightarrow$ *negative* deviation (molecules are held more tightly, lower vapour pressure).
Option B: Ideal solution means all interactions equal – no deviation.
Option D: Higher boiling point of the mixture is characteristic of *negative* deviation (maximum boiling azeotrope), not positive.

Final Answer: A–B interactions weaker than A–A and B–B $\Rightarrow$ positive deviation $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#34

Q35.

Solution

Concept — Non-Newtonian Shear-Thinning (Pseudoplastic) Fluids:
A Newtonian fluid has a constant viscosity $\eta = \tau/\dot{\gamma}$ (shear stress / shear rate). Non-Newtonian fluids have viscosity that depends on $\dot{\gamma}$.

Step 1 — Shear-thinning (pseudoplastic):
In blood (and many polymer solutions, polymer melts, and colloids), the apparent viscosity η_{app} *decreases* with increasing shear rate $\dot{\gamma}$. At low $\dot{\gamma}$, red blood cell ag-

gregates (rouleaux) form, increasing viscosity. At high $\dot{\gamma}$, cells align with the flow and disaggregate, reducing resistance and lowering viscosity.

Step 2 — Clinical relevance:
This shear-thinning behaviour is crucial for cardiovascular physiology – blood flows easily through large vessels (high shear) but can pool in low-shear regions.

Why other options are wrong:
Option A: Shear-thickening (dilatant) behaviour – viscosity increases with shear rate – is observed in some dense suspensions (cornstarch-water), not blood.
Option C: Constant viscosity is the Newtonian response.
Option D: Zero viscosity at all shear rates is physically impossible for a fluid like blood.

Final Answer: Blood is shear-thinning: η_{app} decreases as shear rate increases $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#35

Q36.

Solution

Concept — Debye vs. Einstein Models for Heat Capacity:
Both models describe C_V of crystalline solids, but differ in their treatment of vibrational modes.

Step 1 — Einstein model (1907):
All $3N$ oscillators vibrate at a single Einstein frequency ν_E. At low T: $C_V \propto (h\nu_E/k_BT)^2 e^{-h\nu_E/k_BT}$ – gives an *exponential* decrease, not T^3.

Step 2 — Debye model (1912):
Uses a continuous density of states $g(\nu) \propto \nu^2$ up to the Debye cutoff frequency ν_D. At low $T \ll \theta_D$:

$$C_V = \frac{12\pi^4 N k_B}{5}\left(\frac{T}{\theta_D}\right)^3 \propto T^3$$

This is the Debye T^3 law, which agrees excellently with experiment for many solids.

Why other options are wrong:
Option B: Einstein model gives exponential, not T^3, behaviour at low T.
Option C: Dulong–Petit gives $C_V = 3R$ (constant), valid only at high T.
Option D: Ideal gas gives $C_V = \frac{3}{2}R$, with no temperature-dependent solid-state phonon physics.

Final Answer: Debye model predicts $C_V \propto T^3$ at $T \ll \theta_D \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#36

Q37.

Solution

Concept — Cholesterol and Lipid Bilayer Phase Behaviour:
Lipid bilayers undergo a cooperative gel-to-liquid-crystalline phase transition at the melting temperature T_m.

Step 1 — Effect of cholesterol:
Cholesterol intercalates between phospholipid acyl chains with its rigid sterol ring system. At temperatures below T_m, it disrupts the ordered gel phase (increasing fluidity). At temperatures above T_m, it decreases chain mobility (reducing fluidity). This dual effect creates the *liquid-ordered* (L_o) phase.

Step 2 — Consequence for phase transition:
As cholesterol content increases, the cooperative melting transition broadens and eventually disappears (> 33 mol% cholesterol). The sharp DSC peak at T_m is abolished – no distinct phase transition is observable.

Why other options are wrong:
Option A: Cholesterol can slightly lower T_m for saturated lipids but the *dominant* effect is abolishing the sharp transition, not a large T_m decrease.
Option B: Cholesterol *reduces* ΔH_{trans} (less cooperativity), not increases it.
Option C: Cholesterol dramatically affects phase behaviour – it cannot be said to have no effect.

Final Answer: Cholesterol abolishes the sharp gel $\leftrightarrow$ liquid-crystalline phase transition $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#37

Q38.

Solution

Concept — DNA Melting Temperature Calculation:
The empirical formula for long duplex DNA in 1 M NaCl:

$$T_m\,(^\circ\text{C}) = 69.3 + 0.41 \times (\%\text{GC})$$

Each G–C base pair has three hydrogen bonds (vs. two for A–T), requiring more energy to denature.

Step 1 — Substitute %GC = 60:

$$T_m = 69.3 + 0.41 \times 60 = 69.3 + 24.6 = 93.9\ ^\circ\text{C} \approx 94\ ^\circ\text{C}$$

Step 2 — Sanity check:
For 40% GC: $T_m = 69.3 + 16.4 = 85.7\ ^\circ\text{C}$. For 70% GC: $T_m = 69.3 + 28.7 = 98\ ^\circ\text{C}$.

The trend is consistent – higher GC content raises T_m.

Why other options are wrong:
Option A: 79 °C corresponds to $\%\mathrm{GC} \approx 24\%$ ($69.3 + 0.41 \times 23.7 \approx 79$).
Option B: 87 °C corresponds to $\%\mathrm{GC} \approx 43\%$.
Option D: 100 °C corresponds to $\%\mathrm{GC} \approx 75\%$.

Final Answer: $T_m = 69.3 + 0.41 \times 60 = 93.9 \approx 94\ ^\circ\mathrm{C} \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#38

Q39.

Solution

Concept — Laplace Transform of Exponential Function:
The one-sided Laplace transform is defined as:

$$\mathcal{L}\{f(t)\}(s) = \int_0^\infty f(t)\, e^{-st}\, \mathrm{d}t$$

Step 1 — Apply to $f(t) = e^{-at}$:

$$\mathcal{L}\{e^{-at}\} = \int_0^\infty e^{-at}\, e^{-st}\, \mathrm{d}t = \int_0^\infty e^{-(s+a)t}\, \mathrm{d}t = \left[\frac{e^{-(s+a)t}}{-(s+a)}\right]_0^\infty = \frac{1}{s+a}$$

Valid for $\mathrm{Re}(s) > -a$ (i.e. $s > -a$ for real $a > 0$).

Application in kinetics:
The Laplace transform converts the first-order ODE $\mathrm{d[A]}/\mathrm{d}t = -k[\mathrm{A}]$ (with solution $[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt}$) to an algebraic equation, greatly simplifying analysis of complex reaction networks.

Why other options are wrong:
Option A: $1/(s-a)$ is the Laplace transform of e^{+at} (growing exponential), not e^{-at}.
Option C: $a/(s^2+a^2)$ is the Laplace transform of $\sin(at)$.
Option D: $s/(s^2+a^2)$ is the Laplace transform of $\cos(at)$.

Final Answer: $\mathcal{L}\{e^{-at}\} = 1/(s+a) \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#39

Solution

Concept — Mark–Houwink–Sakurada Equation:
The Mark–Houwink equation $[\eta] = KM^a$ relates intrinsic viscosity to molar mass. The exponent a reflects polymer chain conformation and solvent quality.

Step 1 — Values of a for different cases:

Q40.

- **Compact sphere** (e.g. globular protein): $a \approx 0$ ($[\eta]$ independent of M)
- **Random coil in theta solvent** (Θ conditions): $a = 0.5$ (ideal chain)
- **Random coil in good solvent** (expanded coil): $a \approx 0.6$–0.8 (excluded volume effects)
- **Rigid rod**: $a \approx 1.7$–2 (viscosity strongly dependent on length)

Step 2 — Interpret $a \approx 0.6$–0.8:
In a good solvent, the polymer expands due to excluded volume interactions (Flory exponent $\nu \approx 3/5 = 0.6$). The Mark–Houwink exponent $a = 3\nu - 1 \approx 0.8$, consistent with experimental values for common polymer–good solvent systems.

Why other options are wrong:
Option B: $a \approx 0$ describes a hard sphere – independent of M.
Option C: $a \approx 1.8$ describes a stiff rod (DNA in low salt, xanthan gum).
Option D: $a = 3$ is unphysically high for any real polymer system.

Final Answer: Random coil in good solvent: $a \approx 0.6$–$0.8 \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#40

Answer Key

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