TIFR GS Chemistry

Sample Paper – 8

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 Gibbs-Duhem equation at constant temperature T and pressure P for a binary mixture is:

(A) $n_1\,\mathrm{d}\mu_1 + n_2\,\mathrm{d}\mu_2 = 0$

(B) $\mathrm{d}G = \mu_1\,\mathrm{d}n_1 + \mu_2\,\mathrm{d}n_2$

(C) $\mu_i = (\partial G/\partial n_i)_{T,P,n_j}$

(D) $G = n_1\mu_1 + n_2\mu_2$

Q2. Using the Born-Haber cycle for NaCl, the lattice energy U is calculated from the following data (all in $\mathrm{kJ\,mol^{-1}}$):
$\Delta H_f^\circ(\mathrm{NaCl}) = -411$, $\Delta H_{\mathrm{sub}}(\mathrm{Na}) = +108$, $IE_1(\mathrm{Na}) = +496$, $\frac{1}{2}D(\mathrm{Cl_2}) = +122$, $EA(\mathrm{Cl}) = -349$.
The lattice energy U ($\mathrm{kJ\,mol^{-1}}$) is:

(A) $-411\ \mathrm{kJ\,mol^{-1}}$

(B) $-449\ \text{kJ mol}^{-1}$

(C) $-788\ \text{kJ mol}^{-1}$

(D) $-377\ \text{kJ mol}^{-1}$

Q3. In an S_N1 reaction, the overall rate is independent of the nucleophile concentration. This is because:

(A) The nucleophile attacks the planar carbocation very rapidly after its formation.

(B) The carbocation intermediate is too reactive to differentiate between nucleophiles.

(C) The solvent assists ionisation but does not appear in the rate expression.

(D) The rate-determining step is the unimolecular ionisation of R–X, which does not involve the nucleophile.

Q4. An Arrhenius plot of $\ln k$ versus $1/T$ gives a slope of $-8000\ \text{K}$. The activation energy E_a in kJ mol^{-1} is ($R = 8.314\ \text{J mol}^{-1}\,\text{K}^{-1}$):

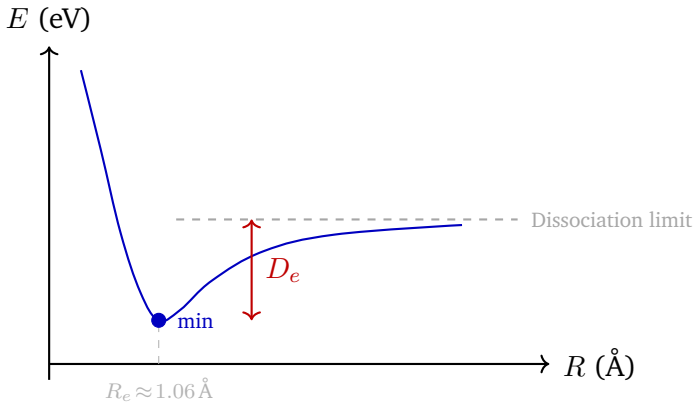
(A) $8.00\ \text{kJ mol}^{-1}$

(B) $66.5\ \text{kJ mol}^{-1}$

(C) $800\ \text{kJ mol}^{-1}$

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

Q5. The Born-Oppenheimer (BO) approximation separates electronic and nuclear motion in molecular quantum mechanics. The diagram below shows the resulting potential energy surface for H_2^+. The BO approximation is valid because:



(A) Electrons are $\approx 1836\times$ lighter than nuclei and move much faster, so they adjust instantaneously to each nuclear configuration (adiabatic separation).

(B) Nuclear and electronic wavefunctions have the same spatial extent.

(C) Electron-nucleus interactions are negligible compared with electron-electron repulsion.

(D) The electronic Hamiltonian commutes with the nuclear kinetic energy operator.

Q6. Which statement *correctly* describes the variational principle in quantum mechanics?

(A) Any trial wavefunction yields the exact ground-state energy E_0.

(B) The variational energy is always *lower* than the true ground-state energy.

(C) For any normalised trial wavefunction $|\psi_{\text{trial}}\rangle$, $\langle\psi_{\text{trial}}|\hat{H}|\psi_{\text{trial}}\rangle \geq E_0$.

(D) The variational principle applies only to excited states, not to the ground state.

Q7. In 1,1-difluoroethylene ($CH_2{=}CF_2$), the two ^{19}F nuclei are chemically equivalent (same chemical shift) yet magnetically *non-equivalent*. This is because:

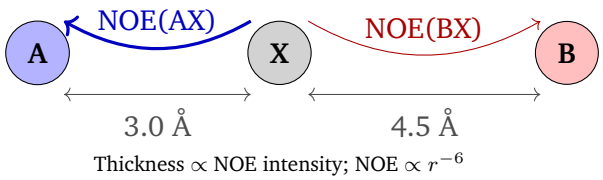
(A) The two ^{19}F nuclei reside in different chemical environments.

(B) Rapid bond rotation breaks the molecular symmetry.

(C) ^{19}F has spin $I = 1/2$, unlike ^{1}H.

(D) Each ^{19}F has a *different* set of coupling constants to the two ^{1}H nuclei (one geminal, one vicinal), so they are not interchangeable by symmetry.

Q8. In a ^{1}H NOESY experiment the NOE enhancement falls off as r^{-6}, where r is the internuclear distance. Proton A is 3.0 Å from proton X; proton B is 4.5 Å from proton X (see schematic below). The ratio $\mathrm{NOE(AX)/NOE(BX)}$ is:



(A) 1.5

(B) 11.4

(C) 2.25

(D) 34.2

Q9. The g-factor of a free electron is $g_e \approx 2.0023$. For a Cu^{2+} ion (d^9 configuration) in a tetragonally distorted octahedral complex, the EPR g-factor is expected to be:

(A) $g > 2.0023$

(B) $g = 2.0023$ exactly

(C) $g < 2.0023$

(D) $g = 0$

Q10. The intense purple colour of permanganate ($\mathrm{MnO_4^-}$) in aqueous solution arises from:

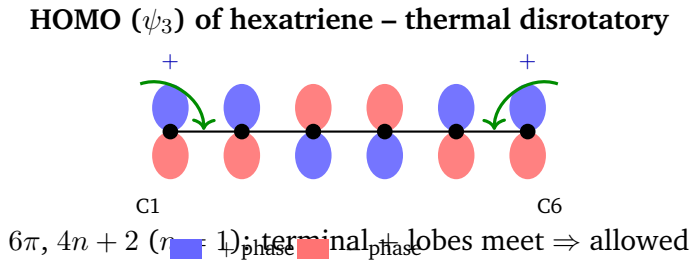
(A) A d–d transition of Mn(VII) (formally d^0).

(B) Metal-to-ligand charge transfer (MLCT) from Mn to the oxo ligands.

(C) Ligand-to-metal charge transfer (LMCT) from filled oxo orbitals to empty Mn d orbitals – a strongly allowed transition.

(D) A $\pi \to \pi^*$ transition of the peroxo ligand.

Q11. According to the Woodward-Hoffmann rules, thermal electrocyclization of $(2E, 4Z, 6E)$-octa-2,4,6-triene (a 6π-electron system) proceeds via which stereochemical mode? (The HOMO symmetry is shown schematically below.)



(A) Conrotatory – thermal, as for a 4π (4-electron) system.

(B) Disrotatory – but only under *photochemical* conditions.

(C) Conrotatory – 6π, photochemical.

(D) Disrotatory – 6π, thermal ($4n+2$ electrons, $n=1$; thermal ⇒ disrotatory by Woodward-Hoffmann).

Q12. The Nazarov cyclization of a divinyl ketone promoted by a Lewis acid gives, as the primary organic product:

(A) Cyclohexenone (six-membered ring ketone).

(B) Cyclopentenone (five-membered ring enone).

(C) Cyclopentadienone (aromatic five-membered dienone).

(D) 1,3-Pentadienyl ketone (ring-opened product).

Q13. In the initiation of Grubbs first-generation catalyst ($[RuCl_2(=CHPh)(PCy_3)_2]$) for olefin metathesis, the catalytically active 14-electron ruthenium carbene species is generated by:

(A) Dissociation of one PCy_3 ligand from the 16-electron precatalyst to give a 14-electron Ru carbene $[RuCl_2(=CHPh)(PCy_3)]$.

(B) Oxidation of Ru(II) to Ru(IV) by the alkene substrate.

(C) Protonation of the benzylidene (=CHPh) ligand by the solvent.

(D) Coordination of the alkene substrate to Ru without prior phosphine dissociation.

Q14. The Swern oxidation converts primary alcohols to aldehydes without over-oxidation to carboxylic acids. The key reason is:

(A) DMSO is thermodynamically a mild enough oxidant to halt at the aldehyde stage.

(B) Oxalyl chloride selectively activates primary alcohols over secondary alcohols.

(C) The reaction is performed at $-78\,^{\circ}\mathrm{C}$; the mechanism generates a chlorosulfonium intermediate that collapses (via Et_3N-mediated elimination of a sulfur ylide) cleanly to give the aldehyde before further oxidation can occur.

(D) Et_3N base deprotonates the aldehyde product to form a stable, unreactive enolate.

Q15. In the Baylis-Hillman reaction between methyl acrylate ($CH_2{=}CHCO_2Me$) and benzaldehyde (PhCHO), catalysed by DABCO, the product is:

(A) Methyl 3-phenylpropanoate (simple 1,4-addition product).

(B) Cinnamaldehyde (aldol/dehydration product).

(C) Methyl cinnamate (E-configured α,β-unsaturated ester).

(D) Methyl 2-(hydroxy(phenyl)methyl)acrylate: $PhCH(OH){-}C(=CH_2)CO_2Me$ (Baylis-Hillman adduct).

Q16. The Stetter reaction employs an N-heterocyclic carbene (NHC) catalyst to generate an *acyl anion equivalent* (umpolung) from an aldehyde. When this species reacts with a Michael acceptor (e.g. an enone), the product is:

(A) A β-hydroxy aldehyde (aldol adduct).

(B) A 1,4-diketone (1,4-dicarbonyl compound, formed by 1,4-addition of the acyl anion to the enone followed by catalyst release).

(C) A cyclopentanol (via intramolecular lactonisation).

(D) An α,β-unsaturated ketone (dehydration product).

Q17. In Evans asymmetric alkylation using a (4R)-benzyl oxazolidinone propionyl imide, the titanium enolate is treated with allyl iodide. Alkylation occurs predominantly on which face of the enolate?

(A) *Re* face – titanium chelates the oxazolidinone and carbonyl oxygens, fixing the conformation so the electrophile attacks from the face *opposite* to the C4-benzyl group.

(B) *Si* face.

(C) Both faces equally (no diastereoselectivity is observed).

(D) The facial selectivity depends only on the alkyl halide, not on the auxiliary.

Q18. The Hajos-Parrish ketone (3,4,8,8a-tetrahydronaphthalene-1,6(2H,7H)-dione derivative), a key intermediate in steroid synthesis, has a carbon skeleton containing:

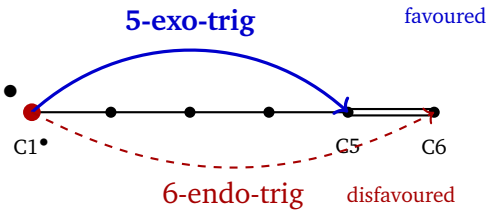
(A) One five-membered ring fused to one six-membered ring.

(B) Three fused six-membered rings (steroid ABC framework).

(C) Two fused six-membered rings (bicyclo[4.4.0]decane/decalin framework).

(D) One six-membered ring fused to one four-membered ring.

Q19. The thermally initiated radical cyclization of the hex-5-en-1-yl radical preferentially follows which pathway? (Schematic shown below.)



5-exo-trig (Baldwin's rules) → cyclopentylmethyl radical

(A) 6-endo-trig

(B) 5-endo-trig

(C) 6-exo-trig

(D) 5-exo-trig

Q20. Treatment of a para-substituted phenol with phenyliodine diacetate [PhI(OAc)$_2$] in MeOH gives, by oxidative dearomatization:

(A) A phenyl ether by simple O-methylation.

(B) A 4-methoxy-4-(para-substituent)cyclohexa-2,5-dien-1-one (MeOH acts as nucleophile attacking the ipso carbon; PhI is the leaving group).

(C) An ortho-iodophenol (electrophilic ortho-iodination product).

(D) Reduction of the phenol to cyclohexanol.

Q21. According to Wade's rules, $[B_{12}H_{12}]^{2-}$ is a *closo* borane. Its cage geometry is:

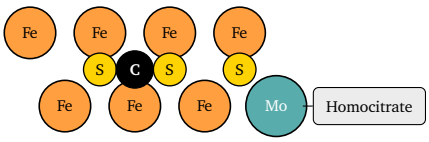
(A) Icosahedral ($n = 12$ vertices, $n + 1 = 13$ skeletal electron pairs, *closo*).

(B) Cuboctahedral.

(C) Octahedral.

(D) Truncated tetrahedron.

Q22. The FeMo cofactor (FeMoco) of nitrogenase contains an interstitial atom at its geometric centre (see schematic). High-resolution X-ray crystallography (2011) identified this atom as:



FeMoco (schematic): central C^{4-} carbide bridged by Fe/S

(A) Nitrogen (N).

(B) Oxygen (O).

(C) Carbon (carbide, C^{4-}).

(D) Sulfur (additional to the bridging S atoms).

Q23. In the Schrock molybdenum complex that catalyses biological-inspired dinitrogen (N_2) reduction, N_2 coordinates in which binding mode?

(A) Side-on (η^2) bridging between two metal centres.

(B) Side-on (η^2) at a single metal centre.

(C) Bridging end-on (μ-η^1:η^1) between two Mo centres.

(D) End-on (η^1) terminal coordination to a single Mo, activating the distal N for PCET (proton-coupled electron transfer).

Q24. Among the isoelectronic carbonyl series $[V(CO)_6]^-$, $[Cr(CO)_6]$, and $[Mn(CO)_6]^+$, which complex has the *lowest* CO stretching frequency ν_{CO}?

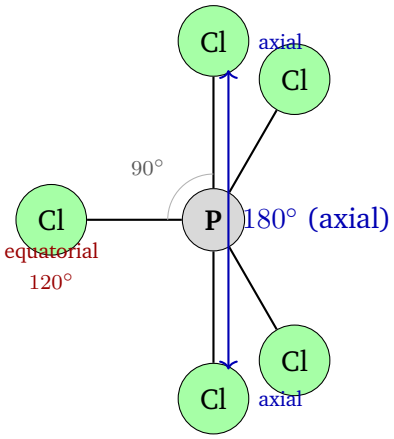
(A) $[Cr(CO)_6]$

(B) $[V(CO)_6]^-$

(C) $[Mn(CO)_6]^+$

(D) All three have identical ν_{CO} (isoelectronic $\Rightarrow$ identical backbonding).

Q25. The geometry of PCl_5 is trigonal bipyramidal (5 bonding pairs, 0 lone pairs). The axial–P–axial bond angle (see diagram) is:



(A) $180°$

(B) $120°$

(C) $90°$

(D) $109.5°$

Q26. Silicone polymers (polysiloxanes) have a backbone of alternating Si–O bonds. Compared with analogous all-carbon polymers, polysiloxanes exhibit:

(A) High flammability and poor thermal stability.

(B) Strongly hydrophilic character due to polar Si–O bonds.

(C) High thermal stability, hydrophobicity, low surface energy, and good electrical insulation (the strong Si–O bond and non-polar organic side groups account for these properties).

(D) Essentially the same physical properties as polyethylene.

Q27. The high-temperature superconductor $YBa_2Cu_3O_7$ (YBCO) has a critical temperature T_c of approximately:

(A) 4 K

(B) 20 K

(C) 40 K

(D) 93 K (above the boiling point of liquid nitrogen, 77 K)

Q28. Lanthanide ions show remarkably sharp, line-like emission spectra. The primary reason is:

(A) The $4f$ electrons are highly delocalised, forming narrow electronic bands.

(B) The $4f$ orbitals are effectively shielded by the outer $5s^2 5p^6$ electrons; crystal-field splitting of $4f$ levels is negligibly small, giving almost atom-like (sharp) transitions.

(C) Lanthanide ions have d–d transitions, which are always sharp by selection rules.

(D) The very high nuclear charge makes all spectroscopic transitions inherently narrow.

Q29. In capillary electrophoresis (CE) with an uncoated fused-silica capillary, the electroosmotic flow (EOF) is directed toward the cathode. This occurs because:

(A) Silanol groups on the capillary wall ionise (Si-OH $\rightarrow$ SiO^-) at neutral/alkaline pH, attracting a cationic diffuse double layer; under the applied field this layer migrates toward the cathode, dragging the bulk solvent with it.

(B) Anions migrate electrophoretically faster than cations in fused silica.

(C) The EOF is directed toward the anode at all pH values in silica capillaries.

(D) Neutral molecules are attracted to the negatively charged capillary wall and are swept toward the cathode.

Q30. In reversed-phase HPLC, gradient elution (mobile phase organic solvent content increasing over the run) compared with isocratic elution:

(A) Increases the column dead volume and reduces resolution.

(B) Keeps the mobile-phase composition constant throughout the run.

(C) Shortens total analysis time and improves peak shape for late-eluting analytes that have a wide range of retention factors k'.

(D) Is applicable only to normal-phase separations with non-polar mobile phases.

Q31. The Van Deemter equation is $H = A + B/u + Cu$, where u is the linear velocity. Given $A = 0.10\ \text{mm}$, $B = 2.0\ \text{mm}^2\,\text{s}^{-1}$, $C = 0.005\ \text{mm}\,\text{s}$, the minimum plate height $H_{\min}$ (in mm) is:

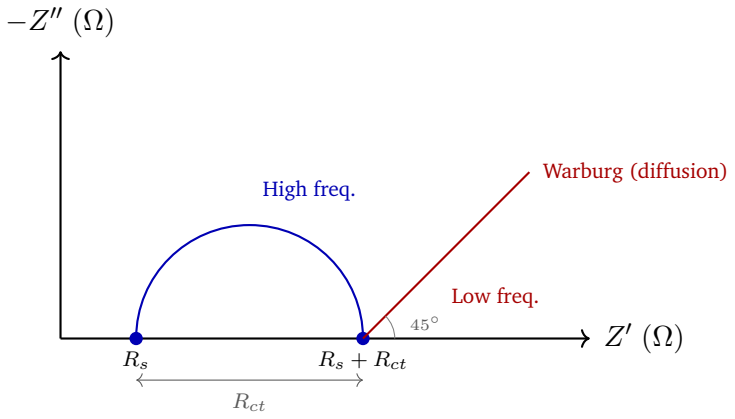
(A) 0.10 mm

(B) 0.20 mm

(C) 0.40 mm

(D) 0.30 mm

Q32. An electrochemical impedance Nyquist plot ($-Z''$ vs. Z') shows a semicircle at high frequencies followed by a 45° straight line at low frequencies (schematic below). This behaviour indicates:



(A) Pure resistive behaviour (vertical line) at all frequencies.

(B) Charge-transfer resistance R_{ct} in parallel with double-layer capacitance C_{dl} at high frequency, followed by semi-infinite linear (Warburg) diffusion control at low frequency.

(C) Pure capacitive behaviour (vertical line in the Nyquist plot) at all frequencies.

(D) Mass-transport (diffusion) control at all frequencies with no charge-transfer contribution.

Q33. For a fully reversible one-electron electrochemical process at $25\,^{\circ}\mathrm{C}$ in cyclic voltammetry (CV), the peak-to-peak separation $\Delta E_p = E_{p,a} - E_{p,c}$ and the anodic-to-cathodic peak current ratio $i_{p,a}/i_{p,c}$ are:

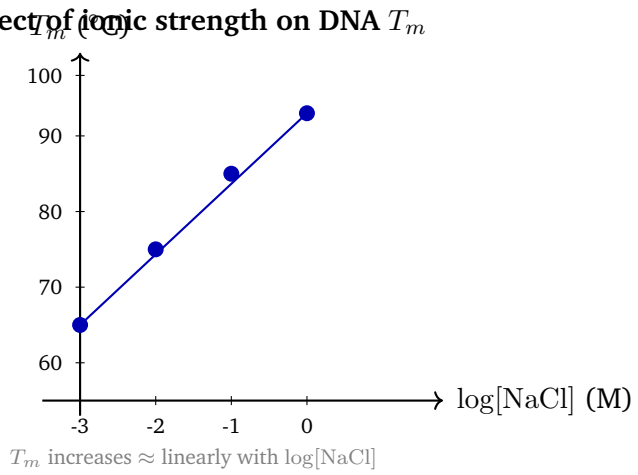
(A) $\Delta E_p \approx 59\ \mathrm{mV},\ \ i_{p,a}/i_{p,c} = 1.00$

(B) $\Delta E_p \approx 0\ \mathrm{mV},\ \ i_{p,a}/i_{p,c} = 1.00$

(C) $\Delta E_p > 200\ \mathrm{mV},\ \ i_{p,a}/i_{p,c} < 1$

(D) $\Delta E_p \approx 59\ \mathrm{mV},\ \ i_{p,a}/i_{p,c} > 2$

Q34. As the NaCl concentration increases from 0.01 M to 1.0 M, the melting temperature T_m of a double-stranded DNA (dsDNA) duplex (see graph):



(A) Decreases monotonically (higher salt destabilises the helix).

(B) Is unaffected – T_m is independent of ionic strength.

(C) Increases – higher ionic strength screens the inter-strand phosphate-phosphate electrostatic repulsion, stabilising the duplex and raising T_m.

(D) First increases then decreases (passes through a maximum near 0.1 M NaCl).

Q35. The radius of gyration R_g of a Gaussian (ideal random-coil) polymer chain with N Kuhn segments each of length b is:

(A) $R_g = Nb$ (fully extended chain contour length)

(B) $R_g = b\sqrt{N}$ (RMS end-to-end distance of the ideal chain)

(C) $R_g = b$ (single-segment length)

(D) $R_g = b\sqrt{N/6}$ (from $R_g^2 = Nb^2/6$ for an ideal Gaussian chain)

Q36. In the grand canonical ensemble a system can exchange both energy and particles with a reservoir at temperature T and chemical potential μ. The grand partition function Ξ is:

(A) $\Xi = \sum_E \exp(-\beta E)$ (canonical partition function)

(B) $\Xi = \sum_N \sum_E \exp[-\beta(E - \mu N)]$

(C) $\Xi = \exp(-\beta G)$ where G is the Helmholtz free energy

(D) $\Xi = \sum_N \exp(-\beta \mu N)$ (particle sector only)

Q37. The Hill equation for ligand binding is $\theta = [L]^n/(K_d^n + [L]^n)$. For haemoglobin, the Hill coefficient $n \approx 2.8$ (not 4, the total number of subunits). This value indicates:

(A) Positive cooperativity ($n > 1$) with partial (not perfect) cooperativity ($n < 4$) – each O_2 bound facilitates binding of subsequent O_2 molecules.

(B) Negative cooperativity ($n < 1$ would be required).

(C) Non-cooperative Langmuir binding ($n = 1$ required).

(D) Anti-cooperative binding in which the first O_2 inhibits subsequent binding.

Q38. The persistence length L_p of double-stranded DNA (dsDNA) under physiological conditions is approximately:

(A) 0.34 nm (rise per base pair in B-DNA).

(B) 3.4 nm (length of one helical turn of B-DNA).

(C) ≈ 50 nm (persistence length; corresponds to ≈ 150 bp).

(D) ≈ 16 μm (contour length of λ-phage DNA).

Q39. In the LCAO-MO treatment of H_2^+, writing $\psi = c_1\phi_1 + c_2\phi_2$ and minimising the energy leads to the secular equation $|\mathbf{H} - E\mathbf{S}| = 0$. Solving the resulting 2×2 determinant gives:

(A) Only one solution exists (the ground-state bonding MO).

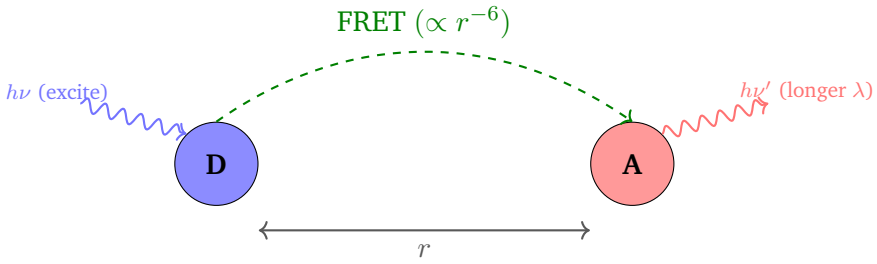
(B) The exact ground-state energy without any approximation.

(C) $E = \alpha$ identically for both bonding and antibonding MOs.

(D) Two solutions: bonding MO $E_+ = (\alpha + \beta)/(1 + S)$ and antibonding MO $E_- = (\alpha - \beta)/(1 - S)$, where α is the Coulomb integral, β the resonance integral, and S the overlap integral.

Q40. The FRET efficiency between a donor (D) and acceptor (A) separated by distance r is $E = R_0^6/(R_0^6 + r^6)$, where R_0 is the Forster radius ($E = 50\%$ at $r = R_0$). The schematic below shows the energy-transfer process. If

the donor-acceptor distance doubles from R_0 to $2R_0$, the FRET efficiency becomes approximately:



$$E = \frac{R_0^6}{R_0^6 + r^6}$$

(A) 25%

(B) $\approx 1.5\%$

(C) 12.5%

(D) 50%

Detailed Solutions

Q1.

Solution

Concept — Gibbs-Duhem Equation (Physical Chemistry):
At constant T and P the total differential of the Gibbs energy of a mixture is $\mathrm{d}G = \sum_i \mu_i \, \mathrm{d}n_i$. Because G is also extensive ($G = \sum_i n_i \mu_i$, the Euler relation), differentiating and subtracting gives the Gibbs-Duhem equation: $\sum_i n_i \, \mathrm{d}\mu_i = 0$, i.e. $n_1 \, \mathrm{d}\mu_1 + n_2 \, \mathrm{d}\mu_2 = 0$.

Why other options are wrong:
Option B: $\mathrm{d}G = \mu_1 \, \mathrm{d}n_1 + \mu_2 \, \mathrm{d}n_2$ is the fundamental equation of the Gibbs energy – *not* the Gibbs-Duhem equation.
Option C: $\mu_i = (\partial G/\partial n_i)_{T,P,n_j}$ is the *definition* of the chemical potential – a different thermodynamic relation.
Option D: $G = n_1\mu_1 + n_2\mu_2$ is Euler's theorem (the integrated form of G), also distinct from the Gibbs-Duhem equation.

Final Answer: $n_1 \, \mathrm{d}\mu_1 + n_2 \, \mathrm{d}\mu_2 = 0 \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#1

Q2.

Solution

Concept — Born-Haber Cycle for NaCl (Thermodynamics):
The Born-Haber cycle equates the formation enthalpy to the sum of all contributing steps:

$$\Delta H_f^\circ = \Delta H_{\text{sub}} + IE_1 + \tfrac{1}{2}D(\text{Cl}_2) + EA(\text{Cl}) + U.$$

Solving for U:

$$U = \Delta H_f^\circ - \Delta H_{\text{sub}} - IE_1 - \tfrac{1}{2}D - EA(\text{Cl}) = -411 - 108 - 496 - 122 - (-349).$$

$$U = -411 - 726 + 349 = -788 \text{ kJ mol}^{-1}.$$

Why other options are wrong:
Option A: -411 kJ mol^{-1} is simply ΔH_f°, not the lattice energy.
Option B: -449 kJ mol^{-1} omits the sign of EA or uses an incorrect formula.
Option D: -377 kJ mol^{-1} corresponds to the sum $\Delta H_{\text{sub}} + IE_1 + \frac{1}{2}D = 726$, subtracted from ΔH_f° without the electron affinity correction.

Final Answer: $U = -788$ kJ mol$^{-1} \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#2

Q3.

Solution

Concept — S_N1 Mechanism: Rate-Determining Unimolecular Ionisation:
The S_N1 mechanism proceeds in two steps: (1) slow, unimolecular ionisation $R-X \xrightarrow{k_1} R^+ + X^-$ (rate-determining step), followed by (2) fast capture of R^+ by the nucleophile. Because the nucleophile does not participate in the RDS, the rate $= k_1[RX]$ is first-order and independent of nucleophile concentration.

Why other options are wrong:
Option A: Although the carbocation is rapidly captured, this *does not explain* why the rate is independent of [Nu] – the relevant point is that capture is *not* the rate-determining step.
Option B: High reactivity of the carbocation is not the criterion for S_N1 kinetics; it explains the lack of stereospecificity, not the rate law.
Option C: Solvent assistance (solvolysis) merely means solvent acts as nucleophile; the rate law is still governed by the RDS, which is unimolecular.

Final Answer: RDS is unimolecular ionisation of R–X $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#3

Q4.

Solution

Concept — Arrhenius Activation Energy from Plot Slope:
The Arrhenius equation in linear form is $\ln k = \ln A - E_a/(RT)$. A plot of $\ln k$ vs. $1/T$ has slope $= -E_a/R$.

Calculation:

$$E_a = -\text{slope} \times R = 8000\ \text{K} \times 8.314\ \text{J mol}^{-1}\,\text{K}^{-1} = 66{,}512\ \text{J mol}^{-1} \approx 66.5\ \text{kJ mol}^{-1}.$$

Why other options are wrong:
Option A: $8.00\ \text{kJ mol}^{-1}$ would correspond to a slope of only ≈ -960 K; the factor of R has been omitted.
Option C: $800\ \text{kJ mol}^{-1}$ is 10× too large (off by a decimal error).
Option D: $96.5\ \text{kJ mol}^{-1}$ arises from using $R \approx 8.314$ with the wrong slope or using Faraday's constant in error.

Final Answer: $E_a \approx 66.5\ \text{kJ mol}^{-1} \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#4

Q5.

Solution

Concept — Born-Oppenheimer Approximation (Quantum Chemistry):
The validity of the BO approximation rests on the mass ratio $m_e/M_{\text{nuc}} \approx 1/1836$ (for a proton). Electrons are $\sim 1836\times$ lighter and consequently adjust $\sim 43\times$ faster to changes in nuclear geometry. Nuclei, being much heavier, move so slowly on the electronic timescale that the electrons effectively "see" nuclei at fixed positions. One can therefore solve the electronic Schrödinger equation at each fixed nuclear geometry R, generating the potential energy surface (PES) shown in the diagram – the PES only exists because of the BO separation.

Why other options are wrong:
Option B: Nuclear and electronic wavefunctions operate on very different spatial and timescales; the approximation exploits their *difference*, not similarity.
Option C: Electron-nucleus attraction is the dominant interaction in a molecule; it is not negligible.
Option D: The electronic Hamiltonian $\hat{H}_e$ does *not* commute with the nuclear kinetic energy $\hat{T}_N$ in general; the BO approximation *neglects* the off-diagonal (non-adiabatic) coupling terms between them.

Final Answer: Electrons $\approx 1836\times$ lighter $\Rightarrow$ adiabatic separation $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#5

Q6.

Solution

Concept — Variational Principle (Quantum Chemistry):
The variational theorem states: for any normalised trial wavefunction $|\psi_{\text{trial}}\rangle$,

$$E_{\text{var}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \geq E_0,$$

where E_0 is the exact ground-state energy. Equality holds *only* if $|\psi_{\text{trial}}\rangle$ is the exact ground-state wavefunction.

Why other options are wrong:
Option A: A trial wavefunction gives the exact energy *only* if it coincides with the exact eigenfunction – impossible in general for a parametrised trial function.
Option B: The variational energy is always $\geq E_0$, never lower; this option reverses the inequality.
Option D: The variational principle applies universally to the ground state (its primary use) and, with orthogonality constraints, to excited states too.

Final Answer: $\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle \geq E_0 \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#6

Q7.

Solution

Concept — Magnetic vs. Chemical Equivalence in NMR:
Two nuclei are *chemically* equivalent if they are related by a symmetry operation of the molecule (same chemical shift). They are *magnetically* equivalent only if, in addition, each has *identical* coupling constants to every other nucleus in the molecule.

In $CH_2{=}CF_2$, the two ^{19}F nuclei are chemically equivalent (related by a C_2 axis). However, F_1 couples to H_1 with a *geminal* constant ^2J and to H_2 with a *vicinal* constant ^3J; F_2 has the reverse. Since $^2J \neq {}^3J$, F_1 and F_2 have different coupling relationships to $H_1 \Rightarrow$ they are magnetically *non-equivalent* (AA'BB' spin system).

Why other options are wrong:
Option A: Both F atoms *are* chemically equivalent (same δ).
Option B: $CH_2{=}CF_2$ is a static planar molecule; bond rotation is irrelevant.
Option C: Spin $I = 1/2$ is a property of both ^1H and ^{19}F and does not explain non-equivalence.

Final Answer: Different coupling constants to each H $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#7

Q8.

Solution

Concept — NOE Intensity and r^{-6} Distance Dependence:
The NOE intensity is proportional to r^{-6}. For protons X and A (separation $r_{AX} = 3.0\,\text{Å}$) and X and B (separation $r_{BX} = 4.5\,\text{Å}$):

Calculation:

$$\frac{\text{NOE(AX)}}{\text{NOE(BX)}} = \left(\frac{r_{BX}}{r_{AX}}\right)^6 = \left(\frac{4.5}{3.0}\right)^6 = (1.5)^6 = \frac{729}{64} \approx 11.4.$$

The AX cross-peak is therefore about 11 times more intense than the BX cross-peak, as indicated by the thicker arrow in the schematic.

Why other options are wrong:
Option A: $1.5 = (4.5/3.0)^1$ – this uses r^{-1} instead of r^{-6}.
Option C: $2.25 = (1.5)^2$ – this uses r^{-2}.
Option D: $34.2 \approx (1.5)^7$ – an incorrect exponent.

Final Answer: $\text{NOE(AX)}/\text{NOE(BX)} \approx 11.4 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#8

Q9.

Solution

Concept — EPR g-Factor of Cu^{2+} (d^9):
Spin-orbit coupling mixes excited states into the ground state, shifting g from the free electron value $g_e = 2.0023$. For a more-than-half-filled d shell (d^9), the spin-orbit coupling constant $\lambda > 0$. The correction is $g \approx g_e + 2\lambda/\Delta_{\text{oct}}$, which gives $g > g_e$. Experimentally, tetragonally elongated Cu^{2+} complexes show $g_{\parallel} \approx 2.20$–$2.30$ and $g_{\perp} \approx 2.05$–2.10.

Why other options are wrong:
Option B: $g = g_e$ only for a free electron or an S-state (no orbital angular momentum to couple); Cu^{2+} has both orbital and spin angular momentum.
Option C: $g < g_e$ would apply to less-than-half-filled d shells ($\lambda < 0$), e.g. V^{3+} (d^2) or Ti^{3+} (d^1).
Option D: $g = 0$ is physically impossible for a $S = 1/2$ system.

Final Answer: $g > 2.0023$ for Cu^{2+} (d^9) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#9

Q10.

Solution

Concept — LMCT in Permanganate (UV-Vis Spectroscopy):
MnO_4^- contains Mn in the +7 oxidation state (d^0) – no d electrons are present. Therefore, d-d transitions are impossible. The intense absorption ($\lambda_{\text{max}} \approx 525$ nm, $\varepsilon \approx 2{,}200\ M^{-1}\,cm^{-1}$) arises from *ligand-to-metal charge transfer* (LMCT): electrons are promoted from filled oxygen $2p$ (π) bonding orbitals into empty Mn $3d$ (e and t_2) orbitals. LMCT bands are strongly allowed (no Laporte restriction) and highly intense.

Why other options are wrong:
Option A: Mn(VII) is d^0; no d-d transitions can exist.
Option B: MLCT requires electron-rich metal d electrons donated *to* ligand π^* orbitals (common in Ru/Fe polypyridyl); Mn(VII) d^0 cannot donate electrons.
Option D: Permanganate contains no peroxo ligand; the oxygen atoms are terminal oxo groups.

Final Answer: LMCT from oxo $2p$ to Mn $3d$ $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#10

Q11.

Solution

Concept — Woodward-Hoffmann Rules: Thermal Electrocyclization (6π):
For an electrocyclic reaction with $4n + 2$ electrons (here $n = 1$, 6 electrons), the

thermal reaction is **disrotatory** and the photochemical reaction is conrotatory. The HOMO of hexatriene is ψ_3 (symmetric, A symmetry under C_2). Disrotatory closure brings both terminal $+$ lobes (on the same face) together $\Rightarrow$ constructive orbital overlap $\Rightarrow$ thermally allowed. Conrotatory closure would bring $+$ and $-$ lobes together $\Rightarrow$ destructive $\Rightarrow$ thermally forbidden.

Why other options are wrong:
Option A: Thermal 4π (4-electron) systems are *conrotatory*, not 6π systems.
Option B: Disrotatory *photochemical* 6π is incorrect; thermal 6π is disrotatory, photochemical 6π is conrotatory.
Option C: Conrotatory under photochemical conditions applies to the $4n+2$ system under photochemical excitation; the question specifies thermal conditions.

Final Answer: 6π, thermal $\Rightarrow$ disrotatory $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#11

Q12.

Solution

Concept — Nazarov Cyclization (Organic Chemistry):
A Lewis acid (e.g. BF_3, $FeCl_3$) coordinates to the carbonyl oxygen of a divinyl ketone, generating a hydroxyl-pentadienyl cation (pentadienyl cation). This 4π electron system undergoes thermal *conrotatory* electrocyclization to give an allyl cyclopentyl cation. Proton loss then gives the cyclopentenone (five-membered ring enone). The 4π thermal conrotatory step is Woodward-Hoffmann allowed for 4-electron systems.

Why other options are wrong:
Option A: Cyclohexenone (6-membered ring) would require a 6-atom electrocyclization; the pentadienyl cation (5 atoms) can only close to a 5-membered ring.
Option C: Cyclopentadienone is an aromatic compound not accessible directly by Nazarov cyclization without additional oxidation/elimination steps.
Option D: Ring opening is the reverse of cyclization; Lewis acid promotes *closure*, not ring opening.

Final Answer: Nazarov $\rightarrow$ cyclopentenone $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#12

Q13.

Solution

Concept — Grubbs 1st-Gen Catalyst Activation (Organometallic Chemistry):
The Grubbs 1st-generation precatalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ is a 16-electron complex. The catalytic cycle is initiated by dissociation of one phosphine

ligand (PCy_3), generating the 14-electron, coordinatively unsaturated species $[RuCl_2(=CHPh)(PCy_3)]$. This square-planar/T-shaped intermediate binds the alkene substrate and enters the Chauvin metallacyclobutane metathesis cycle.

Electron count: Ru(II): 6 e; $2\times Cl^-$: 4 e; PCy_3: 2 e; $=$CHPh: 2 e; total = 14 e.

Why other options are wrong:
Option B: Ru remains Ru(II) throughout the Grubbs 1st-gen cycle; no change in oxidation state to Ru(IV) during initiation.
Option C: Protonation of the benzylidene would destroy the carbene ligand essential for metathesis activity.
Option D: Alkene cannot bind to a 16-electron complex without prior ligand dissociation (18-electron rule would be violated).

Final Answer: PCy_3 dissociation gives 14-electron Ru carbene $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#13

Q14.

Solution

Concept — Swern Oxidation Mechanism (Organic Chemistry):
The Swern oxidation proceeds: (1) DMSO + oxalyl chloride $\rightarrow$ chlorosulfonium ion (Me_2S^+Cl) at $-78\,^\circ$C; (2) Alcohol attacks S $\rightarrow$ alkoxysulfonium intermediate; (3) Et_3N abstracts the α-H, generating a *sulfur ylide*; (4) Intramolecular syn-elimination releases dimethyl sulfide (DMS) and the aldehyde. Operation at $-78\,^\circ$C prevents the Pummerer rearrangement and further oxidation to carboxylic acid; the aldehyde is released at the low temperature before it can be over-oxidised.

Why other options are wrong:
Option A: DMSO alone is a poor oxidant; activation by oxalyl chloride is essential, and selectivity is kinetic (temperature-controlled), not thermodynamic.
Option B: Oxalyl chloride does not discriminate between primary and secondary alcohols; both can be oxidised under Swern conditions.
Option D: Et_3N deprotonates the α-C of the alkoxysulfonium intermediate, not the aldehyde product; aldehydes are not acidic enough under these conditions.

Final Answer: $-78\,^\circ$C + sulfur-ylide elimination $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#14

Q15.

Solution

Concept — Baylis-Hillman Reaction (Organic Chemistry):
DABCO acts as a nucleophilic amine catalyst: it adds to the β-carbon of methyl acrylate generating a zwitterionic enolate, which undergoes aldol-type addition to PhCHO at the α-position. Proton transfer and elimination of DABCO give the allylic alcohol product: **PhCH(OH)-C(=CH_2)CO_2Me** (methyl 2-(hydroxy(phenyl)methyl)acrylate). The α-methylenyl group and the hydroxyl group are both introduced in a single step.

Why other options are wrong:
Option A: Methyl 3-phenylpropanoate would require hydrogenation of both the alkene and loss of the hydroxyl; the Baylis-Hillman does neither.
Option B: Cinnamaldehyde (PhCH=CHCHO) has no ester group; it is not the product of coupling acrylate with benzaldehyde via this mechanism.
Option C: Methyl cinnamate (PhCH=$CHCO_2$Me) results from Wittig or Heck chemistry, not from Baylis-Hillman, which retains the α-methylene and introduces the OH.

Final Answer: Baylis-Hillman adduct = methyl 2-(hydroxy(phenyl)methyl)acrylate $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#15

Q16.

Solution

Concept — Stetter Reaction / Umpolung via NHC Catalysis (Organic Chemistry):
The NHC catalyst (e.g. triazolium or thiazolium salt) adds to an aldehyde RCHO to form the Breslow intermediate, a vinaminol/enaminol that acts as an *acyl anion equivalent*: the carbonyl C becomes nucleophilic (umpolung). This species adds in a 1,4-fashion to the β-carbon of an enone (Michael acceptor), regenerating the NHC catalyst and producing a **1,4-diketone** (1,4-dicarbonyl compound).

Why other options are wrong:
Option A: β-Hydroxy aldehydes are aldol products, which occur without umpolung, via normal carbonyl α-carbon nucleophilicity.
Option C: Cyclopentanol formation requires a different set of conditions (e.g. the Stetter reaction can give lactones intramolecularly, but not cyclopentanol from a simple intermolecular reaction).
Option D: α,β-Unsaturated ketones are Michael *acceptors*, not products of this reaction.

Final Answer: Stetter reaction gives a 1,4-diketone $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#16

Q17.

Solution

Concept — Evans Asymmetric Alkylation (Organic Chemistry):
Titanium chelates both the oxazolidinone ring oxygen and the adjacent carbonyl oxygen, enforcing a rigid *s-cis* enolate conformation. In the $(4R)$-benzyl auxiliary, the C4-benzyl group occupies an equatorial-like position and shields the *Si* face of the enolate. Electrophilic alkylating agents (here allyl iodide) therefore attack from the *Re* face, giving predominantly the $(2R)$-*syn* alkylation product with >95% de.

Why other options are wrong:
Option B: The *Si* face is blocked by the benzyl group; attack from *Si* would give the minor diastereomer.
Option C: Evans auxiliaries are designed precisely to deliver high facial selectivity ($> 90\%$ de); equal face selectivity would be seen only in the absence of the chiral auxiliary.
Option D: The facial selectivity is dominated by the auxiliary's fixed conformation, not by the identity of the alkyl halide.

Final Answer: Electrophile attacks *Re* face (away from benzyl) $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#17

Q18.

Solution

Concept — Hajos-Parrish Ketone Ring System (Organic Chemistry):
The IUPAC name 3,4,8,8a-tetrahydronaphthalene-1,6(2H,7H)-dione identifies the carbon skeleton as a *naphthalene* (two fused six-membered rings, a bicyclo[4.4.0]decane or *trans/cis*-decalin framework), partially saturated by the tetrahydro prefix. It is a bicyclic diketone bearing two carbonyl groups (at positions 1 and 6), used as the Wieland-Miescher/Hajos-Parrish intermediate in total steroid synthesis.

Why other options are wrong:
Option A: A 5-6 fused ring system (like the CD rings of steroids) is not described by the naphthalene (6-6) framework in the IUPAC name.
Option B: Three fused six-membered rings would correspond to a phenanthrene or anthracene skeleton (ABC of steroids), which is beyond the bicyclic Hajos-Parrish ketone.
Option D: A 6-4 bicyclic system is not implied anywhere in the IUPAC name or in the steroid synthetic context.

Final Answer: Two fused six-membered rings (bicyclo[4.4.0]decane) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#18

Solution

Concept — Baldwin's Rules: 5-exo-trig Radical Cyclization:
For the hex-5-en-1-yl radical ($\bullet CH_2CH_2CH_2CH_2CH{=}CH_2$), two ring-closure modes compete:

Q19.

- **5-exo-trig**: radical at C1 attacks C5 (internal alkene carbon) $\rightarrow$ 5-membered ring + exocyclic $\bullet CH_2$ (cyclopentylmethyl radical). Kinetically *favoured* by Baldwin's rules (exo-trig is favoured for 3-7 membered rings) and confirmed by Beckwith's guidelines ($k \approx 10^8\ s^{-1}$ at 25 °C).
- **6-endo-trig**: radical attacks C6 (terminal) $\rightarrow$ cyclohexyl radical. Slower ($k \approx 10^7\ s^{-1}$) and disfavoured (endo-trig for $n = 6$ requires more transition-state strain).

Product ratio strongly favours 5-exo (typically ~5:1 or better).

Why other options are wrong:
Option A: 6-endo-trig is the slower, disfavoured pathway.
Option B: 5-endo-trig violates Baldwin's rules for 5-membered rings (endo-trig for $n = 5$ is disfavoured) and is geometrically strained.
Option C: 6-exo-trig would require a 7-membered chain; hex-5-en-1-yl only has 6 carbons.

Final Answer: 5-exo-trig is kinetically favoured $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#19

Q20.

Solution

Concept — Oxidative Dearomatization with $PhI(OAc)_2$ (Hypervalent Iodine):
Phenyliodine diacetate (PIDA) is an I(III) oxidant. With a para-substituted phenol in MeOH: (1) PIDA activates the phenol at the *ipso* position (adjacent to OH). (2) MeOH (nucleophile) attacks the ipso carbon. (3) PhI is eliminated with loss of aromaticity. Product: 4-(para-substituent)-4-methoxycyclohexa-2,5-dien-1-one – an *oxidative dearomatization* product (cyclohexadienone), widely used in natural product synthesis.

Why other options are wrong:
Option A: O-Methylation (phenyl ether formation) would require a different electrophilic methylating agent (e.g. MeI/K_2CO_3); PIDA is an oxidant, not an O-alkylating agent.
Option C: Ortho-iodination would require a different reagent (e.g. NIS or I_2/oxidant) without nucleophilic solvent participation.
Option D: Reduction of phenol to cyclohexanol requires H_2/Pd or Birch condi-

tions; PIDA is an oxidant.

Final Answer: Oxidative dearomatization gives 4-methoxy cyclohexadienone ⇒ **(B)**

Answer: (B) ← Go Back to Q#20

Q21.

Solution

Concept — Wade's Rules for *Closo* Boranes:

Wade's rules: for $[B_nH_n]^{2-}$ (*closo*), the number of skeletal electron pairs (SEP) $= n + 1$. For $[B_{12}H_{12}]^{2-}$: $n = 12$, SEP $= 13$. The *closo* geometry for $n = 12$ is the **icosahedron** (12 vertices, 20 triangular faces, 30 edges). This is the most symmetric cage available and satisfies the 13-SEP count. $[B_{12}H_{12}]^{2-}$ is an archetypical *closo* borane, highly stable and aromatic (3D aromaticity).

Why other options are wrong:

Option B: Cuboctahedron has 12 vertices but also 24 edges and mixed face types (not all triangular); it does not satisfy the Wade/Jemmis *closo* criterion for boranes.

Option C: Octahedron has 6 vertices, corresponding to $[B_6H_6]^{2-}$ (*closo*, $n = 6$, SEP $= 7$).

Option D: Truncated tetrahedron is not a borane cage geometry predicted by Wade's rules.

Final Answer: $[B_{12}H_{12}]^{2-}$ is icosahedral (*closo*, $n = 12$) ⇒ **(A)**

Answer: (A) ← Go Back to Q#21

Q22.

Solution

Concept — FeMoco Interstitial Atom (Bioinorganic Chemistry):

The iron-molybdenum cofactor (FeMoco) of nitrogenase has the stoichiometry $[Mo - 7Fe - 9S - C - \text{homocitrate}]$. In 2011, Spatzal *et al.* and Lancaster *et al.* independently solved the 1.0 Å resolution X-ray crystal structure of *A. vinelandii* nitrogenase and unambiguously identified the central interstitial atom as **carbon** (a carbide, C^{4-}), *not* nitrogen as earlier lower-resolution structures had suggested. The carbide forms six bonds to six Fe atoms of the cluster.

Why other options are wrong:

Option A: Nitrogen was the incorrect, earlier assignment from lower-resolution structures; high-resolution studies rule it out (N and C scatter X-rays differently at 1.0 Å).

Option B: Oxygen (O) is not consistent with the electron density at that position

nor with ENDOR/Mössbauer spectroscopic evidence.
Option D: Additional sulfur is present as bridging μ_2-S atoms; the interstitial central atom is not sulfur (confirmed by X-ray anomalous scattering).

Final Answer: Central interstitial atom is carbon (C^{4-}) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#22

Q23.

Solution

Concept — N_2 Binding Mode in Schrock Mo Catalyst (Inorganic Chemistry):
In the Schrock Mo(III)/Mo-triamidoamine complex for catalytic N_2 reduction (the Chatt cycle analogue), N_2 coordinates in **end-on** (η^1) fashion through one nitrogen atom to a single Mo centre. This gives a Mo≡N−N unit. The distal N is then sequentially protonated and reduced via PCET (proton-coupled electron transfer), proceeding through nitride, imide, amide, and ammonia intermediates (the "distal" pathway) in the Yandulov-Schrock cycle.

Why other options are wrong:
Option A: Side-on bridging (μ-η^2:η^2) is known for some dinuclear complexes (e.g. $[Mo(N_2)(dppe)_2]_2$) but is not the Schrock Mo mononuclear catalyst.
Option B: Side-on (η^2) at a single Mo is known for other metal systems but not the Schrock triamidoamine Mo complex.
Option C: Bridging end-on (μ-η^1:η^1) occurs in some bimetallic N_2 complexes (e.g. Fe-N_2-Fe in early Chatt-type chemistry) but not in the Schrock mononuclear system.

Final Answer: N_2 binds end-on (η^1) to a single Mo $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#23

Q24.

Solution

Concept — CO Stretching Frequency and π-Backdonation (Inorganic Chemistry):
In an isoelectronic series, the more electron-rich the metal, the greater the $d \rightarrow \pi^*_{CO}$ backdonation, which weakens the C≡O bond and lowers ν_{CO}.

$$[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+.$$

Approximate ν_{CO} values: ~ 1860 (V complex), ~ 1981 (Cr), ~ 2090 cm^{-1} (Mn complex). $[V(CO)_6]^-$ has the lowest effective nuclear charge on V, making V the most electron-rich and thus the strongest π-donor to CO.

Why other options are wrong:
Option A: $[Cr(CO)_6]$ is intermediate; it has a higher ν_{CO} than $[V(CO)_6]^-$.
Option C: $[Mn(CO)_6]^+$ has the *highest* ν_{CO} (least backdonation due to the positive charge on Mn).
Option D: The three complexes are isoelectronic but not iso-*nuclear*; different elements with different charges $\Rightarrow$ different backdonation $\Rightarrow$ different ν_{CO}.

Final Answer: $[V(CO)_6]^-$ has the lowest ν_{CO} $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#24

Solution

Concept — VSEPR Geometry: Trigonal Bipyramidal PCl_5:
In the trigonal bipyramidal (TBP) structure:

Q25.

- Three **equatorial** P-Cl bonds lie in a plane at $120°$ to each other.
- Two **axial** P-Cl bonds are collinear (along the molecular C_3 axis), making an axial-P-axial angle of exactly **180°**.
- Axial-to-equatorial angle: $90°$.

As shown in the diagram, the two axial Cl atoms are directly above and below P, giving a 180° Cl-P-Cl angle along the vertical axis.

Why other options are wrong:
Option B: $120°$ is the *equatorial*-Cl-P-equatorial-Cl angle, not the axial-axial angle.
Option C: $90°$ is the angle between an *axial* and an *equatorial* bond.
Option D: $109.5°$ is the tetrahedral angle seen in sp^3 systems (e.g. CH_4); TBP has neither all-equal bonds nor tetrahedral geometry.

Final Answer: Axial-P-Axial angle $= 180°$ $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#25

Q26.

Solution

Concept — Properties of Polysiloxanes (Silicones):
The Si-O bond (~ 450 kJ mol^{-1}) is significantly stronger than C-C (~ 346 kJ mol^{-1}), giving silicones their high thermal stability (stable to $\sim$ 200-300 °C). The organic side groups (methyl, phenyl) render the surface hydrophobic and give low surface energy ($\gamma \approx 20$ mN m^{-1}). The Si-O backbone is highly polarisable but the valence electrons are tightly bound $\Rightarrow$ excellent electrical insulator. Silicones do not melt sharply (amorphous) and are chemically inert to most conditions.

Why other options are wrong:
Option A: Silicones are flame-retardant and thermally stable; the opposite of

highly flammable.
Option B: Despite polar Si-O bonds in the backbone, the organic side chains make the surface hydrophobic; water contact angles on PDMS exceed $100°$.
Option D: Polyethylene (C-C backbone) has lower thermal stability, higher surface energy, and very different mechanical and electrical properties from silicones.

Final Answer: High thermal stability, hydrophobicity, low surface energy, electrical insulation $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#26

Q27.

Solution

Concept — Critical Temperature of YBCO Superconductor:
$YBa_2Cu_3O_7$ (YBCO) was discovered in 1987 by Wu, Chu et al. and immediately attracted worldwide attention because $T_c \approx 93$ K is above the boiling point of liquid nitrogen (77 K). This made large-scale, cost-effective cooling with liquid N_2 (rather than expensive liquid He at 4 K) feasible for the first time. YBCO belongs to the cuprate perovskite family and has a layered structure with CuO_2 planes responsible for superconductivity.

Why other options are wrong:
Option A: 4 K is the T_c of Hg (first superconductor discovered, 1911) or liquid-He cooled elemental/conventional superconductors (BCS theory regime).
Option B: 20 K is near the range of some heavy-fermion superconductors or early unconventional superconductors.
Option C: 40 K is close to the T_c of MgB_2 (2001 discovery, $T_c = 39$ K); YBCO is more than twice as high.

Final Answer: $T_c(\text{YBCO}) \approx 93$ K $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#27

Q28.

Solution

Concept — Sharp Emission of Lanthanide Ions (Spectroscopy):
The $4f$ orbitals of lanthanide ions are *inner* orbitals, spatially contracted inside the $5s^25p^6$ shell. The outer $5s^25p^6$ electrons shield the $4f$ electrons almost completely from ligand electric fields. Consequently: (1) crystal-field splitting of $4f$ levels is ~ 100 cm^{-1} (vs. $\sim 10{,}000$ cm^{-1} for $3d$ metals); (2) f-f transitions are essentially atomic-like $\Rightarrow$ narrow, sharp emission lines; (3) transition wavelengths shift < 10 nm between different host lattices.

Why other options are wrong:

Option A: $4f$ electrons are *contracted/localized*, not delocalized; band broadening occurs in delocalized systems (e.g. transition metals in oxides).
Option C: Lanthanides have f-f transitions (not d-d); moreover, the sharpness comes from shielding, not merely from the selection rule for d-d.
Option D: High nuclear charge alone does not explain the sharpness; the key factor is the specific shielding of $4f$ by $5s^2 5p^6$.

Final Answer: $4f$ shielded by $5s^2 5p^6 \Rightarrow$ sharp lines $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#28

Q29.

Solution

Concept — Electroosmotic Flow (EOF) in Capillary Electrophoresis:
At $\mathrm{pH} > 3.5$ the silanol groups on the fused-silica capillary wall ionise: Si-OH $\rightarrow$ $SiO^- + H^+$, creating a negatively charged surface. To maintain electroneutrality, cations (Na^+, H_3O^+) accumulate in the diffuse electrical double layer (Gouy-Chapman layer). Under the applied electric field (cathode at the detector), these excess cations migrate toward the cathode, dragging the bulk aqueous plug with them via viscous coupling. This EOF (toward cathode) typically has a flat (plug-flow) velocity profile, superior to the parabolic pressure-driven profile, giving high separation efficiency in CE.

Why other options are wrong:
Option B: Both anions and cations migrate by electrophoresis; the EOF is a *bulk flow* driven by the double layer, not by individual ion electrophoretic velocities.
Option C: EOF in uncoated silica capillaries is directed toward the *cathode* at neutral/alkaline pH; at very acidic pH (below ~3) it may nearly vanish but does not reverse to the anode.
Option D: Neutral analytes are carried by the EOF bulk flow, not attracted electrostatically to the wall.

Final Answer: SiO^- creates cationic double layer migrating toward cathode $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#29

Q30.

Solution

Concept — Gradient Elution in Reversed-Phase HPLC:
In RP-HPLC, the mobile phase starts with high aqueous (weak eluent for non-polar analytes) and the organic solvent (MeOH or MeCN) content increases over time. Benefits over isocratic: (1) **Reduced run time**: non-polar late-eluters are swept

off the column faster. (2) **Improved peak shape**: late-eluting peaks are sharper (less band broadening from diffusion during long isocratic runs). (3) **Wide k' window**: handles samples spanning a large polarity range in one run. (4) After gradient, the column is re-equilibrated before the next injection.

Why other options are wrong:
Option A: Dead volume is a fixed column property; gradient elution does not change it.
Option B: Keeping composition constant is the definition of *isocratic* elution – the opposite of gradient.
Option D: Gradient elution is very common in *reversed-phase* HPLC; it is also used in normal phase, but the statement is not a defining limitation.

Final Answer: Gradient shortens run time and improves late-peak shape ⇒ **(C)**

Answer: (C) ← Go Back to Q#30

Q31.

Solution

Concept — Van Deemter Equation: Minimum Plate Height:
$H = A + B/u + Cu$. The minimum is found by $\mathrm{d}H/\mathrm{d}u = 0$:

$$u_{\text{opt}} = \sqrt{\frac{B}{C}} = \sqrt{\frac{2.0}{0.005}} = \sqrt{400} = 20 \text{ mm s}^{-1}.$$

$H_{\text{min}} = A + 2\sqrt{BC} = 0.10 + 2\sqrt{2.0 \times 0.005} = 0.10 + 2\sqrt{0.010} = 0.10 + 2(0.100) = \mathbf{0.30}$ mm.

Why other options are wrong:
Option A: 0.10 mm equals A alone; it ignores the $B/u + Cu$ terms at the optimum.
Option B: 0.20 mm equals $A + \sqrt{BC}$ (missing the factor of 2 in $H_{\text{min}} = A + 2\sqrt{BC}$).
Option C: 0.40 mm doubles the correct answer; likely a calculation error in the $2\sqrt{BC}$ term.

Final Answer: $H_{\text{min}} = 0.30$ mm ⇒ **(D)**

Answer: (D) ← Go Back to Q#31

Q32.

Solution

Concept — EIS Nyquist Plot Interpretation (Electrochemistry):
A Randles-type EIS spectrum shows:

- **Semicircle (high freq.)**: The R_{ct}-C_{dl} parallel combination gives a perfect semicircle in the Nyquist plot. Diameter $= R_{ct}$; left x-intercept $= R_s$ (solution resistance); right x-intercept $= R_s + R_{ct}$.
- **45° Warburg line (low freq.)**: When diffusion of redox species to the elec-

trode surface limits the current, the Warburg impedance $Z_W = \sigma\omega^{-1/2}(1-j)$ gives equal real and imaginary parts $\Rightarrow$ 45° slope in the Nyquist plot.

Why other options are wrong:
Option A: Pure resistance gives a single point on the Z' axis; a semicircle indicates capacitive/frequency-dependent behaviour.
Option C: Pure capacitance gives a vertical line parallel to the $-Z''$ axis in the Nyquist plot (infinite RC circuit); the semicircle indicates finite R_{ct}.
Option D: Pure diffusion (Warburg) at all frequencies would give a 45° line for the entire spectrum, with no semicircle at high frequency.

Final Answer: $R_{ct} \parallel C_{dl}$ semicircle then Warburg diffusion line $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#32

Q33.

Solution

Concept — Reversible CV: ΔE_p and Peak Current Ratio:
For a *fully reversible* one-electron redox process at $T = 298$ K:

$$\Delta E_p = E_{p,a} - E_{p,c} = \frac{2.303RT}{nF} = \frac{0.05916}{n}\ \text{V} \approx 59\ \text{mV} \quad (n = 1).$$

Because both oxidized and reduced forms are stable and diffusion-limited:

$$\frac{i_{p,a}}{i_{p,c}} = 1.00$$

(from the Randles-Sevcik equation applied to both anodic and cathodic peaks). The formal potential $E^{\circ\prime} = (E_{p,a} + E_{p,c})/2$.

Why other options are wrong:
Option B: $\Delta E_p \approx 0$ would imply ideal (fully equilibrated) bulk electrochemistry, not the semi-infinite diffusion conditions of a CV experiment.
Option C: $\Delta E_p > 200$ mV and $i_{p,a}/i_{p,c} < 1$ describe an *irreversible* or quasi-reversible process with slow electron-transfer kinetics.
Option D: $i_{p,a}/i_{p,c} > 2$ would indicate a coupled chemical reaction (EC mechanism) that generates additional electroactive species on the return scan.

Final Answer: $\Delta E_p \approx 59$ mV, $i_{p,a}/i_{p,c} = 1.00 \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#33

Q34.

Solution

Concept — DNA Melting Temperature vs. Ionic Strength:
The phosphodiester backbone of dsDNA carries one negative charge per nucleotide. At low ionic strength, mutual repulsion between the two negatively charged strands destabilises the duplex and lowers T_m. Adding NaCl screens these charges (Manning condensation of Na^+ on the DNA backbone), reducing the electrostatic penalty for keeping the two strands together. Higher salt $\Rightarrow$ more screening $\Rightarrow$ more stable duplex $\Rightarrow$ higher T_m. Empirically: $T_m \approx T_{m,1M} + 16.6 \log[Na^+]$ (Record's equation), showing a linear increase with $\log[NaCl]$ as in the graph.

Why other options are wrong:
Option A: Higher salt *stabilises* the duplex; T_m increases, not decreases.
Option B: Ionic strength strongly affects T_m; at very low salt, T_m can drop by 20-30 °C relative to physiological conditions.
Option D: There is no maximum; T_m increases monotonically with $\log[NaCl]$ over the physiological range.

Final Answer: T_m increases linearly with $\log[NaCl] \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#34

Q35.

Solution

Concept — Radius of Gyration of a Gaussian Polymer Chain:
For an ideal (Gaussian) random-coil polymer with N Kuhn segments each of length b, the mean-square end-to-end distance is $\langle R^2 \rangle = Nb^2$. The mean-square radius of gyration is:

$$\langle R_g^2 \rangle = \frac{Nb^2}{6} \quad \Rightarrow \quad R_g = b\sqrt{\frac{N}{6}}.$$

The factor of 6 arises from the definition $R_g^2 = (1/N)\sum_i \langle r_i^2 \rangle$ relative to the centre of mass of the chain.

Why other options are wrong:
Option A: $R_g = Nb$ is the *contour length* (fully extended chain); a real polymer is always more compact than this.
Option B: $R_g = b\sqrt{N}$ is the RMS *end-to-end distance* $R = \sqrt{Nb^2}$; R_g is smaller by a factor of $\sqrt{6}$ compared to R.
Option C: $R_g = b$ (one segment length) has no physical meaning for a chain of N segments.

Final Answer: $R_g = b\sqrt{N/6} \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#35

Q36.

Solution

Concept — Grand Canonical Ensemble and Ξ (Statistical Mechanics):
In the grand canonical ensemble the system is in contact with a reservoir at fixed T and μ; both energy and particle number fluctuate. The grand partition function sums over all microstates labelled by (N, E):

$$\Xi = \sum_{N=0}^{\infty} \sum_{E} g(N,E)\, \exp\left[-\frac{E-\mu N}{k_B T}\right] = \sum_{N=0}^{\infty} \sum_{E} \exp[-\beta(E-\mu N)],$$

where $\beta = 1/(k_B T)$ and $g(N,E)$ is the degeneracy. All thermodynamic quantities follow: $\Omega = k_B T \ln \Xi$, $\langle N \rangle = k_B T (\partial \ln \Xi / \partial \mu)_{T,V}$.

Why other options are wrong:
Option A: $\Xi = \sum_E \exp(-\beta E)$ is the *canonical* partition function Z for a fixed-N system, not the grand canonical Ξ.
Option C: $\Xi = \exp(-\beta G)$ is sometimes written for the canonical partition function where G is the Gibbs (or Helmholtz for A) free energy; it does not describe the particle-number sum of the grand canonical ensemble.
Option D: $\Xi = \sum_N \exp(-\beta \mu N)$ omits the energy sum and would not give correct thermodynamic averages.

Final Answer: $\Xi = \sum_N \sum_E \exp[-\beta(E-\mu N)] \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#36

Q37.

Solution

Concept — Hill Equation and Cooperativity in Haemoglobin:
The Hill equation $\theta = [L]^n / (K_d^n + [L]^n)$ models cooperative binding.

- $n = 1$: non-cooperative (Langmuir isotherm).
- $n > 1$: positive cooperativity – binding of one ligand enhances subsequent binding.
- $n < 1$: negative cooperativity (anti-cooperative).

For Hb, $n \approx 2.8$: clearly $> 1 \Rightarrow$ positive cooperativity (T-to-R conformational transition, MWC model). The value < 4 (number of O_2-binding subunits) indicates *partial* cooperativity, not the idealised all-or-nothing limit where $n = 4$.

Why other options are wrong:
Option B: Negative cooperativity would require $n < 1$; $n = 2.8$ is clearly > 1.
Option C: Non-cooperative Langmuir binding requires $n = 1$ exactly; $n = 2.8$ rules this out.
Option D: Anti-cooperative binding (first ligand *inhibits* subsequent binding) gives $n < 1$; haemoglobin shows the opposite – positive cooperativity facilitates efficient

O_2 loading in the lungs and unloading in tissues.

Final Answer: $n \approx 2.8 > 1 \Rightarrow$ positive cooperativity $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#37

Q38.

Solution

Concept — Persistence Length of dsDNA (Worm-Like Chain Model):
The worm-like chain (WLC) model describes semiflexible polymers via the persistence length L_p, the length over which the tangent vector correlation decays: $\langle \hat{t}(0) \cdot \hat{t}(s) \rangle = e^{-s/L_p}$. For dsDNA under physiological conditions (~ 150 mM NaCl, 37 °C):

$$L_p^{\text{dsDNA}} \approx 50 \text{ nm} \approx 150 \text{ bp}.$$

This makes dsDNA *semiflexible*: shorter than L_p it behaves as a rigid rod; much longer it behaves as a random coil. The value has been confirmed by single-molecule force spectroscopy, SAXS, and cryo-EM.

Why other options are wrong:
Option A: 0.34 nm is the rise per base pair in B-form DNA – a structural parameter, not L_p.
Option B: 3.4 nm is the length of one helical turn (10 bp) in B-DNA – also a structural parameter, not L_p.
Option D: ~ 16 μm is the *contour length* of λ-phage DNA ($\sim 48{,}500$ bp), which is $\sim 300 \times L_p$ (well in the random-coil regime).

Final Answer: $L_p(\text{dsDNA}) \approx 50$ nm $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#38

Q39.

Solution

Concept — Secular Determinant in LCAO-MO Theory for H_2^+:
Writing $\psi = c_1\phi_1 + c_2\phi_2$ for two $1s$ hydrogen atomic orbitals and minimising $E = \langle\psi|\hat{H}|\psi\rangle / \langle\psi|\psi\rangle$, we obtain the secular equations in matrix form $(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0$. For H_2^+ with $H_{11} = H_{22} = \alpha$, $H_{12} = H_{21} = \beta$, and $S_{12} = S_{21} = S$:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad \Rightarrow \quad (\alpha - E)^2 = (\beta - ES)^2.$$

This gives two solutions:

$$E_+ = \frac{\alpha + \beta}{1 + S} \text{ (bonding MO)}, \qquad E_- = \frac{\alpha - \beta}{1 - S} \text{ (antibonding MO)}.$$

Why other options are wrong:
Option A: A 2×2 secular determinant always gives *two* solutions; only one solution would require a degenerate (1×1) system.
Option B: The LCAO-MO result is an *approximation* (uses a limited basis set); the exact solution requires numerical methods beyond simple LCAO.
Option C: $E = \alpha$ for both MOs would mean $\beta = 0$ (no resonance integral, i.e. no bonding interaction), which is unphysical for H_2^+.

Final Answer: Two MO energies: $E_+ = (\alpha+\beta)/(1+S)$, $E_- = (\alpha-\beta)/(1-S) \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#39

Q40.

Solution

Concept — FRET Efficiency and r^{-6} Dependence:
The FRET efficiency is:

$$E = \frac{R_0^6}{R_0^6 + r^6}.$$

At $r = 2R_0$ (donor-acceptor distance doubled from R_0):

$$E = \frac{R_0^6}{R_0^6 + (2R_0)^6} = \frac{R_0^6}{R_0^6 + 64R_0^6} = \frac{1}{65} \approx 0.0154 \approx 1.5\%.$$

The strong r^{-6} dependence (shown by the FRET arrow in the schematic) means that doubling the distance reduces FRET efficiency from 50% (at $r = R_0$) to only $\sim 1.5\%$ – a 33-fold drop.

Why other options are wrong:
Option A: 25% corresponds to $r = R_0 \cdot 2^{1/6} \approx 1.12R_0$ (not double).
Option C: 12.5% would require $(R_0/r)^6 = 0.125$, i.e. $r \approx 1.26R_0$ (not double).
Option D: 50% is the FRET efficiency at $r = R_0$ by definition of the Forster radius; doubling r to $2R_0$ reduces E drastically.

Final Answer: $E(r = 2R_0) = 1/65 \approx 1.5\% \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#40

Answer Key

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