TIFR GS Chemistry

Sample Paper – 5

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 enthalpy of vaporisation of water is $\Delta H_{\text{vap}} = 40.7$ kJ mol^{-1}. The vapour pressure at 373 K is 1.013×10^5 Pa. Using the Clausius–Clapeyron equation,

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$

estimate the vapour pressure at 413 K. ($R = 8.314$ J mol^{-1}K^{-1})

(A) 1.5×10^5 Pa

(B) 3.6×10^5 Pa

(C) 5.2×10^5 Pa

(D) 7.1×10^5 Pa

Q2. Which of the following expressions correctly states the **Gibbs–Helmholtz equation**?

(A) $\left[\dfrac{\partial(\Delta G/T)}{\partial T}\right]_P = -\dfrac{\Delta H}{T^2}$

(B) $\left[\dfrac{\partial \Delta G}{\partial T}\right]_P = -\Delta S$

(C) $\Delta G = \Delta H - T\Delta S$ (valid only at constant temperature and pressure)

(D) $\left[\dfrac{\partial \Delta G}{\partial P}\right]_T = \Delta V$

Q3. The rate constant for a first-order reaction is $k_1 = 3.0 \times 10^{-3}$ s^{-1} at 300 K and $k_2 = 2.0 \times 10^{-2}$ s^{-1} at 310 K. Calculate the enthalpy of activation $\Delta H^{\ddagger}$ (in kJ mol^{-1}). ($R = 8.314$ J mol^{-1}K^{-1})

(A) 92 kJ mol^{-1}

(B) 121 kJ mol^{-1}

(C) 146 kJ mol^{-1}

(D) 175 kJ mol^{-1}

Q4. For an enzyme-catalysed reaction obeying Michaelis–Menten kinetics, the initial rate $v_0 = V_{\max}/2$ when $[\mathrm{S}] = 4.0$ mM. What is the Michaelis constant K_m?

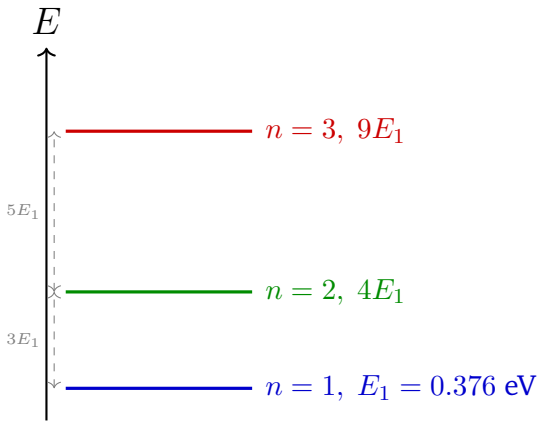
(A) 1.0 mM

(B) 2.0 mM

(C) 8.0 mM

(D) 4.0 mM

Q5. An electron is confined in a one-dimensional box of length $L = 1.0$ nm. Given that the ground-state energy $E_1 = h^2/(8m_eL^2) = 0.376$ eV, what is the energy of the $n = 3$ state?



(A) 3.38 eV

(B) 1.13 eV

(C) 1.50 eV

(D) 9.02 eV

Q6. The radial probability distribution function for the $2s$ orbital of the hydrogen atom has its *outer* maximum at approximately which value of r (in Bohr radii a_0)?

(A) $1.0\ a_0$

(B) $5.2\ a_0$

(C) $3.0\ a_0$

(D) $9.0\ a_0$

Q7. Arrange the following CH_3 groups in order of **increasing** ^{1}H NMR chemical shift (δ, ppm): CH_3–alkyl, CH_3–C=O (ketone), CH_3–O (ether), CH_3–NO_2 (nitro).

(A) $NO_2 < O < C{=}O <$ alkyl

(B) alkyl $< O < NO_2 < C{=}O$

(C) alkyl $< C{=}O < O < NO_2$

(D) $C{=}O <$ alkyl $< O < NO_2$

Q8. How many distinct ^{1}H NMR signals does **ethyl propanoate** ($CH_3CH_2OCOCH_2CH_3$) show?

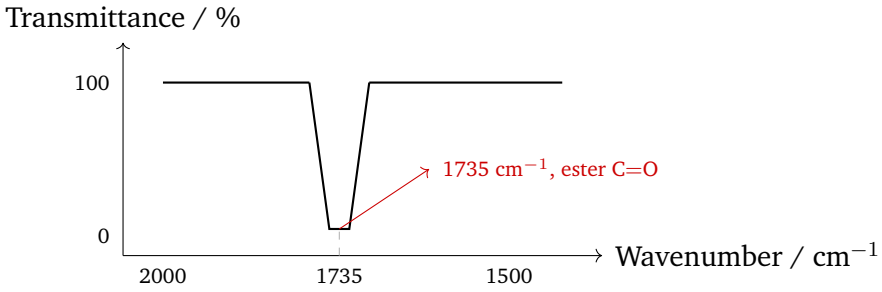
(A) 2

(B) 3

(C) 6

(D) 4

Q9. A carbonyl absorption at 1735 cm^{-1} in the IR spectrum shown below is characteristic of which functional group?



(A) Ester

(B) Aldehyde

(C) Ketone

(D) Carboxylic acid

Q10. A solution has molar absorptivity $\varepsilon = 1.00 \times 10^3$ L mol^{-1}cm^{-1}. In a 1.0 cm cell the measured absorbance is $A = 0.50$. What is the molar concentration (in mmol L^{-1})?

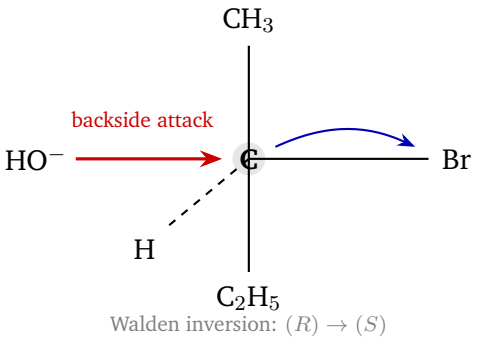
(A) 0.20 mmol L^{-1}

(B) 0.50 mmol L^{-1}

(C) 2.0 mmol L^{-1}

(D) 5.0 mmol L^{-1}

Q11. Treatment of (R)-2-bromobutane with aqueous NaOH under S_N2 conditions gives which product?



Walden inversion: $(R) \rightarrow (S)$

(A) (R)-butan-2-ol

(B) Racemic butan-2-ol

(C) (S)-butan-2-ol

(D) 1-Butanol

Q12. Treatment of 2-bromo-2-methylbutane with KOH in ethanol (E2 conditions) gives predominantly which alkene (Zaitsev's rule)?

(A) 2-Methylbut-1-ene

(B) 3-Methylbut-1-ene

(C) 2-Methylbut-3-ene

(D) 2-Methylbut-2-ene

Q13. Which substituent on a benzene ring acts as an **ortho/para director** in electrophilic aromatic substitution?

(A) $-NH_2$

(B) $-NO_2$

(C) $-CN$

(D) $-COOH$

Q14. The initial product of **base-catalysed aldol condensation** of two molecules of acetaldehyde (CH_3CHO) is:

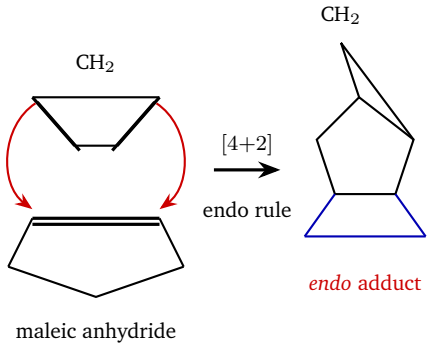
(A) But-2-enal (α,β-unsaturated aldehyde, dehydration product)

(B) 3-Hydroxybutanal (β-hydroxy aldehyde, aldol adduct)

(C) Butanal (simple chain elongation product)

(D) 2-Methylpropanal (branched isomer)

Q15. The $[4+2]$ cycloaddition of cyclopentadiene with maleic anhydride preferentially gives which product?



(A) *exo*-Norbornene-2,3-dicarboxylic anhydride

(B) A 1:1 mixture of *endo* and *exo* adducts

(C) *endo*-Norbornene-2,3-dicarboxylic anhydride

(D) An open-chain addition product

Q16. Reaction of methylmagnesium bromide (MeMgBr) with acetone (propan-2-one) followed by aqueous workup gives:

(A) Methanol

(B) Propan-1-ol

(C) Propan-2-ol

(D) 2-Methylpropan-2-ol

Q17. In the Sharpless asymmetric epoxidation of (E)-but-2-en-1-ol using $(+)$-diethyl tartrate (DET), Ti(Oi-Pr)$_4$, and TBHP, the epoxide oxygen is delivered to which face of the double bond?

(A) β-face (top face)

(B) α-face (bottom face)

(C) Both faces equally (racemic product)

(D) No epoxidation occurs without the chiral tartrate ligand

Q18. Which single reagent converts cyclohexanone to cyclohexanol in one synthetic step?

(A) H_2, Pd/C

(B) $NaBH_4$

(C) *m*-CPBA (meta-chloroperoxybenzoic acid)

(D) MeMgBr (Grignard reagent)

Q19. Which of the following correctly ranks **free radicals** in order of **decreasing stability**?

(A) methyl $>$ primary $>$ secondary $>$ tertiary

(B) tertiary $>$ secondary $>$ methyl $>$ primary

(C) tertiary $>$ secondary $>$ primary $>$ methyl

(D) primary $>$ secondary $>$ tertiary $>$ methyl

Q20. Treatment of 2-methylcyclohexan-1-one with LDA at -78°C generates predominantly which enolate?

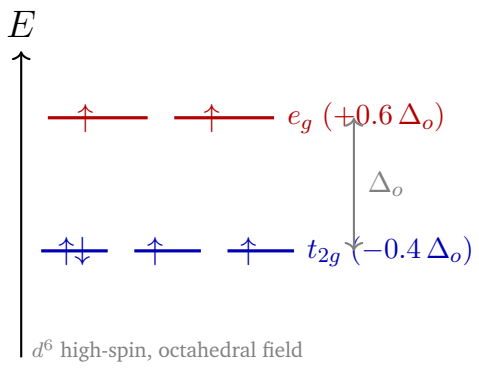
(A) The thermodynamic (more substituted) enolate at C-2

(B) The enolate at C-5

(C) A mixture of kinetic and thermodynamic enolates

(D) The kinetic (less substituted) enolate at C-6

Q21. Calculate the crystal field stabilisation energy (CFSE) in units of Δ_o for $[Fe(H_2O)_6]^{2+}$, a d^6 **high-spin** octahedral complex.



(A) $-0.4\ \Delta_o$

(B) $-2.4\ \Delta_o$

(C) $-0.6\ \Delta_o$

(D) 0

Q22. Which d-electron configuration shows the **strongest Jahn–Teller distortion** in an octahedral complex?

(A) d^3

(B) d^9

(C) d^6 low-spin

(D) d^{10}

Q23. Which of the following is an **18-electron complex**?

(A) $[\mathrm{V(CO)_6}]$ (17-electron species)

(B) $[\mathrm{Mn(CO)_5}]^+$ (16-electron species)

(C) $[\mathrm{Cr(CO)_6}]$ (18-electron species)

(D) $[\mathrm{Fe(CO)_4}]$ (16-electron species)

Q24. How many **geometric isomers** does the square planar complex $[\mathrm{Pt(NH_3)_2Cl_2}]$ have?

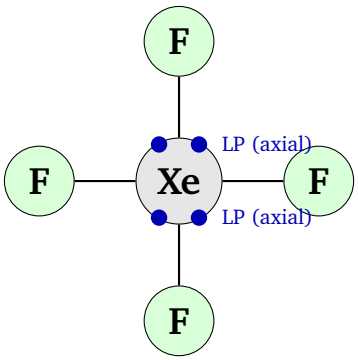
(A) 1

(B) 3

(C) 4

(D) 2

Q25. According to VSEPR theory, the molecular geometry of $\mathrm{XeF_4}$ is:



Square planar, AX_4E_2

(A) Square planar

(B) Tetrahedral

(C) See-saw

(D) Square pyramidal

Q26. Arrange the chlorine oxoacids in order of **increasing acid strength**: $HClO$, $HClO_2$, $HClO_3$, $HClO_4$.

(A) $HClO_4 < HClO_3 < HClO_2 < HClO$

(B) $HClO < HClO_2 < HClO_3 < HClO_4$

(C) $HClO_2 < HClO < HClO_4 < HClO_3$

(D) $HClO_3 < HClO_2 < HClO < HClO_4$

Q27. The packing efficiency of a **face-centred cubic (FCC / ccp)** unit cell is closest to:

(A) 52.4%

(B) 68.0%

(C) 74.1%

(D) 90.7%

Q28. Which metal ion is present at the active site of **cobalamin** (vitamin B_{12})?

(A) Iron

(B) Copper

(C) Zinc

(D) Cobalt

Q29. A 0.500 g sample of impure $CaCO_3$ ($M = 100$ g mol^{-1}) was dissolved in 25.0 mL of 0.200 M HCl. The excess HCl was back-titrated with 0.100 M NaOH, consuming 12.5 mL. What is the **percentage purity** of $CaCO_3$? ($CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + CO_2$)

(A) 37.5%

(B) 50.0%

(C) 62.5%

(D) 75.0%

Q30. Two chromatographic peaks have retention times $t_{R1} = 10.0$ min and $t_{R2} = 11.0$ min, each with baseline peak width $w = 0.50$ min. Using $R_s = 2(t_{R2} - t_{R1})/(w_1 + w_2)$, the resolution is:

(A) $R_s = 1.0$

(B) $R_s = 2.0$

(C) $R_s = 0.5$

(D) $R_s = 4.0$

Q31. At 25°C, the theoretical Nernst response slope for a **monovalent cation** ion-selective electrode (ISE) is:

(A) 29.6 mV per decade

(B) 118.3 mV per decade

(C) 59.2 mV per decade

(D) 25.7 mV per decade

Q32. A current of 2.00 A flows for 965 s through a $CuSO_4$ solution. What mass of copper ($M = 63.5$ g mol^{-1}, $n = 2$) is deposited at the cathode? ($F = 96500$ C mol^{-1})

(A) 0.317 g

(B) 1.270 g

(C) 1.905 g

(D) 0.635 g

Q33. For the galvanic cell $\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s)$, given $E^\circ(\mathrm{Zn}^{2+}/\mathrm{Zn}) = -0.76$ V and $E^\circ(\mathrm{Cu}^{2+}/\mathrm{Cu}) = +0.34$ V, the standard cell potential E°_{cell} is:

(A) $+1.10$ V

(B) -1.10 V

(C) $+0.42$ V

(D) $+0.76$ V

Q34. A solution is prepared by dissolving 10.0 g of glucose ($M = 180$ g mol^{-1}) in 100 g of water. Given $K_b(\text{water}) = 0.512$ K kg mol^{-1}, the boiling-point elevation ΔT_b is:

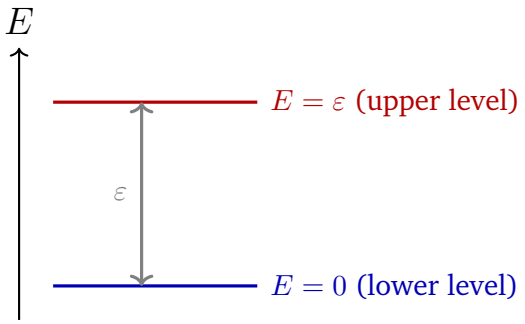
(A) 0.14 K

(B) 0.28 K

(C) 0.56 K

(D) 1.12 K

Q35. A system has two non-degenerate energy levels with energies $E = 0$ and $E = \varepsilon$. As $T \to \infty$, the ratio of the population in the *upper* level to that in the *lower* level approaches:



(A) 0

(B) $\exp(-\varepsilon/kT)$

(C) 1

(D) ∞

Q36. Two energy levels are separated by 200 cm^{-1}. At $T = 300$ K, what is the ratio n_2/n_1 of upper-to-lower level populations? ($hc/k = 1.4388$ cm K)

(A) 0.95

(B) 0.51

(C) 0.63

(D) 0.38

Q37. The standard free energy of ATP hydrolysis is $\Delta G^{\circ\prime} = -30.5$ kJ mol^{-1}. Under cellular conditions ([ATP] $= 10$ mM, [ADP] $= 1$ mM, [P$_i$] $= 10$ mM) at 310 K, the actual ΔG for ATP hydrolysis is approximately: ($R = 8.314 \times 10^{-3}$ kJ mol^{-1}K^{-1})

(A) -48 kJ mol^{-1}

(B) -30.5 kJ mol^{-1}

(C) -13 kJ mol^{-1}

(D) -65 kJ mol^{-1}

Q38. A buffer contains a weak acid with p$K_a = 6.80$ and its conjugate base, with $[\text{A}^-]/[\text{HA}] = 4.0$. The pH of the buffer is:

(A) 6.20

(B) 7.40

(C) 6.80

(D) 8.00

Q39. For the first-order reaction A $\rightarrow$ B, the rate equation $d[\text{B}]/dt = k([\text{A}]_0 - [\text{B}])$ with $[\text{B}]_0 = 0$ is most directly solved by which mathematical method?

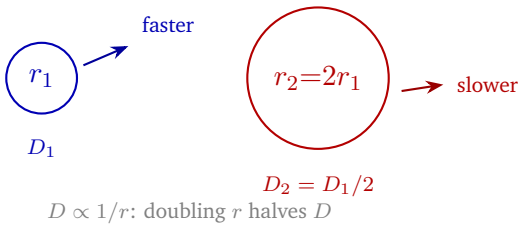
(A) Laplace transform (the only valid approach)

(B) Fourier transform

(C) Separation of variables

(D) Finite difference method

Q40. The Stokes–Einstein diffusion coefficient is $D = kT/(6\pi\eta r)$. If the radius of a spherical particle is **doubled** while temperature and viscosity remain constant, how does D change?



(A) Doubles

(B) Quadruples

(C) Decreases to one-quarter of its original value

(D) Decreases to one-half of its original value

Detailed Solutions

Q1.

Solution

Concept — Clausius–Clapeyron Equation:

The Clausius–Clapeyron equation $\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2)$ relates vapour pressure to temperature via the enthalpy of vaporisation.

Step 1 — Compute the temperature factor:

$T_1 = 373$ K, $T_2 = 413$ K

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{373} - \frac{1}{413} = \frac{413 - 373}{373 \times 413} = \frac{40}{154049} = 2.597 \times 10^{-4}\ \text{K}^{-1}$$

Step 2 — Evaluate $\ln(P_2/P_1)$:

$$\frac{\Delta H_{\text{vap}}}{R} = \frac{40700}{8.314} = 4893\ \text{K}$$

$$\ln(P_2/P_1) = 4893 \times 2.597 \times 10^{-4} = 1.271$$

$$P_2 = 1.013 \times 10^5 \times e^{1.271} = 1.013 \times 10^5 \times 3.564 = 3.61 \times 10^5\ \text{Pa}$$

Why other options are wrong:

Option A: 1.5×10^5 Pa corresponds to a much smaller temperature difference.

Option C: 5.2×10^5 Pa overestimates by using an incorrect exponent.

Option D: 7.1×10^5 Pa would require $T_2 > 450$ K.

Final Answer: $P_2 \approx 3.6 \times 10^5$ Pa $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#1

Q2.

Solution

Concept — Gibbs–Helmholtz Equation:

The Gibbs–Helmholtz equation arises from the temperature derivative of G/T at constant pressure and gives the temperature dependence of ΔG via ΔH.

Step 1 — Identify the correct form:

Starting from $G = H + T(\partial G/\partial T)_P$, one obtains: $[\partial(\Delta G/T)/\partial T]_P = -\Delta H/T^2$. This is the Gibbs–Helmholtz equation (option A).

Why other options are wrong:

Option B: $(\partial \Delta G/\partial T)_P = -\Delta S$ is a valid thermodynamic identity but is not the Gibbs–Helmholtz equation.

Option C: $\Delta G = \Delta H - T\Delta S$ holds at any temperature, not only at constant T.

Option D: $(\partial \Delta G/\partial P)_T = \Delta V$ is correct but defines the pressure dependence of ΔG, not the Gibbs–Helmholtz relation.

Final Answer: $[\partial(\Delta G/T)/\partial T]_P = -\Delta H/T^2$ $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#2

Q3.

Solution

Concept — Eyring / Arrhenius Two-Temperature Method:
Using $\ln(k_2/k_1) = (\Delta H^\ddagger/R)(1/T_1 - 1/T_2)$ with two rate constants at two temperatures allows direct calculation of the activation enthalpy.

Step 1 — Compute the rate ratio and temperature factor:
$k_2/k_1 = (2.0 \times 10^{-2})/(3.0 \times 10^{-3}) = 6.667$
$\ln(6.667) = 1.897$
$1/T_1 - 1/T_2 = 1/300 - 1/310 = 10/(300 \times 310) = 1.075 \times 10^{-4}$ K^{-1}

Step 2 — Solve for $\Delta H^\ddagger$:
$\Delta H^\ddagger = R\ \ln(k_2/k_1)\ /\ (1/T_1 - 1/T_2) = 8.314 \times 1.897\ /\ 1.075 \times 10^{-4} = 15.77\ /\ 1.075 \times 10^{-4} \approx 146{,}700$ J mol^{-1} ≈ 147 kJ mol^{-1}
Nearest option: **146 kJ mol^{-1}** (option C).

Why other options are wrong:
Option A: 92 kJ mol^{-1} arises from using a 10-fold rate ratio with a 20 K gap.
Option B: 121 kJ mol^{-1} corresponds to an incorrect temperature interval.
Option D: 175 kJ mol^{-1} overestimates $\Delta H^\ddagger$.

Final Answer: $\Delta H^\ddagger \approx 146$ kJ mol^{-1} $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#3

Q4.

Solution

Concept — Michaelis–Menten Half-Maximum Condition:
The Michaelis–Menten equation is $v_0 = V_{\max}[\mathrm{S}]/(K_m + [\mathrm{S}])$. When $v_0 = V_{\max}/2$, solving gives $K_m = [\mathrm{S}]$ directly.

Step 1 — Apply the half-maximum condition:
$$\frac{V_{\max}}{2} = \frac{V_{\max}[\mathrm{S}]}{K_m + [\mathrm{S}]}$$
$K_m + [\mathrm{S}] = 2[\mathrm{S}] \quad \Rightarrow \quad K_m = [\mathrm{S}] = 4.0$ mM

Why other options are wrong:
Option A: 1.0 mM would give $v_0 = V_{\max}/5$.
Option B: 2.0 mM would give $v_0 = V_{\max}/3$.
Option C: 8.0 mM would give $v_0 = V_{\max}/3$ at $[\mathrm{S}] = 4$ mM.

Final Answer: $K_m = 4.0$ mM $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#4

Q5.

Solution

Concept — Particle in a 1D Box Energy Levels:
For a particle in a 1D box, the quantised energies are $E_n = n^2h^2/(8m_eL^2) = n^2E_1$. Levels are spaced in proportion to n^2, not linearly.

Step 1 — Calculate E_3:
$E_3 = 3^2 \times E_1 = 9 \times 0.376$ eV $= 3.38$ eV

Why other options are wrong:
Option B: 1.13 eV $= 3 \times 0.376$ uses a linear (incorrect) scaling.
Option C: 1.50 eV does not correspond to any n for $E_1 = 0.376$ eV.
Option D: 9.02 eV would require $E_1 \approx 1.00$ eV (wrong L).

Final Answer: $E_3 = 9E_1 = 3.38$ eV $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#5

Q6.

Solution

Concept — Hydrogen Atom 2s Radial Probability Distribution:
The $2s$ radial wavefunction has one radial node at $r = 2a_0$. The radial probability distribution $P(r) = r^2|R_{2s}|^2$ has an inner maximum near $r \approx 0.76\,a_0$ and an outer maximum at $r \approx 5.2\,a_0$.

Step 1 — Locate the outer maximum:
Setting $dP/dr = 0$ for the $2s$ function gives the outer maximum at $r_{\text{max}} = 5.2\,a_0$. This is the most probable radial position for an electron in the $2s$ orbital.

Why other options are wrong:
Option A: $1.0\,a_0$ corresponds to the $1s$ orbital outer maximum.
Option C: $3.0\,a_0$ is near the nodal position, not a maximum.
Option D: $9.0\,a_0$ is the outer maximum of the $2p$ orbital (approximately).

Final Answer: outer maximum at $\approx 5.2\,a_0 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#6

Q7.

Solution

Concept — Deshielding and ^{1}H Chemical Shifts:
Electron-withdrawing groups remove electron density from the attached CH_3 protons, reducing shielding and shifting the signal downfield (higher δ). The more electron-withdrawing the group, the higher the chemical shift.

Step 1 — Assign approximate δ values:
CH_3–alkyl: $\delta \approx 0.9$ ppm (most shielded)

CH_3–C=O (ketone): $\delta \approx 2.1$ ppm
CH_3–O (ether): $\delta \approx 3.3$ ppm
CH_3–NO_2 (nitro): $\delta \approx 4.3$ ppm (most deshielded)

Step 2 — Order of increasing δ:
alkyl $<$ C=O $<$ O $<$ NO_2 (option C).

Why other options are wrong:
Option A: Reverses the entire order; alkyl is the most shielded, not least.
Option B: Places O before NO_2 incorrectly and puts C=O last.
Option D: Places C=O below alkyl, which contradicts observed shifts.

Final Answer: alkyl $<$ C=O $<$ O $<$ NO_2 $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#7

Q8.

Solution

Concept — Counting Distinct ^{1}H NMR Environments:
Ethyl propanoate is CH_3CH_2–O–CO–CH_2CH_3. Each chemically non-equivalent set of protons gives one NMR signal.

Step 1 — Identify the four environments:
(1) $-$O$-$**CH_2**$-CH_3$: $\delta \approx 4.1$ ppm (quartet, ester O-methylene)
(2) $-$O$-CH_2-$**CH_3**: $\delta \approx 1.3$ ppm (triplet, ester terminal methyl)
(3) $-$CO$-$**CH_2**$-CH_3$: $\delta \approx 2.3$ ppm (quartet, acyl methylene)
(4) $-$CO$-CH_2-$**CH_3**: $\delta \approx 1.1$ ppm (triplet, acyl terminal methyl)
Total: **4 distinct signals**.

Why other options are wrong:
Option A: 2 signals would require a symmetric ester such as diethyl carbonate.
Option B: 3 signals – would result from accidental overlap of two environments.
Option C: 6 signals – over-counts individual carbon groups rather than environments.

Final Answer: 4 distinct ^{1}H NMR signals $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#8

Q9.

Solution

Concept — IR Carbonyl Stretching Frequencies:
The C=O stretching frequency is sensitive to the electronic environment. Conjugation and lone-pair donation lower the frequency; inductive withdrawal raises it. Esters absorb at higher frequency than ketones or carboxylic acids because of the

inductive effect of the OR oxygen on the carbonyl.

Step 1 — Match frequency to functional group:
Ester C=O: 1735–1750 cm^{-1} (matches the observed 1735 cm^{-1})
Aldehyde: $\approx$ 1720–1725 cm^{-1}
Ketone: $\approx$ 1710–1720 cm^{-1}
Carboxylic acid: $\approx$ 1700–1715 cm^{-1}

Why other options are wrong:
Option B: Aldehyde absorbs at $\sim$1725 cm^{-1}, lower than 1735.
Option C: Ketone C=O absorbs near 1715 cm^{-1}.
Option D: Carboxylic acid has a broad OH stretch and C=O near 1710 cm^{-1}.

Final Answer: 1735 cm^{-1} is characteristic of an ester C=O $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#9

Q10.

Solution

Concept — Beer–Lambert Law:
The Beer–Lambert law states $A = \varepsilon l c$, where A is absorbance, ε is molar absorptivity (L $\text{mol}^{-1}\text{cm}^{-1}$), l is path length (cm), and c is molar concentration.

Step 1 — Solve for concentration:
$$c = \frac{A}{\varepsilon l} = \frac{0.50}{1.00 \times 10^3 \times 1.0} = 5.0 \times 10^{-4} \text{ mol L}^{-1} = 0.50 \text{ mmol L}^{-1}$$

Why other options are wrong:
Option A: 0.20 mmol L^{-1} would give $A = 0.20$, not 0.50.
Option C: 2.0 mmol L^{-1} results from dividing by 250 instead of 1000.
Option D: 5.0 mmol L^{-1} omits the factor of 1000 in converting mol to mmol.

Final Answer: $c = 0.50$ mmol L^{-1} $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#10

Q11.

Solution

Concept — S_N2 Stereochemistry (Walden Inversion):
S_N2 reactions proceed via backside attack of the nucleophile, inverting the configuration at the tetrahedral carbon. Starting from the (R) enantiomer invariably gives the (S) product.

Step 1 — Assign the product configuration:
(R)-2-bromobutane: chiral centre is C-2 with groups Br, CH_3, C_2H_5, H.
HO^- attacks from the face opposite Br.
All three remaining groups invert their spatial arrangement.

The product is (S)-butan-2-ol.

Why other options are wrong:
Option A: (R)-butan-2-ol would require retention – only possible via S_N1 or double-inversion.
Option B: Racemic product forms in S_N1, not S_N2.
Option D: 1-Butanol would result from a different regiochemistry (S_N2 at C-1).

Final Answer: Walden inversion gives (S)-butan-2-ol $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#11

Q12.

Solution

Concept — E2 Elimination and Zaitsev's Rule:
Under E2 conditions with a strong base, the more substituted (thermodynamically more stable) alkene is the major product (Zaitsev's rule). More substituted alkenes have lower energy due to hyperconjugation.

Step 1 — Identify possible products from 2-bromo-2-methylbutane:
Structure: $CH_3C(Br)(CH_3)CH_2CH_3$.
Loss of H from C-1 methyl: gives $CH_2{=}C(CH_3)CH_2CH_3$ (2-methylbut-1-ene, disubstituted).
Loss of H from C-3 methylene: gives $CH_3C(CH_3){=}CHCH_3$ (2-methylbut-2-ene, trisubstituted).

Step 2 — Apply Zaitsev's rule:
2-Methylbut-2-ene (trisubstituted) is more stable $\rightarrow$ major product.

Why other options are wrong:
Option A: 2-Methylbut-1-ene is the Hofmann (minor) product.
Option B: 3-Methylbut-1-ene cannot form from this substrate by simple E2.
Option C: 2-Methylbut-3-ene does not exist from this substrate.

Final Answer: 2-Methylbut-2-ene (Zaitsev product) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#12

Q13.

Solution

Concept — EAS Directing Effects:
Ortho/para directors are electron-donating groups that stabilise the arenium ion intermediate via resonance donation into the ring. Meta directors are electron-withdrawing groups that destabilise all positions but destabilise ortho/para positions most.

Step 1 — Classify each substituent:
$-NH_2$: lone pair on N donates into ring via resonance $\rightarrow$ strong o/p director.
$-NO_2$, $-CN$, $-COOH$: all electron-withdrawing $\rightarrow$ meta directors.

Why other options are wrong:
Option B: $-NO_2$ withdraws electrons via both resonance and induction; meta director.
Option C: $-CN$ (nitrile) withdraws electrons via resonance; meta director.
Option D: $-COOH$ withdraws via resonance and induction; meta director.

Final Answer: $-NH_2$ is the ortho/para director $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#13

Q14.

Solution

Concept — Aldol Condensation Mechanism:
Base-catalysed aldol: base abstracts an α-proton from one carbonyl compound to form an enolate, which then attacks the carbonyl carbon of a second molecule, giving a β-hydroxy carbonyl compound (the aldol adduct). Dehydration (elimination) requires heating to give the α,β-unsaturated product.

Step 1 — Apply to acetaldehyde:
$CH_3CHO \xrightarrow{\text{base}} {}^{-}CH_2CHO$ (enolate)
Enolate attacks second $CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$ = 3-hydroxybutanal.

Why other options are wrong:
Option A: But-2-enal (α,β-unsaturated) is the product only after heating/dehydration.
Option C: Butanal would require a different reaction (reduction).
Option D: 2-Methylpropanal requires a different substrate.

Final Answer: Initial product is 3-hydroxybutanal $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#14

Q15.

Solution

Concept — Diels–Alder Endo Rule:
The $[4+2]$ cycloaddition is concerted, stereospecific, and suprafacial on both components. The endo transition state is kinetically favoured due to secondary orbital interactions between the substituents of the dienophile and the diene's π system, even though the exo product is thermodynamically more stable.

Step 1 — Identify the products:

Cyclopentadiene (diene, locked in s-cis) + maleic anhydride (dienophile) gives a bicyclo[2.2.1] (norbornene) skeleton. The anhydride groups can be endo (under the bridge) or exo (away from the bridge).

Step 2 — Apply the endo rule:
Secondary orbital interaction between C=O of anhydride and diene π orbitals stabilises the endo transition state. Product: *endo*-norbornene-2,3-dicarboxylic anhydride.

Why other options are wrong:
Option A: *exo* adduct is thermodynamically favoured but kinetically minor.
Option B: The reaction is highly stereoselective; endo strongly predominates.
Option D: $[4+2]$ cycloaddition always gives a cyclic product.

Final Answer: *endo*-bicyclic anhydride (endo rule) $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#15

Q16.

Solution

Concept — Grignard Addition to Ketones:
A Grignard reagent (RMgX) acts as a carbanion nucleophile (R^-). Addition to a ketone gives a tertiary alkoxide, which yields a tertiary alcohol upon aqueous workup.

Step 1 — Write the reaction:
$CH_3MgBr + (CH_3)_2C{=}O \rightarrow (CH_3)_3C{-}O^-MgBr^+$
Aqueous workup: $(CH_3)_3C{-}OH$ = 2-methylpropan-2-ol (*t*-butanol, tertiary alcohol).

Why other options are wrong:
Option A: Methanol (CH_3OH) would need formaldehyde as the substrate.
Option B: Propan-1-ol would result from MeMgBr + ethylene oxide.
Option C: Propan-2-ol would arise if H^- were added to acetone ($NaBH_4$ product).

Final Answer: MeMgBr + acetone $\rightarrow$ 2-methylpropan-2-ol $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#16

Q17.

Solution

Concept — Sharpless Asymmetric Epoxidation:
In the Sharpless epoxidation the Ti-tartrate catalyst delivers the oxidant (TBHP) to a specific face of the allylic alcohol. Using the mnemonic: draw the allylic alcohol with OH at the lower right; (+)-DET delivers oxygen to the β-face (top face).

Step 1 — Apply the Sharpless mnemonic:
(E)-but-2-en-1-ol drawn with OH at lower right, double bond at left.
$(+)$-diethyl tartrate $\rightarrow$ epoxide oxygen from the top (β-face).

Why other options are wrong:
Option B: α-face (bottom) epoxidation is obtained with $(-)$-DET.
Option C: The chiral tartrate ligand provides full enantioselectivity; racemic product is not formed.
Option D: Ti(Oi-Pr)$_4$ + TBHP alone does epoxidise; the tartrate controls facial selectivity.

Final Answer: $(+)$-DET delivers oxygen to the β-face $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#17

Q18.

Solution

Concept — Selective Reduction of Ketones:
$NaBH_4$ is a mild hydride reducing agent that selectively reduces aldehydes and ketones to primary and secondary alcohols, respectively. It does not reduce isolated alkenes, esters, or amides.

Step 1 — Evaluate each reagent:
H_2/Pd/C: chiefly hydrogenates alkenes and alkynes; not selective for isolated ketones.
$NaBH_4$: delivers H^- to the carbonyl carbon of cyclohexanone $\rightarrow$ cyclohexanol.
m-CPBA: a peracid oxidant used for epoxidation, not reduction.
MeMgBr: Grignard addition would give 1-methylcyclohexanol (tertiary), not cyclohexanol.

Why other options are wrong:
Option A: H_2/Pd/C does not efficiently reduce saturated ketones under mild conditions.
Option C: *m*-CPBA oxidises; it cannot reduce a ketone to an alcohol.
Option D: MeMgBr gives a different alcohol (tertiary, not secondary).

Final Answer: $NaBH_4$ cleanly converts cyclohexanone to cyclohexanol $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#18

Q19.

Solution

Concept — Free Radical Stability:
Free radical stability increases with the number of alkyl substituents on the radical carbon. Hyperconjugation from adjacent C–H bonds delocalises the unpaired

electron, stabilising higher-order radicals. The order is: tertiary $>$ secondary $>$ primary $>$ methyl.

Step 1 — Rank the radicals:
Methyl radical: no stabilisation (no α-C–H hyperconjugation).
Primary: 1 adjacent carbon donating via hyperconjugation.
Secondary: 2 adjacent carbons donating.
Tertiary: 3 adjacent carbons donating – most stable.

Why other options are wrong:
Option A: Completely reverses the correct order.
Option B: Places methyl above primary, which is incorrect.
Option D: Primary before secondary and tertiary – reverses the trend.

Final Answer: tertiary $>$ secondary $>$ primary $>$ methyl $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#19

Q20.

Solution

Concept — Kinetic vs Thermodynamic Enolate:
LDA is a bulky, non-nucleophilic, strong base. At $-78°$C (irreversible conditions) it abstracts the kinetically more accessible (less hindered) α-proton, giving the kinetic (less substituted) enolate. Thermodynamic conditions (weak base, equilibrating) give the more substituted enolate.

Step 1 — Identify the α-positions of 2-methylcyclohexan-1-one:
C-2 is α to the carbonyl and is more substituted (bears a methyl group).
C-6 is α to the carbonyl on the other side and is less substituted.
LDA at $-78°$C $\rightarrow$ kinetic enolate at C-6 (less hindered).

Why other options are wrong:
Option A: Thermodynamic enolate (C-2) requires equilibrating conditions (e.g., base + heat).
Option B: C-5 is not adjacent to the carbonyl; no enolate forms there.
Option C: LDA at low temperature gives essentially one enolate (kinetic control).

Final Answer: LDA/$-78°$C gives kinetic enolate at C-6 $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#20

Q21.

Solution

Concept — Crystal Field Stabilisation Energy (CFSE):
In an octahedral crystal field, d orbitals split into t_{2g} (at $-0.4\,\Delta_o$ each) and e_g (at

$+0.6\,\Delta_o$ each). CFSE = sum over all d electrons of their energy relative to the barycentre.

Step 1 — Determine the d^6 high-spin configuration:
High-spin d^6: fill by Hund's rule first, then pair.
$t_{2g}^4\, e_g^2$: four electrons in t_{2g}, two in e_g.

Step 2 — Calculate CFSE:
$\text{CFSE} = 4 \times (-0.4\,\Delta_o) + 2 \times (+0.6\,\Delta_o) = -1.6\,\Delta_o + 1.2\,\Delta_o = -0.4\,\Delta_o$

Why other options are wrong:
Option B: $-2.4\,\Delta_o$ corresponds to low-spin d^6 ($t_{2g}^6\, e_g^0$).
Option C: $-0.6\,\Delta_o$ is the CFSE for d^3 (t_{2g}^3).
Option D: CFSE = 0 only for d^0, d^5 high-spin, or d^{10}.

Final Answer: CFSE $= -0.4\,\Delta_o$ for $[Fe(H_2O)_6]^{2+} \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#21

Q22.

Solution

Concept — Jahn–Teller Distortion:
Jahn–Teller (JT) distortion occurs when a non-linear molecule has an orbitally degenerate ground state. The distortion is strongest when the degenerate e_g set is asymmetrically occupied, because the energy gained by elongation or compression is largest.

Step 1 — Check each configuration:
d^3: t_{2g}^3, symmetric t_{2g} occupancy $\rightarrow$ weak JT (only via t_{2g}).
d^9 (Cu^{2+}): $t_{2g}^6\, e_g^3$, one hole in e_g $\rightarrow$ strong JT distortion.
d^6 low-spin: $t_{2g}^6\, e_g^0$, no e_g occupancy $\rightarrow$ no JT.
d^{10}: all orbitals full $\rightarrow$ no degeneracy, no JT.

Why other options are wrong:
Option A: d^3 has a symmetric t_{2g}^3; only weak distortion possible.
Option C: Low-spin d^6 (t_{2g}^6) has no e_g electrons; no JT.
Option D: d^{10} is completely filled with no degeneracy.

Final Answer: d^9 shows the strongest Jahn–Teller distortion $\Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#22

Q23.

Solution

Concept — 18-Electron Rule for Organometallics:
The 18-electron rule states that stable transition metal complexes tend to have

18 valence electrons (d electrons of metal + electrons donated by ligands). CO donates 2 electrons.

Step 1 — Count electrons for each complex:
$[V(CO)_6]$: V(0) has 5 d-electrons; $+6 \times 2 = 12$ from CO $\rightarrow$ **17e**.
$[Mn(CO)_5]^+$: Mn(I) has 6 d-electrons; $+5 \times 2 = 10$ from CO $\rightarrow$ **16e**.
$[Cr(CO)_6]$: Cr(0) has 6 d-electrons; $+6 \times 2 = 12$ from CO $\rightarrow$ **18e**.
$[Fe(CO)_4]$: Fe(0) has 8 d-electrons; $+4 \times 2 = 8$ from CO $\rightarrow$ **16e**.

Why other options are wrong:
Option A: $V(CO)_6$ is a 17-electron radical species.
Option B: $[Mn(CO)_5]^+$ is a 16-electron square pyramidal cation.
Option D: $Fe(CO)_4$ is a 16-electron species.

Final Answer: $[Cr(CO)_6]$ is the 18-electron complex $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#23

Q24.

Solution

Concept — Geometric Isomerism in Square Planar Complexes:
For a square planar complex $[MA_2B_2]$, two arrangements are possible: *cis* (A ligands adjacent, 90° apart) and *trans* (A ligands opposite, 180° apart).

Step 1 — Enumerate isomers:
$[Pt(NH_3)_2Cl_2]$: *cis*-platin (both NH_3 cis) and *trans*-platin (both NH_3 trans). No other geometric arrangements exist for $[MA_2B_2]$.
Total: **2** geometric isomers.

Why other options are wrong:
Option A: 1 isomer would imply no geometric isomerism, which is incorrect.
Option B: 3 isomers occur for $[MA_2B_2C]$ in octahedral geometry.
Option C: 4 isomers would require additional ligand types.

Final Answer: 2 geometric isomers (*cis* and *trans*) $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#24

Q25.

Solution

Concept — VSEPR Theory for XeF_4:
Count electron domains around Xe: 4 bonding pairs (to 4 F atoms) + 2 lone pairs = 6 total. The electron geometry is **octahedral**. The 2 lone pairs occupy axial positions (mutually trans, 180° apart) to minimise repulsion. The 4 F atoms sit in the equatorial plane.

Step 1 — Determine molecular geometry:
Removing the lone pairs from the picture, the 4 F atoms define a **square planar** molecular geometry. VSEPR notation: AX_4E_2.

Why other options are wrong:
Option B: Tetrahedral requires 4 bonding pairs and 0 lone pairs (e.g., CH_4).
Option C: See-saw (AX_4E_1) has only 1 lone pair (e.g., SF_4).
Option D: Square pyramidal (AX_5E_1) has 5 bonding pairs and 1 lone pair.

Final Answer: XeF_4 is square planar $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#25

Q26.

Solution

Concept — Oxoacid Strength and Number of Oxygen Atoms:
For oxoacids of the same central element, acid strength increases with the number of non-bonded (additional) oxygen atoms attached to the central atom, because more oxygens withdraw electron density from the O–H bond, facilitating proton release.

Step 1 — Count oxygens and rank:
HClO: 1 O (hypochlorous, weakest acid).
$HClO_2$: 2 O (chlorous).
$HClO_3$: 3 O (chloric).
$HClO_4$: 4 O (perchloric, strongest acid, nearly completely ionised).
Increasing strength: $HClO < HClO_2 < HClO_3 < HClO_4$.

Why other options are wrong:
Option A: This is the decreasing order – completely reversed.
Option C: Non-monotonic order; $HClO_4$ should be last (strongest), not third.
Option D: Reverses the first three members; HClO should be weakest.

Final Answer: $HClO < HClO_2 < HClO_3 < HClO_4 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#26

Q27.

Solution

Concept — FCC Packing Efficiency:
In the face-centred cubic (FCC, cubic close-packed) structure, there are 4 atoms per unit cell with radius r and cell parameter $a = 2\sqrt{2}\,r$.

Step 1 — Calculate packing efficiency:
Volume of atoms $= 4 \times \dfrac{4}{3}\pi r^3$

Volume of cell $= a^3 = (2\sqrt{2}\,r)^3 = 16\sqrt{2}\,r^3$

Efficiency $= \dfrac{4 \times (4\pi r^3/3)}{16\sqrt{2}\,r^3} = \dfrac{16\pi/3}{16\sqrt{2}} = \dfrac{\pi}{3\sqrt{2}} \approx 74.05\%$

Why other options are wrong:

Option A: 52.4% is the packing efficiency of the simple cubic cell.

Option B: 68.0% is the packing efficiency of the body-centred cubic (BCC) cell.

Option D: 90.7% exceeds the physical maximum for sphere packing.

Final Answer: FCC packing efficiency $\approx 74.1\% \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#27

Q28.

Solution

Concept — Metal Centre in Vitamin B_{12}:

Cobalamin (vitamin B_{12}) belongs to the corrinoid family. The corrin ring coordinates a central cobalt ion that can exist in $+1$, $+2$, or $+3$ oxidation states and is essential for the cofactor's radical and organometallic reactivity.

Step 1 — Identify the metal:

Cobalamin = cobalt-containing corrinoid.

The Co–C bond (cobalt-carbon σ-bond) is the defining feature of the coenzyme form, adenosylcobalamin.

Why other options are wrong:

Option A: Iron is the metal in haemoglobin, myoglobin, and haem enzymes.

Option B: Copper is found in azurin, ceruloplasmin, and cytochrome c oxidase.

Option C: Zinc is the metal in carbonic anhydrase, carboxypeptidase, and zinc-finger proteins.

Final Answer: Cobalt (Co) is at the active site of vitamin $B_{12} \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#28

Q29.

Solution

Concept — Back Titration Calculation:

Excess reagent from the primary reaction is titrated with a second standard solution. Moles of $CaCO_3$ = (moles HCl added − moles NaOH used) /2 (stoichiometry of the $CaCO_3$ + 2 HCl reaction).

Step 1 — Moles of HCl and NaOH:

$n(\text{HCl}) = 0.0250\ \text{L} \times 0.200\ \text{mol L}^{-1} = 5.00 \times 10^{-3}\ \text{mol}$

$n(\text{NaOH}) = 0.0125\ \text{L} \times 0.100\ \text{mol L}^{-1} = 1.25 \times 10^{-3}\ \text{mol}$

Step 2 — Moles of HCl reacted with $CaCO_3$:

$n(\text{HCl, reacted}) = 5.00 \times 10^{-3} - 1.25 \times 10^{-3} = 3.75 \times 10^{-3}$ mol
$n(\text{CaCO}_3) = 3.75 \times 10^{-3}/2 = 1.875 \times 10^{-3}$ mol
$m(\text{CaCO}_3) = 1.875 \times 10^{-3} \times 100 = 0.1875$ g
Purity $= (0.1875/0.500) \times 100 = 37.5\%$

Why other options are wrong:
Option B: 50.0% arises from neglecting the factor of 2 in the stoichiometry.
Option C: 62.5% results from using $n(\text{HCl, reacted})$ directly as $n(\text{CaCO}_3)$.
Option D: 75.0% would require $n(\text{CaCO}_3) = 3.75 \times 10^{-3}$ mol.

Final Answer: Percentage purity $= 37.5\% \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#29

Q30.

Solution

Concept — Chromatographic Resolution:
The resolution $R_s = 2(t_{R2} - t_{R1})/(w_1 + w_2)$ measures the degree of separation between two adjacent peaks. $R_s \geq 1.5$ indicates baseline separation.

Step 1 — Substitute values:
$$R_s = \frac{2(11.0 - 10.0)}{0.50 + 0.50} = \frac{2 \times 1.0}{1.0} = 2.0$$

Why other options are wrong:
Option A: $R_s = 1.0$ would require peaks only half as far apart.
Option C: $R_s = 0.5$ means poor separation; peaks heavily overlap.
Option D: $R_s = 4.0$ would need twice the retention-time difference or half the widths.

Final Answer: $R_s = 2.0 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#30

Q31.

Solution

Concept — Nernst Slope for Ion-Selective Electrodes:
The Nernst equation gives the electrode potential: $E = E^\circ + (RT/nF)\ln a$. At 25°C: $RT/F = 0.02569$ V. For a monovalent cation ($n = 1$), the slope of E vs log(activity) is $2.303 \times RT/F = 0.05916$ V ≈ 59.2 mV per decade.

Step 1 — Calculate the slope:
Slope $= 2.303 \times 0.02569$ V $= 0.05916$ V $= 59.16$ mV per decade ≈ 59.2 mV/decade.

Why other options are wrong:
Option A: 29.6 mV/decade applies to a divalent cation ($n = 2$; slope halved).
Option B: 118.3 mV/decade would require $n = 0.5$ (non-physical for simple ions).

Option D: 25.7 mV/decade is RT/F itself (without the 2.303 factor).

Final Answer: Nernst slope ≈ 59.2 mV/decade for monovalent cation $\Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#31

Q32.

Solution

Concept — Faraday's Law of Electrolysis:

Mass deposited: $m = \dfrac{I \cdot t \cdot M}{n \cdot F}$, where I = current (A), t = time (s), M = molar mass, n = number of electrons transferred, F = Faraday constant.

Step 1 — Substitute values:

$$m = \frac{2.00\ \text{A} \times 965\ \text{s} \times 63.5\ \text{g mol}^{-1}}{2 \times 96500\ \text{C mol}^{-1}} = \frac{122{,}510}{193{,}000} = 0.635\ \text{g}$$

Why other options are wrong:

Option A: 0.317 g uses $n = 1$ (incorrect; Cu^{2+} requires 2 electrons).

Option B: 1.270 g results from forgetting to include $n = 2$ (dividing numerator by 1).

Option C: 1.905 g has an arithmetic error in the product.

Final Answer: Mass of Cu deposited $= 0.635$ g $\Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#32

Q33.

Solution

Concept — Standard Cell Potential:

For a galvanic cell, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ (reduction potentials). The cathode is the site of reduction (higher E°) and the anode is the site of oxidation (lower E°).

Step 1 — Identify cathode and anode:

$Cu^{2+} + 2e^- \rightarrow Cu$: $E^\circ = +0.34$ V (cathode, reduction).

$Zn \rightarrow Zn^{2+} + 2e^-$: $E^\circ(\text{oxidation}) = +0.76$ V; $E^\circ(\text{reduction}) = -0.76$ V (anode).

Step 2 — Compute E°_{cell}:

$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10$ V

Why other options are wrong:

Option B: -1.10 V would indicate a non-spontaneous cell (reversed).

Option C: $+0.42$ V results from $0.34 + 0.08$ (incorrect arithmetic).

Option D: $+0.76$ V is only the Zn half-cell potential, not the full cell.

Final Answer: $E^\circ_{\text{cell}} = +1.10$ V $\Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#33

Q34.

Solution

Concept — Boiling-Point Elevation (Colligative Property):
$\Delta T_b = K_b \cdot m$, where m is the molality of the solution (mol solute per kg solvent). For a non-electrolyte, the van't Hoff factor $i = 1$.

Step 1 — Calculate molality:
$n(\text{glucose}) = 10.0\ \text{g}/180\ \text{g mol}^{-1} = 0.05556\ \text{mol}$
$m = 0.05556\ \text{mol}/0.100\ \text{kg} = 0.5556\ \text{mol kg}^{-1}$

Step 2 — Calculate ΔT_b:
$\Delta T_b = 0.512\ \text{K kg mol}^{-1} \times 0.5556\ \text{mol kg}^{-1} = 0.285\ \text{K} \approx 0.28\ \text{K}$

Why other options are wrong:
Option A: 0.14 K uses half the correct molality (error of a factor of 2).
Option C: 0.56 K doubles the molality (uses 200 g solvent erroneously).
Option D: 1.12 K is four times the correct value.

Final Answer: $\Delta T_b \approx 0.28\ \text{K} \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#34

Q35.

Solution

Concept — Boltzmann Statistics in the High-Temperature Limit:
For a two-level system, the Boltzmann population ratio is $n_{\text{upper}}/n_{\text{lower}} = \exp(-\varepsilon/kT)$. As $T \to \infty$, $\varepsilon/kT \to 0$, so the exponential factor $\to e^0 = 1$, giving equal populations in both levels.

Step 1 — Evaluate the limit:
$\lim_{T\to\infty} e^{-\varepsilon/(kT)} = e^0 = 1$
The upper and lower levels become equally populated.

Why other options are wrong:
Option A: 0 is the $T \to 0$ limit (all population in lower level).
Option B: $\exp(-\varepsilon/kT)$ is the ratio at finite T, not its limiting value.
Option D: ∞ is not physically reachable; the ratio is bounded by 1 at most for a two-level system.

Final Answer: $n_{\text{upper}}/n_{\text{lower}} \to 1$ as $T \to \infty \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#35

Q36.

Solution

Concept — Boltzmann Distribution for Spectroscopic Levels:
$n_2/n_1 = g_2/g_1 \cdot \exp(-\Delta\tilde{\nu} \cdot hc/(kT))$. With both levels non-degenerate ($g_2/g_1 = 1$) and using $hc/k = 1.4388$ cm K: $\Delta E/(kT) = \Delta\tilde{\nu} \cdot hc/(kT) = \Delta\tilde{\nu} \times 1.4388/T$.

Step 1 — Calculate the exponent:
$\Delta E/(kT) = 200\ \text{cm}^{-1} \times 1.4388\ \text{cm K}/300\ \text{K} = 287.76/300 = 0.9592$

Step 2 — Evaluate the population ratio:
$n_2/n_1 = e^{-0.9592} = 1/e^{0.9592} \approx 1/2.610 \approx 0.383 \approx 0.38$

Why other options are wrong:
Option A: 0.95 would correspond to a separation near $14\ \text{cm}^{-1}$.
Option B: 0.51 corresponds to $\Delta\tilde{\nu} \approx 140\ \text{cm}^{-1}$.
Option C: $0.63 \approx e^{-0.46}$ corresponds to $\Delta\tilde{\nu} \approx 96\ \text{cm}^{-1}$.

Final Answer: $n_2/n_1 \approx 0.38 \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#36

Q37.

Solution

Concept — Actual Free Energy of ATP Hydrolysis:
$\Delta G = \Delta G^{\circ\prime} + RT \ln Q$, where $Q = [\text{ADP}][\text{P}_i]/[\text{ATP}]$ under cellular conditions. Because cellular [ATP]/[ADP] is maintained far from equilibrium, ΔG is substantially more negative than $\Delta G^{\circ\prime}$.

Step 1 — Compute the reaction quotient:
$$Q = \frac{[\text{ADP}][\text{P}_i]}{[\text{ATP}]} = \frac{10^{-3}\ \text{M} \times 10^{-2}\ \text{M}}{10^{-2}\ \text{M}} = 10^{-3}$$

Step 2 — Evaluate ΔG:
$RT = 8.314 \times 10^{-3} \times 310 = 2.577\ \text{kJ mol}^{-1}$
$RT \ln(10^{-3}) = 2.577 \times (-6.908) = -17.8\ \text{kJ mol}^{-1}$
$\Delta G = -30.5 + (-17.8) = -48.3\ \text{kJ mol}^{-1} \approx -48\ \text{kJ mol}^{-1}$

Why other options are wrong:
Option B: $-30.5\ \text{kJ mol}^{-1}$ is the standard value, ignoring cellular concentrations.
Option C: $-13\ \text{kJ mol}^{-1}$ would require $Q \gg 1$.
Option D: $-65\ \text{kJ mol}^{-1}$ overestimates the Q-correction term.

Final Answer: $\Delta G \approx -48\ \text{kJ mol}^{-1} \Rightarrow$ **(A)**

Answer: (A) ← Go Back to Q#37

Q38.

Solution

Concept — Henderson–Hasselbalch Equation:
$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$. This equation is exact for an ideal buffer and allows rapid calculation of pH from the ratio of conjugate base to weak acid.

Step 1 — Substitute values:
$\text{pH} = 6.80 + \log(4.0) = 6.80 + 0.602 = 7.402 \approx 7.40$

Why other options are wrong:
Option A: 6.20 would require $\log([\text{A}^-]/[\text{HA}]) = -0.60$, i.e., ratio $= 0.25$.
Option C: 6.80 is the pH when $[\text{A}^-]/[\text{HA}] = 1$ (equimolar buffer, not ratio 4).
Option D: 8.00 would require $\log(\text{ratio}) = 1.2$, i.e., ratio ≈ 16.

Final Answer: $\text{pH} = 7.40 \Rightarrow$ **(B)**

Answer: (B) ← Go Back to Q#38

Q39.

Solution

Concept — Separation of Variables for First-Order ODE:
The rate equation $d[\text{B}]/dt = k([\text{A}]_0 - [\text{B}])$ is a first-order linear ODE that is directly separable. Rearranging: $d[\text{B}]/([\text{A}]_0 - [\text{B}]) = k\,dt$.

Step 1 — Integrate (separation of variables):
$$\int_0^{[\text{B}]} \frac{d[\text{B}]'}{[\text{A}]_0 - [\text{B}]'} = \int_0^t k\,dt'$$
$$-\ln\left(\frac{[\text{A}]_0 - [\text{B}]}{[\text{A}]_0}\right) = kt$$
$$[\text{B}](t) = [\text{A}]_0\left(1 - e^{-kt}\right)$$

Why other options are wrong:
Option A: Laplace transforms give the same result but are far more complex; not the "most direct" method.
Option B: Fourier transforms apply to linear PDEs with periodic boundary conditions.
Option D: Finite difference methods are numerical approximations, not analytical solutions.

Final Answer: Separation of variables gives $[\text{B}] = [\text{A}]_0(1 - e^{-kt}) \Rightarrow$ **(C)**

Answer: (C) ← Go Back to Q#39

Q40.

Solution

Concept — Stokes–Einstein Diffusion and Particle Size:
The Stokes–Einstein equation $D = kT/(6\pi\eta r)$ shows that $D \propto 1/r$ at constant T

and η. Increasing the particle radius reduces the diffusion coefficient inversely.

Step 1 — Apply the inverse proportionality:
If $r \to 2r$, then $D_{\text{new}} = \dfrac{kT}{6\pi\eta(2r)} = \dfrac{1}{2} \cdot \dfrac{kT}{6\pi\eta r} = \dfrac{D_1}{2}$
The diffusion coefficient **decreases to one-half** its original value.

Why other options are wrong:
Option A: Doubling would occur if $D \propto r$ (incorrect – D decreases with r).
Option B: Quadrupling would arise if $D \propto 1/r^2$ (also incorrect).
Option C: One-quarter reduction requires $r \to 4r$ (not a doubling of r).

Final Answer: Doubling r halves $D \Rightarrow$ **(D)**

Answer: (D) ← Go Back to Q#40

Answer Key

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