TIFR GS Chemistry

Sample Paper – 6

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. The most probable speed u_{mp} for $\mathrm{N_2}$ gas ($M = 28\ \mathrm{g\,mol^{-1}}$) at $300\ \mathrm{K}$ is given by $u_{\mathrm{mp}} = \sqrt{2RT/M}$ ($R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$). Its approximate numerical value is:

(A) $300\ \mathrm{m\,s^{-1}}$

(B) $515\ \mathrm{m\,s^{-1}}$

(C) $422\ \mathrm{m\,s^{-1}}$

(D) $600\ \mathrm{m\,s^{-1}}$

Q2. A crystal of $\mathrm{N_2O}$ contains molecules that can adopt either a head-to-tail ($\mathrm{N{\equiv}N{-}O}$) or a tail-to-head ($\mathrm{O{-}N{\equiv}N}$) orientation at random with equal probability. The residual molar entropy of this crystal at $0\ \mathrm{K}$ is approximately:

(A) 0

(B) $R\ln 4 \approx 11.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$

(C) $R/2 \approx 4.16\ \mathrm{J\,mol^{-1}\,K^{-1}}$

(D) $R\ln 2 \approx 5.76\ \mathrm{J\,mol^{-1}\,K^{-1}}$

Q3. In Marcus theory for outer-sphere electron transfer, the activation free energy is $\Delta G^{\ddagger} = \dfrac{(\Delta G^{\circ} + \lambda)^2}{4\lambda}$, where λ is the reorganisation energy. For a self-exchange reaction ($\Delta G^{\circ} = 0$), $\Delta G^{\ddagger}$ equals:

(A) $\lambda/4$

(B) $\lambda/2$

(C) λ

(D) 0

Q4. Species A undergoes two competing parallel first-order reactions: $\mathrm{A} \rightarrow \mathrm{B}$ ($k_1 = 0.010\ \mathrm{s^{-1}}$) and $\mathrm{A} \rightarrow \mathrm{C}$ ($k_2 = 0.030\ \mathrm{s^{-1}}$). The molar ratio $[\mathrm{B}]/[\mathrm{C}]$ at any time $t > 0$ is:

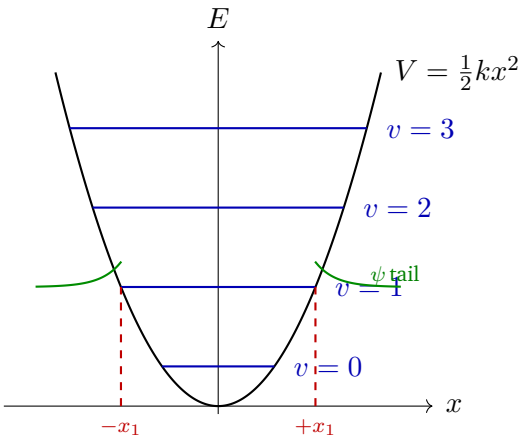
(A) $3:1$

(B) $1:3$

(C) $1:1$

(D) $1:9$

Q5. The diagram below shows the parabolic potential $V = \frac{1}{2}kx^2$ of a quantum-mechanical harmonic oscillator with the first four quantised energy levels ($v = 0, 1, 2, 3$). Dashed red lines mark the classical turning points for $v = 1$; green tails indicate the penetration of ψ into the classically forbidden region. Which of the following statements about this system is **incorrect**?



(A) The zero-point energy of the ground state ($v = 0$) is $\frac{1}{2}h\nu$.

(B) Consecutive energy levels are equally spaced with spacing $h\nu$.

(C) The vibrational wavefunction is strictly zero beyond the classical turning points for every level v.

(D) The ground-state ($v = 0$) wavefunction has a Gaussian (bell-curve) form.

Q6. Which of the following molecules is infrared **inactive** (shows no IR absorption bands)?

(A) HCl

(B) CO

(C) H_2O

(D) N_2

Q7. In a DEPT-135 experiment, which type of carbon gives a **negative (downward-pointing)** signal?

(A) CH_2

(B) CH

(C) CH_3

(D) Quaternary C (no attached H)

Q8. Which factor does **not** significantly affect the magnitude of the vicinal $^1H-^1H$ coupling constant (^3J)?

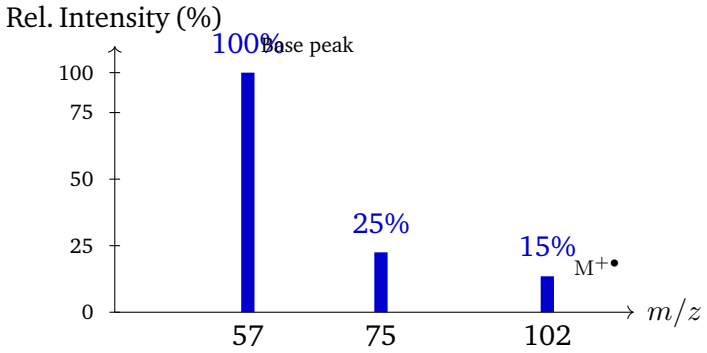
(A) Dihedral angle between C–H bonds (Karplus equation)

(B) Chemical shift difference ($\Delta\delta$) between the two coupled protons

(C) Electronegativity of substituents on the vicinal carbons

(D) C–C–H bond angle

Q9. The mass spectrum below shows the molecular ion at $m/z = 102$ and a base peak at $m/z = 57$ (loss of 45 u). The neutral fragment of mass 45 lost from $M^{+\bullet}$ is most consistent with:



(A) CH_3 ($m/z = 15$)

(B) OCH_3 ($m/z = 31$)

(C) OC_2H_5 (ethoxy, $m/z = 45$)

(D) CHO ($m/z = 29$)

Q10. Butadiene (2 conjugated C=C bonds) absorbs at $\lambda_{max} = 217$ nm; hexatriene (3 conjugated C=C bonds) absorbs at ≈ 258 nm. Each additional conjugated double bond shifts λ_{max} by approximately $+30$ nm. The expected λ_{max} for an all-*E*-octatetraene (4 conjugated C=C bonds) is approximately:

(A) 217 nm

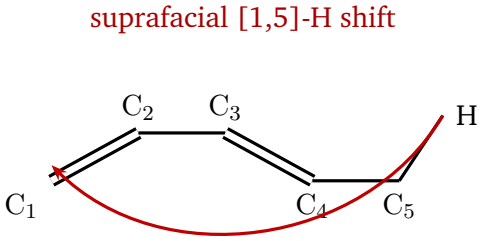
(B) 258 nm

(C) 270 nm

(D) 290 nm

Q11. Heating (Z)-penta-1,3-diene brings about a [1,5]-sigmatropic hydrogen

shift (shown schematically below). This thermal reaction is allowed by the Woodward–Hoffmann rules because:



(A) It involves 6 electrons and is thermally allowed in a suprafacial fashion by the Woodward–Hoffmann rules.

(B) It proceeds with inversion of configuration at the migrating carbon.

(C) It requires photochemical activation; only the photochemical pathway is suprafacially allowed.

(D) It is actually a [1,3]-H shift, not a [1,5]-H shift.

Q12. The Cope rearrangement of hexa-1,5-diene is a thermally allowed [3,3]-sigmatropic rearrangement proceeding via a chair-like six-membered transition state. Which statement about this reaction is **correct**?

(A) The reaction is strongly exothermic ($\approx 100\ \mathrm{kJ\,mol^{-1}}$) because a new σ bond is formed.

(B) For hexa-1,5-diene the reaction is degenerate – the product is chemically identical to the starting material.

(C) The Cope rearrangement requires a transition-metal catalyst to proceed.

(D) The Cope rearrangement is photochemically allowed only and proceeds via a triplet excited state.

Q13. When fluorobenzene is treated with $\mathrm{NaNH_2}$ in liquid ammonia at low temperature, which highly reactive intermediate is formed?

(A) Phenyl anion ($\mathrm{C_6H_5^-}$)

(B) Phenyl cation ($\mathrm{C_6H_5^+}$)

(C) Benzyne (1,2-didehydrobenzene)

(D) Phenyl radical ($C_6H_5^{\bullet}$)

Q14. Treatment of cyclohexanone with *meta*-chloroperoxybenzoic acid (mCPBA) under Baeyer–Villiger oxidation conditions gives which product?

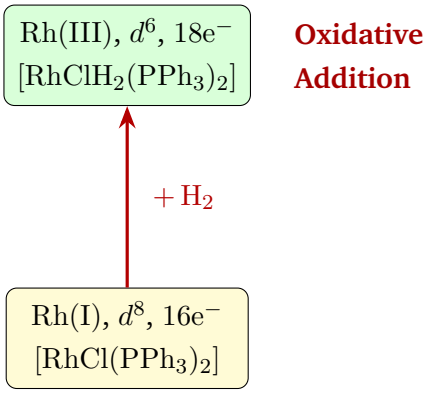
(A) Cyclohexanol

(B) Cyclohexane-1,2-diol

(C) Adipic acid (hexanedioic acid)

(D) ε-Caprolactone (oxepan-2-one, a 7-membered ring lactone)

Q15. In the catalytic cycle of Wilkinson's catalyst $[RhCl(PPh_3)_3]$ for homogeneous alkene hydrogenation (schematic below), which step involves molecular hydrogen (H_2) **first**?



Rh oxidation state: $+1 \rightarrow +3$ Coordination number: $4 \rightarrow 6$

(A) Oxidative addition of H_2 to $Rh(I)$, giving a $Rh(III)$ dihydride complex

(B) Migratory (1,2-)insertion of the alkene into a Rh–H bond

(C) Reductive elimination to release the saturated alkane product

(D) Dissociative substitution of PPh_3 to create a vacant site for alkene coordination

Q16. The Mannich reaction of acetone with formaldehyde and dimethylamine (Me_2NH) gives which β-aminocarbonyl (Mannich base) product?

(A) N,N-Dimethylaminomethanol

(B) 4-(Dimethylamino)butan-2-one

(C) But-3-en-2-one (methyl vinyl ketone)

(D) 1-(Dimethylamino)propan-2-ol

Q17. In the Birch reduction of anisole ($\mathrm{PhOCH_3}$) with Na / liquid $\mathrm{NH_3}$ / *t*-BuOH, reduction of the ring occurs preferentially at the positions:

(A) 1,2-positions (adjacent to $\mathrm{OCH_3}$)

(B) 1,4-positions including the $\mathrm{OCH_3}$-bearing carbon

(C) 2,5-positions (not bearing $\mathrm{OCH_3}$), giving 2,5-dihydroanisole

(D) Complete reduction to cyclohexyl methyl ether

Q18. Wittig reactions using **stabilised** (conjugated) phosphorus ylides with aldehydes give predominantly:

(A) The Z-alkene exclusively

(B) A racemic mixture of enantiomers

(C) Equal amounts of E- and Z-alkene (non-stereospecific)

(D) Predominantly the E-alkene

Q19. Which of the following carbanions is the **most stable**?

(A) Diethyl malonate anion $\mathrm{(EtOOC)_2CH^-}$

(B) Benzyl anion $\mathrm{PhCH_2^-}$

(C) Acetone enolate $\mathrm{CH_3COCH_2^-}$

(D) Acetylide anion $\mathrm{HC{\equiv}C^-}$

Q20. Which compound reacts **fastest** with sodium borohydride ($\mathrm{NaBH_4}$) in methanol?

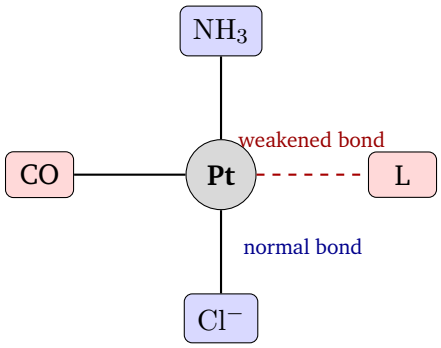
(A) Acetamide ($\mathrm{CH_3CONH_2}$)

(B) Acetaldehyde ($\mathrm{CH_3CHO}$)

(C) Methyl acetate ($\mathrm{CH_3COOCH_3}$)

(D) Acetone ($\mathrm{CH_3COCH_3}$)

Q21. The diagram shows a square planar Pt(II) complex. A strong trans influence ligand placed at one axial position (West) weakens the bond to the ligand located *trans* to it (East, shown as a dashed bond). Which ligand exerts the **strongest trans influence**?



(A) NH_3

(B) Cl^-

(C) CO

(D) F^-

Q22. Which of the following metal carbonyl species has the **highest** CO stretching frequency (ν_{CO})?

(A) $[V(CO)_6]^-$ (anionic; most electron-rich)

(B) $Cr(CO)_6$ (neutral)

(C) $[Mn(CO)_5Br]$ (neutral, one CO replaced by Br)

(D) $[Mn(CO)_6]^+$ (cationic; least electron-rich)

Q23. According to Wade's rules, B_5H_9 is classified as a **nido** borane. Which skeletal electron pair (SEP) count is consistent with this classification?

(A) 7 SEP ($= n + 2$, nido – octahedron with one vertex missing)

(B) 6 SEP ($= n + 1$, closo – closed polyhedral cage)

(C) 8 SEP ($= n + 3$, arachno – two vertices missing)

(D) 5 SEP ($= n$, hypo structure)

Q24. The tris(ethylenediamine)cobalt(III) complex $[Co(en)_3]^{3+}$ (en = 1,2-diaminoethan

is chiral and shows optical activity. How many optical isomers (stereoisomers related by non-superimposable mirror images) does it have?

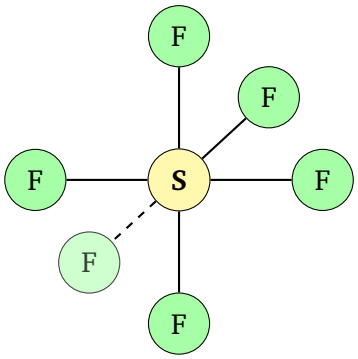
(A) 1

(B) 2

(C) 3

(D) 4

Q25. According to VSEPR theory, the molecular geometry of SF_6 (6 bonding pairs, 0 lone pairs on S) is:



SF_6 **– Octahedral**

(A) Trigonal prismatic

(B) Trigonal bipyramidal

(C) Octahedral

(D) Square antiprismatic

Q26. Which of the following alkali metal hydrides has the **highest thermal stability** (highest decomposition temperature)?

(A) CsH

(B) RbH

(C) NaH

(D) LiH

Q27. In the diamond cubic unit cell, the atomic packing efficiency (fraction of the unit cell volume occupied by atoms) is approximately:

(A) 34%

(B) 52%

(C) 68%

(D) 74%

Q28. The **primary** cause of the lanthanide contraction (anomalously small increase in ionic radius across La to Lu) is:

(A) Increasing nuclear charge alone (a common periodic trend in all rows)

(B) Ineffective shielding of nuclear charge by the 4f electrons

(C) Increased electron–electron repulsion in the contracted 4f subshell

(D) Decreasing number of valence electrons across the lanthanide series

Q29. In molecular fluorimetry, the **Stokes shift** refers to:

(A) The ratio of fluorescence emission intensity to absorbance of the sample

(B) The quantum yield of fluorescence (Φ_F)

(C) The difference between the excitation and emission wavelengths (emission occurs at longer λ than excitation)

(D) The full-width at half-maximum (FWHM) of the emission band

Q30. In atomic absorption spectroscopy (AAS), the hollow cathode lamp (HCL) is used as the radiation source because:

(A) It provides a continuous broadband spectrum spanning the entire UV-Vis range.

(B) It produces intense broadband UV radiation to maximise total photon flux.

(C) It generates a high-temperature plasma for atomisation of the sample solution.

(D) It emits element-specific sharp spectral lines that exactly match the narrow absorption profile of free analyte atoms in the flame/furnace.

Q31. In HPLC, the retention factor (capacity factor) $k' = (t_R - t_0)/t_0$. If a solute elutes at $t_R = 12.0$ min and the dead time is $t_0 = 2.0$ min, the value of k' is:

(A) 5.0

(B) 6.0

(C) 0.17

(D) 12.0

Q32. For a rotating disk electrode (RDE), the Levich equation gives a limiting current $i_L \propto \omega^{1/2}$, where ω is the angular rotation speed. If ω is increased by a factor of 4, the limiting current i_L increases by a factor of:

(A) 4

(B) 2

(C) 8

(D) 16

Q33. At large anodic overpotentials, the Butler-Volmer equation reduces to the Tafel equation $\eta = a + b \log i$ (a linear $\log i$ vs. η relationship). This simplification arises because:

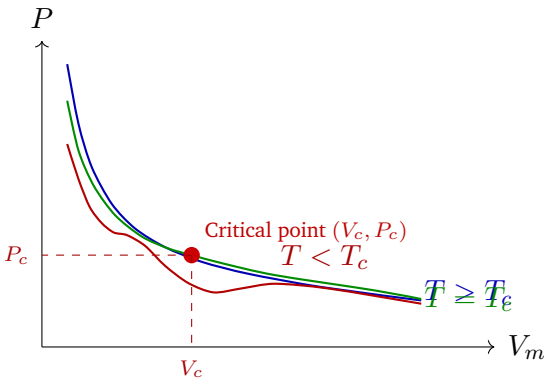
(A) Diffusion overpotential becomes the sole rate-controlling factor at high η.

(B) The electric double-layer capacitance is fully discharged at large overpotentials.

(C) The cathodic exponential term in the Butler-Volmer equation becomes negligibly small at large positive η.

(D) The charge-transfer resistance falls to zero, giving linear current–voltage behaviour.

Q34. For a van der Waals gas (constants a, b; gas constant R), P–V_m isotherms at three temperatures are shown below. Which set of expressions for the **critical constants** is correct?



(A) $T_c = \dfrac{a}{27Rb}, \quad P_c = \dfrac{a}{27b^2}, \quad V_c = 3b$

(B) $T_c = \dfrac{8a}{27Rb}, \quad P_c = \dfrac{a}{27b^2}, \quad V_c = b$

(C) $T_c = \dfrac{8a}{27Rb}, \quad P_c = \dfrac{a}{3b^2}, \quad V_c = 3b$

(D) $T_c = \dfrac{8a}{27Rb}, \quad P_c = \dfrac{a}{27b^2}, \quad V_c = 3b$

Q35. The osmotic pressure of a polymer solution is $\pi = 0.240$ atm for $w = 1.00$ g dissolved in $V = 100$ mL at $T = 300$ K. Using $\pi = \dfrac{wRT}{MV}$ with $R = 0.08206\ \text{L atm mol}^{-1}\,\text{K}^{-1}$, the molar mass M is approximately:

(A) $1000\ \text{g mol}^{-1}$

(B) $500\ \text{g mol}^{-1}$

(C) $2000\ \text{g mol}^{-1}$

(D) $250\ \text{g mol}^{-1}$

Q36. In the Einstein model of the heat capacity of solids, at temperatures $T \gg \theta_E$ (the Einstein temperature), the molar constant-volume heat capacity C_V approaches:

(A) 0

(B) $3R$

(C) $3R/2$

(D) $R \ln 3$

Q37. For the thermal unfolding of a globular protein in aqueous solution, the difference in heat capacity $\Delta C_p = C_{p,\text{unfolded}} - C_{p,\text{folded}}$ is typically:

(A) Negative (folded state has higher heat capacity)

(B) Zero (heat capacity is the same in both states)

(C) Positive (unfolded state has higher heat capacity)

(D) Entirely determined by and proportional to the protein's molecular weight

Q38. A competitive inhibitor raises the apparent K_m while leaving $V_{\max}$ unchanged. On a Lineweaver–Burk plot ($1/v$ vs. $1/[\mathrm{S}]$), competitive inhibition is characterised by:

(A) Lines intersecting on the x-axis ($-1/K_m$ axis)

(B) A family of parallel lines with the same slope but different intercepts

(C) Lines intersecting in the second quadrant (negative $1/[\mathrm{S}]$, negative $1/v$)

(D) Lines intersecting on the y-axis (same $1/V_{\max}$ intercept, different slopes)

Q39. In Fourier-transform NMR (FT-NMR), the mathematical technique used to convert the free induction decay (FID, time-domain signal) into the conventional NMR spectrum (frequency domain) is the:

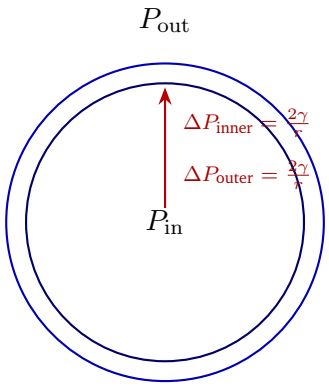
(A) Fourier transform

(B) Laplace transform

(C) Wavelet transform

(D) Z-transform

Q40. The Young–Laplace equation gives the excess pressure across a *single* spherical interface: $\Delta P = 2\gamma/r$. A soap bubble (radius $r = 1.0$ cm, surface tension $\gamma = 0.025\ \mathrm{N\,m^{-1}}$) has **two** liquid–air interfaces (inner and outer, as shown). The total pressure difference between the inside and outside of the bubble is:



$$\Delta P_{\text{total}} = \frac{4\gamma}{r}$$

(A) 5 Pa

(B) 10 Pa

(C) 2.5 Pa

(D) 20 Pa

Detailed Solutions

Q1.

Solution

Concept — Maxwell-Boltzmann Speed Distribution:
The most probable speed is the speed at the peak of the Maxwell-Boltzmann distribution, given by $u_{\text{mp}} = \sqrt{2RT/M}$.

Step 1 — Substitute values:
$M = 28\ \text{g mol}^{-1} = 0.028\ \text{kg mol}^{-1}$, $T = 300\ \text{K}$, $R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$:

$$u_{\text{mp}} = \sqrt{\frac{2 \times 8.314 \times 300}{0.028}} = \sqrt{\frac{4988.4}{0.028}} = \sqrt{178157} \approx 422\ \text{m s}^{-1}.$$

Why other options are wrong:
Option A (300 m/s): This is below even the root-mean-square speed at much lower temperatures; it underestimates the kinetic energy at $300\ \text{K}$.
Option B (515 m/s): This corresponds to $u_{\text{rms}} = \sqrt{3RT/M}$ rather than $u_{\text{mp}} = \sqrt{2RT/M}$; it is the rms speed, not the most probable speed.
Option D (600 m/s): This significantly overestimates u_{mp}; numerically inconsistent with the formula.

Final Answer: $u_{\text{mp}} = 422\ \text{m s}^{-1} \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#1

Q2.

Solution

Concept — Residual (Positional) Entropy:
When N_A molecules each independently adopt one of Ω equally probable orientations, the residual molar entropy at $0\ \text{K}$ is $S_{\text{res}} = R \ln \Omega$.

Step 1 — Identify Ω:
Each N_2O molecule can orient in **2** ways ($N{\equiv}N{-}O$ or $O{-}N{\equiv}N$), so $\Omega = 2$.

Step 2 — Calculate:
$S_{\text{res}} = R \ln 2 = 8.314 \times 0.693 \approx 5.76\ \text{J mol}^{-1}\,\text{K}^{-1}$.

Why other options are wrong:
Option A (0): Zero residual entropy would require a perfectly ordered crystal with a unique ground state, but N_2O has head-to-tail disorder.
Option B ($R \ln 4$): This would apply if each molecule had *four* orientations (e.g. CO on a 2D surface); N_2O has only two.
Option C ($R/2$): This value has no thermodynamic basis for this problem; $R/2$ is not a residual entropy formula.

Final Answer: $S_{\text{res}} = R\ln 2 \approx 5.76\ \text{J mol}^{-1}\,\text{K}^{-1} \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#2

Q3.

Solution

Concept — Marcus Theory; Self-Exchange Reaction:
The Marcus activation energy is $\Delta G^{\ddagger} = (\Delta G^{\circ} + \lambda)^2/(4\lambda)$. For a self-exchange reaction, $\Delta G^{\circ} = 0$ by definition (reactant and product are the same couple).

Step 1 — Substitute $\Delta G^{\circ} = 0$:

$$\Delta G^{\ddagger} = \frac{(0+\lambda)^2}{4\lambda} = \frac{\lambda^2}{4\lambda} = \frac{\lambda}{4}.$$

Why other options are wrong:
Option B ($\lambda/2$): Arises from incorrectly not squaring the numerator or from misapplying the formula.
Option C (λ): This would be the reorganisation energy itself, not the barrier height.
Option D (0): Zero activation energy would mean the reaction is barrierless, which only occurs when $\Delta G^{\circ} = -\lambda$ (the activationless region), not for self-exchange.

Final Answer: $\Delta G^{\ddagger} = \lambda/4 \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#3

Q4.

Solution

Concept — Parallel First-Order Reactions; Product Ratio:
For two concurrent first-order reactions from a common reactant A, the amounts of products B and C formed are proportional to their respective rate constants at *all* times $t > 0$.

Step 1 — Derive product ratio:
$\frac{d[\text{B}]}{dt} = k_1[\text{A}]$ and $\frac{d[\text{C}]}{dt} = k_2[\text{A}]$. Dividing: $\frac{d[\text{B}]}{d[\text{C}]} = \frac{k_1}{k_2} = \frac{0.010}{0.030} = \frac{1}{3}$.

Step 2 — Confirm time-independence:
Since both numerator and denominator share the same $[\text{A}](t)$ factor, the ratio $[\text{B}]/[\text{C}] = k_1/k_2 = 1/3$ at every instant.

Why other options are wrong:
Option A (3:1): This inverts k_1/k_2; B is formed *slower* than C.
Option C (1:1): Only holds when $k_1 = k_2$; here $k_1 \neq k_2$.

Option D (1:9): This would result from $k_1/k_2 = (0.010)^2/(0.030)^2$, which has no kinetic justification.

Final Answer: $[\mathrm{B}]/[\mathrm{C}] = 1/3 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#4

Q5.

Solution

Concept — Quantum Harmonic Oscillator; Tunnelling into Forbidden Region:
The quantum-mechanical harmonic oscillator differs fundamentally from its classical counterpart: wavefunctions decay exponentially into the classically forbidden region rather than terminating abruptly at the turning points.

Step 1 — Evaluate each statement:
(A) True: Ground-state energy $E_0 = \frac{1}{2}h\nu$ – the zero-point energy – is an exact result from $\hat{H}\psi_0 = E_0\psi_0$.
(B) True: $E_v = (v + \frac{1}{2})h\nu$, so $E_{v+1} - E_v = h\nu$ for all v.
(C) *False* (correct answer): The wavefunction does NOT vanish at the classical turning points; it continues as an exponentially decaying tail into the forbidden region (quantum tunnelling / barrier penetration). The probability of finding the particle beyond the turning points is small but non-zero for all v.
(D) True: $\psi_0 \propto \exp(-\alpha x^2)$, a Gaussian, which is a consequence of solving the Schrödinger equation for $V = \frac{1}{2}kx^2$.

Why other options are wrong:
Option A: Correct statement, not the answer.
Option B: Correct statement, not the answer.
Option D: Correct statement, not the answer.

Final Answer: Statement C is incorrect $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#5

Q6.

Solution

Concept — IR Selection Rule; Dipole Moment Change:
A vibrational mode is IR active only if the *dipole moment changes* during the vibration ($\partial\mu/\partial Q \neq 0$).

Step 1 — Assess each molecule:
HCl: polar, $\mu \neq 0$, vibration changes μ – **IR active**.
CO: polar (small μ), vibration changes μ – **IR active**.
H_2O: bent, polar – both symmetric and antisymmetric stretches change μ – **IR active**.

N_2: *homonuclear diatomic*, $\mu = 0$ at all bond lengths by symmetry – **IR inactive**.

Why other options are wrong:
Option A (HCl): Has a permanent dipole that changes upon vibration; strongly IR active (fundamental at $\approx 2890\ \text{cm}^{-1}$).
Option B (CO): Despite small μ, the vibration is IR active (band at $\approx 2143\ \text{cm}^{-1}$).
Option C (H_2O): Both stretching and bending modes are IR active; well-known atmospheric absorber.

Final Answer: N_2 is IR inactive $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#6

Q7.

Solution

Concept — DEPT-135; Phase of Carbon Signals:
In DEPT-135, the phase of a signal depends on the number of attached protons: CH and CH_3 give *positive* (upward) peaks; CH_2 gives a *negative* (downward) peak; quaternary carbons give *no* signal.

Step 1 — Recall the DEPT-135 phase rule:
The signal intensity in DEPT-135 is proportional to $\sin\theta\ \cos^{n-1}\theta$ evaluated at $\theta = 135^\circ$ (the final pulse angle). For $n = 1$ (CH): $\sin 135^\circ = +0.707 > 0$ (positive).
For $n = 2$ (CH_2): $\sin 135^\circ \cos 135^\circ = (+0.707)(-0.707) = -0.5 < 0$ (**negative**).
For $n = 3$ (CH_3): $\sin 135^\circ \cos^2 135^\circ = (+0.707)(0.5) = +0.354 > 0$ (positive).

Why other options are wrong:
Option B (CH): CH gives a positive (upward) peak in DEPT-135.
Option C (CH_3): CH_3 gives a positive (upward) peak.
Option D (quaternary C): Quaternary carbons have no attached H and give no signal in any DEPT experiment.

Final Answer: CH_2 gives the negative peak $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#7

Q8.

Solution

Concept — Vicinal Coupling Constant ^3J; Karplus Equation:
The Karplus equation $^3J = A\cos^2\phi - B\cos\phi + C$ shows that ^3J depends on the *dihedral angle* ϕ, the electronegativity of substituents, and bond angles. It does *not* depend on the chemical shift difference between the coupled nuclei.

Step 1 — Analyse each factor:
(A) Dihedral angle: Directly governs ^3J via the Karplus equation – ^3J varies from

≈ 0 (gauche, $\phi = 60°$) to $\approx$10–12 Hz (anti, $\phi = 180°$). *Significant*.
(B) $\Delta\delta$: The chemical shift difference $\Delta\delta$ affects the *appearance* of the multiplet (first- vs. second-order), but NOT the magnitude of J itself. J is a fixed property of the molecular electronic structure. *No significant effect on J.*
(C) Electronegativity: Electronegative substituents reduce ${}^3J$ by withdrawing electron density from the C–H bonds. *Significant*.
(D) Bond angle: Alters the overlap integral and thus modulates ${}^3J$. *Significant*.

Why other options are wrong:
Options A, C, D: Each is a genuine, experimentally verified determinant of ${}^3J$ magnitude and is not the answer.

Final Answer: $\Delta\delta$ does not affect ${}^3J \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#8

Q9.

Solution

Concept — Mass Spectrometry; Neutral Loss of 45 u:
A neutral fragment of mass 45 u from an ester is most commonly an ethoxy radical ($OC_2H_5^{\bullet}$, $M = 45$ u). Loss of OEt from an ester $M^{+\bullet}$ gives the acylium ion $[RCO]^+$.

Step 1 — Identify the compound:
$M = 102$ u. Possible ethyl ester: ethyl propanoate $CH_3CH_2COOC_2H_5$, $M = 102$ u. Loss of OEt (45 u) gives $[CH_3CH_2CO]^+ =$ propanoyl cation at $m/z = 57$. Consistent!

Step 2 — Verify fragment masses:
m/z 57: $CH_3CH_2CO^+$ (acylium), MW = 57. ✓
m/z 75: $[M - 27]^+$ (loss of C_2H_3), a minor fragment.
m/z 102: molecular ion $M^{+\bullet}$.

Why other options are wrong:
Option A (CH_3, 15 u): Would give $m/z = 102 - 15 = 87$, not 57.
Option B (OCH_3, 31 u): Would give $m/z = 102 - 31 = 71$, not 57.
Option D (CHO, 29 u): Would give $m/z = 102 - 29 = 73$, not 57.

Final Answer: Loss of OEt (45 u) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#9

Q10.

Solution

Concept — UV-Vis Spectroscopy; Extension of Conjugation (Woodward Rules):

Each additional conjugated C=C double bond red-shifts (bathochromic shift) λ_{max} by approximately 30 nm.

Step 1 — Build the series:
Butadiene (2 C=C): $\lambda_{max} = 217$ nm.
Hexatriene (3 C=C): $217 + 30 = 247$ nm (empirical: ≈ 258 nm, given in the question).
Octatetraene (4 C=C): $258 + 30 \approx 288 \approx 290$ nm.

Step 2 — Select answer:
λ_{max} for 4 conjugated double bonds ≈ 290 nm.

Why other options are wrong:
Option A (217 nm): This is butadiene (2 C=C); ignores the bathochromic shift from extra conjugation.
Option B (258 nm): This is hexatriene (3 C=C), one double bond fewer than requested.
Option C (270 nm): Intermediate value; does not match the $+30$ nm rule applied to the hexatriene baseline.

Final Answer: $\lambda_{max} \approx 290$ nm $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#10

Q11.

Solution

Concept — Woodward-Hoffmann Rules; [1,5]-Sigmatropic H Shift:
A [1,5]-sigmatropic hydrogen shift is a pericyclic reaction involving a 6-electron, 6-centre transition state (C–H σ bond: 2e + diene π system: 4e = 6e total).

Step 1 — Apply the Woodward-Hoffmann selection rule:
For sigmatropic shifts with $4n + 2$ electrons thermally: suprafacial migration is *allowed*. Here $4n + 2 = 6$ requires $n = 1$. The [1,5]-H shift is therefore thermally allowed suprafacially.

Step 2 — Physical consequence:
The H migrates across the top face (suprafacially) of the conjugated diene from C_5 to C_1 through an aromatic-like 6-membered cyclic transition state, with *retention* of configuration at the migrating carbon.

Why other options are wrong:
Option B: Inversion at the migrating H is not possible (H has no stereochemistry); the shift proceeds with retention via the suprafacial pathway.
Option C: The [1,5]-H shift is thermally (not photochemically) allowed. The photochemical pathway is antara-facial, which is geometrically inaccessible.
Option D: A [1,3]-H shift involves only 4 electrons (4n, $n = 1$) and is thermally

forbidden suprafacially; the observed shift in pentadiene is [1,5].

Final Answer: Suprafacial, 6-electron, thermally allowed ⇒ **(A)**

Answer: (A) ← Go Back to Q#11

Q12.

Solution

Concept — Cope Rearrangement; Degenerate Pericyclic Reaction:
The Cope rearrangement is a thermally allowed [3,3]-sigmatropic rearrangement proceeding through a chair-like six-membered transition state.

Step 1 — Identify degeneracy:
In hexa-1,5-diene ($H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$), the two C=C double bonds are identical and symmetrically placed. The [3,3]-shift interconverts one 1,5-hexadiene arrangement with an identical one: starting material and product have the same connectivity → *degenerate*.

Step 2 — Energetics and mechanism:
Because the reaction is degenerate, $\Delta H^\circ \approx 0$; it is not exothermic. The reaction requires no metal catalyst and is thermal, not photochemical.

Why other options are wrong:
Option A: The reaction is nearly thermoneutral ($\Delta H \approx 0$) for hexa-1,5-diene; $\approx 100\ \text{kJ mol}^{-1}$ exothermicity is incorrect.
Option C: The Cope rearrangement is an uncatalysed concerted pericyclic reaction; no metal catalyst is required (contrast with the aza-Cope/Mannich variant).
Option D: The reaction is thermally allowed via $4n+2=6$ electrons in a suprafacial/suprafacial (supra/supra) sense; it does not require a photon.

Final Answer: Degenerate rearrangement; product = starting material ⇒ **(B)**

Answer: (B) ← Go Back to Q#12

Q13.

Solution

Concept — Benzyne Intermediate; Elimination-Addition Mechanism:
Strongly basic amide ion (NH_2^-) removes an ortho proton from fluorobenzene; concerted or subsequent loss of F^- then generates **benzyne** (1,2-didehydrobenzene).

Step 1 — Mechanism:
1. NH_2^- abstracts H ortho to F → aryl carbanion / concerted E2.
2. Loss of F^- gives benzyne (a highly strained triple-bond equivalent in the ring).
3. NH_3 (nucleophile/electrophile) adds across the triple bond → aniline or iso-

meric products.

Step 2 — Evidence:
The Maitland-Jones "isotope labelling" experiments and the formation of a 1:1 mixture of aniline isomers confirm benzyne as intermediate.

Why other options are wrong:
Option A (phenyl anion): A phenyl carbanion is not formed; fluorobenzene does not undergo simple nucleophilic displacement at sp^2 carbon without forming benzyne first.
Option B (phenyl cation): Requires heterolytic ionisation; not generated under these strongly basic conditions.
Option D (phenyl radical): Radical mechanisms require radical initiators or photolysis; $NaNH_2$ acts as a base/nucleophile, not a radical agent.

Final Answer: Benzyne (1,2-didehydrobenzene) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#13

Q14.

Solution

Concept — Baeyer-Villiger Oxidation; Migration Aptitude:
Peracids convert ketones to esters (or cyclic ketones to lactones) by oxidative insertion of an oxygen atom between the carbonyl carbon and the carbon with the greater migratory aptitude.

Step 1 — Identify the migrating group:
In cyclohexanone, the two α-carbons are equivalent. Migration of one $C-C$ bond (a secondary α-carbon) from the carbonyl carbon gives ring expansion. The "Criegee intermediate" (tetrahedral peracid adduct) undergoes migration of the more electron-rich carbon, inserting O into the C–C bond.

Step 2 — Product identification:
Insertion of O into the ring gives a 7-membered ring lactone: ε-caprolactone (oxepan-2-one), MW = 114.

Why other options are wrong:
Option A (cyclohexanol): Reduction of ketone to alcohol; peracids are *oxidants*, not reductants; not formed by Baeyer-Villiger.
Option B (diol): Diols result from dihydroxylation (OsO_4 / mCPBA of alkenes); cyclohexanone has no alkene.
Option C (adipic acid): Requires oxidative ring-opening with stronger conditions (e.g. $KMnO_4$, HNO_3); not Baeyer-Villiger product.

Final Answer: ε-Caprolactone $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#14

Q15.

Solution

Concept — Wilkinson's Catalyst; Oxidative Addition of H_2:
$[RhCl(PPh_3)_3]$ is a d^8, Rh(I), square-planar 16-electron complex. After loss of one PPh_3 to generate a 14e species, it reacts with H_2.

Step 1 — Oxidative Addition:
H_2 undergoes **oxidative addition** to the electron-rich Rh(I) centre:

$$\mathrm{Rh(I)}(d^8,\ 16\mathrm{e}) + H_2 \longrightarrow \mathrm{Rh(III)}(d^6,\ 18\mathrm{e})\ (\text{dihydride})$$

Rh is oxidised from $+1$ to $+3$ and gains two H ligands; both the oxidation state and coordination number increase by 2.

Step 2 — Subsequent steps:
After H_2 addition, the alkene coordinates, migratory insertion (step 2) forms Rh–alkyl, then reductive elimination (step 3) releases the alkane and regenerates Rh(I).

Why other options are wrong:
Option B: Migratory insertion occurs *after* H_2 oxidative addition and alkene coordination.
Option C: Reductive elimination is the *last* step, releasing the hydrogenated product.
Option D: PPh_3 dissociation occurs before H_2 addition to open a coordination site, but the question asks specifically about the first step *involving* H_2.

Final Answer: Oxidative addition of H_2 $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#15

Q16.

Solution

Concept — Mannich Reaction; β-Aminocarbonyl Formation:
The Mannich reaction proceeds: (1) condensation of Me_2NH with $HCHO$ gives the iminium ion $[Me_2N{=}CH_2]^+$ (Mannich electrophile); (2) the enol of acetone attacks the iminium carbon; (3) proton transfer gives the β-aminoketone.

Step 1 — Trace the product:
Acetone enol ($CH_2{=}C(OH)CH_3$) attacks $CH_2{=}N^+Me_2$ at C-1 of the iminium:

$$CH_3COCH_3 + HCHO + Me_2NH \longrightarrow CH_3CO\underbrace{CH_2CH_2NMe_2}_{\text{new } \beta\text{-position}}$$

Product: 4-(dimethylamino)butan-2-one ($CH_3COCH_2CH_2NMe_2$).

Why other options are wrong:

Option A (N,N-dimethylaminomethanol): This is the hemiaminal Me_2NCH_2OH; it is the initial condensation product of amine and aldehyde, not the Mannich base.

Option C (but-3-en-2-one): Methyl vinyl ketone would require elimination of $NHMe_2$; not the direct Mannich product.

Option D (1-(dimethylamino)propan-2-ol): This is an alcohol, not a ketone; it would require reduction of the Mannich base.

Final Answer: 4-(Dimethylamino)butan-2-one $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#16

Q17.

Solution

Concept — Birch Reduction; Effect of Electron-Donating Groups:

In the Birch reduction, the ring is reduced by dissolving-metal electrons. Electron-*donating* substituents (e.g. OCH_3, NR_2) direct reduction to the *unsubstituted* positions (2,5) of the ring, leaving the substituted carbon part of the residual double bond.

Step 1 — Mechanistic reasoning:

The radical anion is stabilised at positions where the LUMO coefficient is largest. For electron-donating substituents, the LUMO has highest coefficient at positions *not* bearing the substituent. Protonation at these positions (2 and 5 in anisole) leaves a 1,4-diene with the OCH_3 still on the ring: 2,5-dihydroanisole (1-methoxy-1,4-cyclohexadiene).

Why other options are wrong:

Option A (1,2-positions): 1,2-reduction would give a strained 1,2-cyclohexadiene; not observed under Birch conditions with an EDG.

Option B (1,4 including OCH_3 carbon): This pattern applies to electron-*withdrawing* groups (e.g. $COOH$), not EDGs.

Option D (complete reduction): Complete reduction to the cyclohexyl ether requires excess metal and protic acid; not observed under standard Birch conditions.

Final Answer: Reduction at 2,5-positions (EDG rule), giving 2,5-dihydroanisole $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#17

Q18.

Solution

Concept — Wittig Reaction Stereochemistry; Stabilised vs. Non-stabilised Ylides:
Unstabilised (alkyl) ylides react fast, reversibly through an oxetane, giving predominantly *Z*-alkene. *Stabilised* (conjugated, EWG-containing) ylides are less reactive; the rate-limiting step is the [2+2] cycloaddition, and the betaine/oxetane collapses preferentially to the *E*-product.

Step 1 — Rationalise E-selectivity:
Stabilised ylides form a betaine intermediate that is sufficiently long-lived to equilibrate to the more stable, less hindered E-configured oxetane. The E-alkene is thermodynamically and kinetically preferred due to steric interaction between the large $\mathrm{Ph_3P=O}$ fragment and the substituent of the aldehyde in the Z-transition state.

Why other options are wrong:
Option A (Z-exclusively): Z-selectivity is characteristic of unstabilised (non-conjugated, e.g. simple alkyl) ylides, not stabilised ones.
Option B (racemic): The Wittig reaction forms C=C double bonds (prochiral); it does not create a stereogenic centre, so enantiomers are irrelevant.
Option C (equal E and Z): Non-stereospecific mixtures occur with reactive but poorly selective ylides; stabilised ylides give high E-selectivity.

Final Answer: Predominantly E-alkene ⇒ **(D)**

Answer: (D) ← Go Back to Q#18

Q19.

Solution

Concept — Carbanion Stability; Multiple Resonance Stabilisation:
Carbanion stability increases with: (a) increased s-character of the orbital; (b) resonance delocalisation (especially into EWG); (c) induction. The pKa of the conjugate acid is the quantitative measure (lower pKa = more stable carbanion).

Step 1 — Compare pKa values:
Diethyl malonate $\mathrm{(EtOOC)_2CH_2}$: $\mathrm{p}K_a \approx 13$ (two ester groups provide double resonance stabilisation). **Most stable**.
Acetone $\mathrm{CH_3COCH_3}$: $\mathrm{p}K_a \approx 20$ (single keto group).
Acetylene $\mathrm{HC{\equiv}CH}$: $\mathrm{p}K_a \approx 25$ (sp carbon, high s-character).
Toluene $\mathrm{PhCH_3}$: $\mathrm{p}K_a \approx 43$ (benzyl, limited stabilisation).

Step 2 — Conclusion:
The diethyl malonate anion, stabilised by *two* ester groups via resonance and induction, is the most stable (lowest $\mathrm{p}K_a$).

Why other options are wrong:
Option B (benzyl): $pK_a \approx 43$; much higher than malonate, hence much less stable anion.
Option C (acetone enolate): $pK_a \approx 20$; one ester provides less stabilisation than two.
Option D (acetylide): $pK_a \approx 25$; s-character stabilisation, but weaker than double-ester resonance.

Final Answer: Diethyl malonate anion (most stable) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#19

Q20.

Solution

Concept — Nucleophilic Addition to Carbonyl; Reactivity Order:
$NaBH_4$ is a hydride donor that attacks electrophilic carbonyl carbons. Reactivity depends on (a) electrophilicity of the carbonyl carbon and (b) steric accessibility.

Step 1 — Reactivity series of carbonyl compounds:
General order toward nucleophiles:

$$RCHO > R_2CO \gg RCOOR' \approx RCOSR' > RCONR_2 \approx RCOO^-$$

Among the given options: acetaldehyde (aldehyde) $>$ acetone (ketone) $\gg$ methyl acetate (ester) $>$ acetamide (amide; essentially unreactive with $NaBH_4$).

Step 2:
Acetaldehyde has less steric shielding than acetone (one methyl vs. two) and is more electrophilic. It therefore reacts fastest with $NaBH_4$.

Why other options are wrong:
Option A (acetamide): Amides are essentially inert to $NaBH_4$; they require a stronger hydride such as $LiAlH_4$.
Option C (methyl acetate): Esters react very slowly with $NaBH_4$; they also require $LiAlH_4$ for efficient reduction.
Option D (acetone): A ketone is less reactive than the corresponding aldehyde due to greater steric hindrance and lower electrophilicity.

Final Answer: Acetaldehyde reacts fastest $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#20

Q21.

Solution

Concept — Trans Influence; Ground-State Weakening of Trans Bond:
The trans influence is the *thermodynamic* (ground-state) weakening of the bond trans to a ligand. Strong σ-donors and ligands with good π-acceptor ability exert the largest trans influence.

Step 1 — Trans influence series:
$CO > CN^- \approx PR_3 > Cl^- > NH_3 > F^-$

CO is simultaneously a very strong σ-donor to the metal via the carbon lone pair and a very strong π-acceptor via its π^*. This dual character places electron density trans to CO into an elongated, weakened bond.

Step 2 — Compare given ligands:
Among NH_3 (moderate σ-donor, no π effects), Cl^- (moderate σ, π-donor), F^- (weak σ, strong π-donor), and CO: **CO has by far the strongest trans influence**.

Why other options are wrong:
Option A (NH_3): Weak σ-donor, no back-bonding; very low trans influence.
Option B (Cl^-): Moderate trans influence (π-donor, weak σ); weaker than CO.
Option D (F^-): Strong π-donor but poor σ-donor; smaller net trans influence than CO.

Final Answer: CO has the strongest trans influence $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#21

Q22.

Solution

Concept — CO Stretching Frequency; π-Backbonding:
CO forms π-backbonds: metal d-electrons donate into the CO π^* orbital, weakening the C≡O bond. More electron-rich metals $\Rightarrow$ more backbonding $\Rightarrow$ lower ν_{CO}.

Step 1 — Rank electron richness of the metal centres:
$[V(CO)_6]^-$: V(0), *anionic* complex – most electron-rich. $\Rightarrow$ most backbonding $\Rightarrow$ *lowest* ν_{CO} ($\approx 1860\ cm^{-1}$).
$Cr(CO)_6$: Cr(0), neutral – intermediate. ($\approx 2000\ cm^{-1}$).
$[Mn(CO)_5Br]$: Mn(I), Br withdraws slightly. ($\approx 2013\ cm^{-1}$).
$[Mn(CO)_6]^+$: Mn(I), *cationic* – least electron-rich, least backbonding $\Rightarrow$ *highest* ν_{CO} ($\approx 2090\ cm^{-1}$).

Why other options are wrong:
Option A ($[V(CO)_6]^-$): Anionic; lowest ν_{CO}, not highest.
Option B ($Cr(CO)_6$): Neutral, intermediate ν_{CO}.
Option C ($[Mn(CO)_5Br]$): Slightly lower ν_{CO} than the cation because Br donates

electron density relative to a vacant site.

Final Answer: $[\mathrm{Mn(CO)_6}]^+$ (highest ν_{CO}) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#22

Q23.

Solution

Concept — Wade's Rules; SEP Count for Boranes:
Wade's rules classify polyhedral boranes by the number of skeletal electron pairs (SEP): closo $(n+1)$, nido $(n+2)$, arachno $(n+3)$, where n is the number of cage vertices.

Step 1 — Count SEP for $\mathrm{B_5H_9}$:
Each BH unit contributes 2 skeletal electrons; each additional (bridging or extra) H contributes 1 electron to the skeleton.
$\mathrm{B_5H_9}$: 5 BH groups $\rightarrow 5 \times 2 = 10$ skeleton e; 4 additional bridging H $\rightarrow 4 \times 1 = 4$ e.
Total skeletal electrons = 14; SEP = $14/2 = 7$.

Step 2 — Assign structure type:
$n = 5$ vertices; SEP $= 7 = n + 2 = 5 + 2 \Rightarrow$ **nido** structure (octahedron with one vertex missing: a square pyramid).

Why other options are wrong:
Option B (6 SEP = $n+1$): This would imply a closo (closed, spherical) cage; $\mathrm{B_5H_9}$ has one vertex missing, so it is nido.
Option C (8 SEP = $n+3$): This is the arachno classification; would require two missing vertices and correspond to $\mathrm{B_5H_{11}}$.
Option D (5 SEP = n): A hypo cage; not a standard Wade category and inconsistent with the actual electron count.

Final Answer: 7 SEP $= n + 2$; nido structure $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#23

Q24.

Solution

Concept — Optical Isomerism in Tris-chelate Octahedral Complexes:
$[\mathrm{Co(en)_3}]^{3+}$ is a propeller-like complex with D_3 symmetry. The three bidentate en ligands wrap around Co in either a right-handed (Δ) or left-handed (Λ) helical fashion.

Step 1 — Identify stereoisomers:
The Δ (right-handed) and Λ (left-handed) configurations are non-superimposable

mirror images → they are **enantiomers**. No other geometric isomers exist for a tris-bidentate complex of this type. Total optical isomers = **2**.

Step 2 — Verify chirality:
The D_3 point group has no improper rotation axis (S_n), so the complex is *chiral*: both enantiomers are optically active and rotate plane-polarised light in opposite directions.

Why other options are wrong:
Option A (1): A single isomer would imply the molecule is identical to its mirror image (achiral); $[\mathrm{Co(en)_3}]^{3+}$ is chiral.
Option C (3): No meso or third geometric form exists for $[\mathrm{M(en)_3}]^{3+}$; all three en are equivalent.
Option D (4): Four isomers would require at least two independent stereogenic elements; a tris-chelate complex has only one (Δ/Λ).

Final Answer: 2 optical isomers (Δ and Λ) ⇒ **(B)**

Answer: (B) ← Go Back to Q#24

Q25.

Solution

Concept — VSEPR Theory; $\mathrm{SF_6}$:
VSEPR predicts geometry from the number of electron domains (bonding pairs + lone pairs) around the central atom.

Step 1 — Electron domain count for $\mathrm{SF_6}$:
S has 6 valence electrons. Each F claims 1 electron from S to form 6 S–F bonds. Remaining lone pairs on S = $6 - 6 = 0$. Total electron domains on S = 6 bonding + 0 lone = 6 ⇒ **octahedral** geometry (all bond angles $90°$).

Step 2 — Confirm symmetry:
$\mathrm{SF_6}$ belongs to the O_h point group; all 6 S–F bonds are equivalent by symmetry. Experimental measurements confirm octahedral geometry with $d(\mathrm{S{-}F) = 156\ pm}$ and bond angles $90°$.

Why other options are wrong:
Option A (trigonal prismatic): A trigonal prism has 6 vertices but requires a different arrangement of ligands; it has D_{3h} symmetry, not O_h. $\mathrm{SF_6}$ adopts the lower-energy octahedral geometry.
Option B (trigonal bipyramidal): Only 5 electron domains; relevant for $\mathrm{PCl_5}$ or $\mathrm{SF_4}$ (4 bonds + 1 lone pair), not for $\mathrm{SF_6}$.
Option D (square antiprismatic): Requires 8 ligands; irrelevant for a 6-coordinate compound.

Final Answer: Octahedral ⇒ **(C)**

Answer: (C) ← Go Back to Q#25

Q26.

Solution

Concept — Thermal Stability of Alkali Metal Hydrides:
Alkali metal hydrides (MH) are ionic solids with increasing lattice energy as the cation size decreases (down the group: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$).

Step 1 — Lattice energy argument:
Higher lattice energy $\Rightarrow$ higher thermal stability. Lattice energy is greatest for LiH because Li^+ is the smallest alkali cation, giving the shortest interionic distance and strongest ionic attraction.

Step 2 — Decomposition temperatures:
Approximate values: LiH :$\approx 850\,^\circ$C; NaH :$\approx 425\,^\circ$C; RbH, CsH: decompose well below $300\,^\circ$C.

Why other options are wrong:
Option A (CsH): Cs^+ is the largest alkali cation; lattice energy and thermal stability are lowest in the group.
Option B (RbH): Similar reasoning; second-lowest stability.
Option C (NaH): Thermally less stable than LiH; widely used in synthesis but decomposes well below LiH's temperature.

Final Answer: LiH (highest thermal stability) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#26

Q27.

Solution

Concept — Diamond Cubic Packing Efficiency:
The diamond cubic structure has 8 carbon atoms per unit cell in a face-centred cubic lattice with 4 additional atoms occupying alternating tetrahedral voids.

Step 1 — Geometric calculation:
In diamond cubic, atoms touch along the body diagonal of the sub-cube of side $a/2$: contact distance $= 2r = \dfrac{a\sqrt{3}}{4}$, so $r = \dfrac{a\sqrt{3}}{8}$.

Volume of 8 atoms $= 8 \times \dfrac{4\pi}{3} r^3 = 8 \times \dfrac{4\pi}{3} \left(\dfrac{a\sqrt{3}}{8}\right)^3 = \dfrac{\pi a^3 \sqrt{3}}{16}$.

Packing efficiency $= \dfrac{\pi\sqrt{3}}{16} \approx \dfrac{3.1416 \times 1.732}{16} \approx 0.340 = 34\%$.

Why other options are wrong:
Option B (52%): This is the packing efficiency of a simple cubic lattice (1 atom/cell).
Option C (68%): This is the body-centred cubic (BCC) packing efficiency.

Option D (74%): This is the face-centred cubic (FCC) / hexagonal close-packed (HCP) packing efficiency; the maximum possible for equal spheres.

Final Answer: Packing efficiency $\approx 34\% \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#27

Q28.

Solution

Concept — Lanthanide Contraction; 4f Orbital Shielding:
Across the lanthanide series (La to Lu), the nuclear charge Z increases by 1 at each element, but the corresponding electron is added to the *4f* subshell. 4f orbitals are diffuse, poorly directed, and experience strong electron–electron repulsion that limits their shielding effectiveness.

Step 1 — Shielding factor of 4f electrons:
The shielding constant for an added 4f electron by the existing 4f electrons $\sigma_{4f \leftarrow 4f} \approx 0.35$ (Slater), whereas for inner shells $\sigma \approx 0.85$–1.00. Because $\sigma < 1$, each added f-electron fails to fully shield the nucleus, so Z_{eff} *increases* across the series. The increased Z_{eff} contracts the 5s, 5p, 6s shells, reducing the ionic radius.

Why other options are wrong:
Option A (nuclear charge only): Increasing Z is the *proximate* cause in all periods; the *key* is that 4f electrons are unusually poor shields, making the contraction anomalously large.
Option C (e^-–e^- repulsion): Repulsion would tend to expand the orbitals; it is not the primary cause of contraction.
Option D (decreasing electron number): The number of electrons increases across the series, not decreases.

Final Answer: Ineffective 4f shielding $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#28

Q29.

Solution

Concept — Fluorimetry; Stokes Shift:
After absorption of a photon, a fluorescent molecule rapidly relaxes vibrationally to the lowest vibrational level of S_1 (Kasha's rule) before emitting. This internal vibrational relaxation means the emitted photon has *less energy* (longer wavelength) than the absorbed photon.

Step 1 — Definition:
The **Stokes shift** $= \lambda_{\text{em}} - \lambda_{\text{ex}}$ (always positive; emission is at longer λ). A large Stokes shift is analytically beneficial because excitation and emission can be sepa-

rated without overlap.

Step 2 — Physical origin:
Energy is lost via: (i) vibrational relaxation in S_1; (ii) solvent reorganisation (if the excited state has a different dipole moment).

Why other options are wrong:
Option A (intensity/absorbance ratio): This ratio is related to quantum yield, not Stokes shift.
Option B (quantum yield Φ_F): Quantum yield = photons emitted / photons absorbed; a dimensionless ratio unrelated to wavelength shift.
Option D (FWHM): The bandwidth describes the width of the emission band; the Stokes shift is the *position* difference between absorption and emission maxima.

Final Answer: Stokes shift $= \lambda_{\text{em}} - \lambda_{\text{ex}} \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#29

Q30.

Solution

Concept — Atomic Absorption Spectroscopy; Hollow Cathode Lamp:
Free analyte atoms in the flame or graphite furnace have very narrow absorption profiles (Doppler-broadened linewidths ≈ 0.001 nm). A broadband source would spread light over many wavelengths, most of which are not absorbed; sensitivity would be negligible.

Step 1 — Role of the HCL:
The HCL contains the same element as the analyte as the cathode material. Sputtered atoms are excited by the discharge and emit the element's characteristic spectral lines at exactly the same wavelengths as the analyte absorbs. This specificity ensures that only the analyte absorbs the incident radiation $\Rightarrow$ high selectivity and sensitivity.

Why other options are wrong:
Option A (continuous spectrum): A continuous source (tungsten lamp, deuterium lamp) is used in UV-Vis spectrophotometry, not in conventional AAS; it would give inadequate sensitivity because only a tiny fraction of the light overlaps with the analyte's narrow absorption.
Option B (broad UV radiation): Broadband UV radiation disperses signal over many wavelengths; the fraction absorbed by narrow atomic lines is too small to measure accurately.
Option C (plasma atomisation): The HCL is a *radiation source*, not an atomiser; atomisation is achieved by the flame or electrothermal furnace.

Final Answer: Element-specific sharp spectral lines from the HCL match the ana-

lyte absorption exactly ⇒ **(D)**

Answer: (D) ← Go Back to Q#30

Q31.

Solution

Concept — HPLC Retention Factor (Capacity Factor):
The retention factor $k' = (t_R - t_0)/t_0$ expresses how much longer a solute is retained on the column relative to an unretained species.

Step 1 — Substitute values:
$t_R = 12.0$ min, $t_0 = 2.0$ min:

$$k' = \frac{12.0 - 2.0}{2.0} = \frac{10.0}{2.0} = 5.0.$$

Why other options are wrong:
Option B (6.0): This would result from $k' = t_R/t_0 = 12/2 = 6$, which incorrectly omits the subtraction of t_0 in the numerator.
Option C (0.17): This inverts the formula: $t_0/t_R = 2/12 \approx 0.17$; dimensionally and operationally incorrect.
Option D (12.0): This is simply t_R expressed numerically; it confuses the retention time with the retention factor.

Final Answer: $k' = 5.0 \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#31

Q32.

Solution

Concept — Rotating Disk Electrode; Levich Equation:
The Levich equation for the diffusion-limited current at a rotating disk electrode is $i_L = 0.620\, nFAD^{2/3}\nu^{-1/6}C\omega^{1/2}$, where ω is the angular rotation rate.

Step 1 — Apply the proportionality:
$i_L \propto \omega^{1/2}$. If ω increases by factor 4:

$$\frac{i_{L,\text{new}}}{i_{L,\text{old}}} = \left(\frac{4\omega}{\omega}\right)^{1/2} = 4^{1/2} = 2.$$

The limiting current doubles.

Step 2 — Physical interpretation:
Faster rotation thins the diffusion layer (Nernst layer thickness $\delta \propto \omega^{-1/2}$), so more analyte reaches the electrode per unit time.

Why other options are wrong:
Option A (4): Would apply if $i_L \propto \omega$ (linear dependence), which is not the case.
Option C (8): No physical basis; $4^{3/2} = 8$ but the exponent is 1/2, not 3/2.
Option D (16): Would require $i_L \propto \omega^2$; incorrect Levich scaling.

Final Answer: i_L increases by factor 2 $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#32

Q33.

Solution

Concept — Butler-Volmer → Tafel Limit; Large Anodic Overpotential:
The Butler-Volmer equation is: $i = i_0\left[\exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right)\right]$.

Step 1 — Large positive η:
At large anodic overpotential, $\eta \gg 0$, so the cathodic exponential $\exp[-(1-\alpha)F\eta/RT] \to 0$. The equation simplifies to:

$$i \approx i_0 \exp\left(\frac{\alpha F\eta}{RT}\right)$$

Taking the logarithm: $\log i = \log i_0 + \frac{\alpha F}{2.303RT}\eta$, which is the Tafel equation with $b = RT/(2.303\alpha F)$.

Why other options are wrong:
Option A (diffusion overpotential): Diffusion limitation causes a concentration overpotential and a levelling of i, not a Tafel linear region; they are separate phenomena.
Option B (double-layer capacitance): Capacitive charging is a transient effect; it does not generate the steady-state Tafel linearity.
Option D (zero charge-transfer resistance): If $R_{ct} = 0$, the system is in the mass-transport limit, not the activation-control (Tafel) limit.

Final Answer: Cathodic term in Butler-Volmer becomes negligible $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#33

Q34.

Solution

Concept — Van der Waals Critical Constants:
The van der Waals equation is $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$. At the critical point, $(\partial P/\partial V_m)_T = 0$ and $(\partial^2 P/\partial V_m^2)_T = 0$ simultaneously.

Step 1 — Derive from conditions at critical point:

Setting both derivatives to zero and solving the system of equations gives:

$$V_c = 3b, \qquad P_c = \frac{a}{27b^2}, \qquad T_c = \frac{8a}{27Rb}.$$

These are the exact van der Waals critical constants.

Step 2 — Verify dimensionally:
Check: $P_cV_c/(RT_c) = \frac{a}{27b^2}\cdot 3b \Big/ \left(R\cdot\frac{8a}{27Rb}\right) = \frac{3a}{27b}\cdot\frac{27Rb}{8aR} = \frac{3}{8}$ (the van der Waals critical compressibility factor $Z_c = 3/8$). ✓

Why other options are wrong:
Option A: $T_c = a/(27Rb)$ misses the factor of 8 in the numerator.
Option B: $V_c = b$ (not $3b$); incorrect by a factor of 3.
Option C: $P_c = a/(3b^2)$ misses the factor of 9 in the denominator ($27 = 3 \times 9$; the correct denominator is $27b^2$).

Final Answer: $T_c = 8a/(27Rb)$, $P_c = a/(27b^2)$, $V_c = 3b \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#34

Q35.

Solution

Concept — Osmometry; Molar Mass from Osmotic Pressure:
The van't Hoff osmotic pressure equation $\pi = \frac{n}{V}RT = \frac{w}{MV}RT$ relates osmotic pressure to concentration. Rearranging: $M = \frac{wRT}{\pi V}$.

Step 1 — Substitute values:
$w = 1.00$ g, $R = 0.08206$ L atm mol^{-1} K^{-1}, $T = 300$ K, $\pi = 0.240$ atm, $V = 100$ mL $= 0.100$ L:

$$M = \frac{1.00 \times 0.08206 \times 300}{0.240 \times 0.100} = \frac{24.618}{0.0240} \approx 1026 \text{ g mol}^{-1} \approx 1000 \text{ g mol}^{-1}.$$

Why other options are wrong:
Option B (500 g/mol): Would require $\pi \approx 0.49$ atm, about twice the measured value; M has been halved incorrectly.
Option C (2000 g/mol): Would require $\pi \approx 0.12$ atm, half the measured value; M has been doubled incorrectly.
Option D (250 g/mol): About 4-fold too small; would imply an unreasonably high osmotic pressure for such small dissolved amounts.

Final Answer: $M \approx 1000$ g mol$^{-1} \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#35

Q36.

Solution

Concept — Einstein Model; High-Temperature Limit (Dulong-Petit):
In the Einstein model, each of the N atoms in a solid is treated as an independent quantum harmonic oscillator with the same frequency ν_E. The molar heat capacity is:

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}, \quad \theta_E = h\nu_E/k_B.$$

Step 1 — Take the high-T limit:
For $T \gg \theta_E$, define $x = \theta_E/T \ll 1$. Then $e^x \approx 1 + x$, so $(e^x - 1) \approx x$:

$$C_V \approx 3Rx^2\frac{1+x}{x^2} \approx 3R(1+x) \approx 3R.$$

This is the classical Dulong-Petit limit.

Why other options are wrong:
Option A (0): $C_V \to 0$ is the *low*-temperature limit ($T \ll \theta_E$), where $e^x \to \infty$ and the occupation number is negligible.
Option C ($3R/2$): This is the translational/rotational heat capacity of an ideal gas; it underestimates the solid's heat capacity, which has both kinetic and potential contributions ($3R$, not $3R/2$).
Option D ($R\ln 3$): This quantity ($\approx 9.1\ \mathrm{J\,mol^{-1}\,K^{-1}}$) has no relevance to the high-T heat capacity limit.

Final Answer: $C_V \to 3R$ (Dulong-Petit limit) $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#36

Q37.

Solution

Concept — Protein Unfolding Thermodynamics; $\Delta C_p > 0$:
The change in heat capacity upon protein unfolding is consistently *positive* and large (typically 1–10 $\mathrm{kJ\,mol^{-1}\,K^{-1}}$ for globular proteins).

Step 1 — Physical origin:
Folded proteins bury hydrophobic residues in the core. Upon unfolding, these non-polar groups are exposed to water. Water molecules form structured "icelike" cages (hydrophobic hydration) around exposed non-polar surfaces. These ordered water structures have a high heat capacity because hydrogen-bond network disruption requires energy with a large temperature coefficient $\Rightarrow C_p(\text{unfolded}) > C_p(\text{folded})$.

Step 2 — Consequence:
Because $\Delta C_p > 0$, ΔH and ΔS of unfolding both increase with temperature, leading to the phenomenon of *cold denaturation* at low T.

Why other options are wrong:

Option A (negative): $\Delta C_p < 0$ is observed for folding, not unfolding; (the sign depends on the direction of the process). The question asks for $C_{p,\text{unfolded}} - C_{p,\text{folded}}$, which is positive.
Option B (zero): Zero would imply no exposure of hydrophobic residues upon unfolding and no differential solvation; inconsistent with decades of calorimetric data.
Option D: While larger proteins expose more surface and tend to have larger $|\Delta C_p|$, the *sign* (positive) is a universal feature, not merely a function of MW.

Final Answer: $\Delta C_p > 0$ (positive) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#37

Q38.

Solution

Concept — Enzyme Inhibition; Lineweaver-Burk Analysis of Competitive Inhibition:
The Michaelis-Menten equation with a competitive inhibitor is: $v = V_{\max}[\text{S}]/(K_m^{\text{app}} + [\text{S}])$ where $K_m^{\text{app}} = K_m(1 + [\text{I}]/K_i) > K_m$; $V_{\max}$ is unchanged.

Step 1 — Lineweaver-Burk form:
Taking reciprocals:

$$\frac{1}{v} = \underbrace{\frac{K_m^{\text{app}}}{V_{\max}}}_{\text{slope}} \cdot \frac{1}{[\text{S}]} + \underbrace{\frac{1}{V_{\max}}}_{y\text{-intercept}} .$$

The y-intercept $(1/V_{\max})$ is *the same* with and without inhibitor. The slope $(K_m^{\text{app}}/V_{\max})$ *increases* with inhibitor.

Step 2 — Identify the graph feature:
Different slopes but the same y-intercept $\Rightarrow$ lines fan out from a **common point on the y-axis**.

Why other options are wrong:
Option A (x-axis intersection): Lines meeting on the x-axis (same x-intercept $= -1/K_m^{\text{app}}$) is NOT observed; $-1/K_m^{\text{app}}$ changes with $[\text{I}]$.
Option B (parallel lines): Parallel lines (same slope, different intercepts) is the signature of *uncompetitive* inhibition, not competitive.
Option C (second quadrant intersection): Intersection in the second quadrant is the signature of *non-competitive* inhibition.

Final Answer: Lines intersect on the y-axis (common $1/V_{\max}$ intercept) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#38

Q39.

Solution

Concept — FT-NMR; Time-Domain to Frequency-Domain Conversion:
In FT-NMR, all NMR-active nuclei are excited simultaneously by a short radiofrequency pulse. The detected signal (the FID) is a superposition of all precessing magnetisation components – a complex, oscillating time-domain signal. To recover the familiar frequency-domain NMR spectrum, a mathematical transform is required.

Step 1 — Identify the transform:
The **Fourier transform** (FT) decomposes a time-domain function $f(t)$ into its frequency components: $F(\nu) = \int_{-\infty}^{\infty} f(t)\, e^{-2\pi i \nu t}\, dt$. Applying FT to the FID yields the NMR spectrum with peaks at the Larmor precession frequencies of each chemically distinct nucleus.

Why other options are wrong:
Option B (Laplace transform): The Laplace transform is used for linear systems analysis and solving differential equations (e.g. in control theory and electrochemical impedance); it is not used for NMR data processing.
Option C (wavelet transform): Wavelets analyse multi-resolution time-frequency properties; used in signal denoising applications but not the primary transform for NMR spectral conversion.
Option D (Z-transform): The Z-transform is the discrete-time analogue of the Laplace transform, used in digital signal processing filter design; not used for NMR spectral acquisition.

Final Answer: Fourier transform converts FID to NMR spectrum $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#39

Q40.

Solution

Concept — Young-Laplace Equation; Soap Bubble (Two Interfaces):
The Young-Laplace equation $\Delta P = 2\gamma/r$ applies to a *single* spherical liquid–gas interface. A soap bubble is a thin liquid film bounded by *two* concentric spherical interfaces (inner and outer surfaces of the film).

Step 1 — Apply to both interfaces:
Each interface contributes $2\gamma/r$ (assuming film thickness $\ll r$, so both interfaces have essentially the same radius r):

$$\Delta P_{\text{total}} = \frac{2\gamma}{r} + \frac{2\gamma}{r} = \frac{4\gamma}{r}.$$

Step 2 — Substitute numerical values:

$\gamma = 0.025\ \text{N m}^{-1}$, $r = 1.0\ \text{cm} = 0.010\ \text{m}$:

$$\Delta P = \frac{4 \times 0.025}{0.010} = \frac{0.10}{0.010} = 10\ \text{Pa}.$$

Why other options are wrong:
Option A (5 Pa): This applies $\Delta P = 2\gamma/r$ (single interface only); it ignores the outer surface of the soap film.
Option C (2.5 Pa): Would require either $r = 4\ \text{cm}$ (wrong) or $\gamma = 0.00625\ \text{N m}^{-1}$ (wrong); numerically inconsistent.
Option D (20 Pa): This overestimates by a factor of 2; it would correspond to 4 interfaces, or to using $r = 0.005\ \text{m}$ instead of $0.010\ \text{m}$.

Final Answer: $\Delta P = 4\gamma/r = 10\ \text{Pa} \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#40

Answer Key

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