IIT JAM Chemistry

Sample Paper – 3

Instructions

- This paper contains **60 questions** carrying a maximum of **100 marks**. Duration: **3 hours (180 minutes)**.
- **Section A** (**Q1–Q30**, MCQ): Q1–Q10 carry **+1 mark** each; wrong response: $-\frac{1}{3}$ mark. Q11–Q30 carry **+2 marks** each; wrong response: $-\frac{2}{3}$ mark. Choose the **single best** option.
- **Section B** (**Q31–Q40**, MSQ): Each carries **+2 marks**. **No negative marking. One or more** options may be correct; full marks only if *all* correct options are selected; no partial credit.
- **Section C** (**Q41–Q60**, NAT): Q41–Q50 carry **+1 mark**; Q51–Q60 carry **+2 marks**. **No negative marking.** Enter the numerical value using the virtual keypad (integer or decimal as appropriate).
- **Calculator policy:** Personal calculators are **strictly prohibited**. A virtual scientific calculator is provided in the CBT interface. Rough sheets are supplied at the examination centre.
- Once you move to the next section, you cannot return to a previous section. Manage time accordingly.

Section A — Multiple Choice Questions (MCQ)

***Q1–Q10**: 1 mark each ($-\frac{1}{3}$ for wrong). Choose the **single** correct option.*

Q1. The Pauling electronegativity values of the second-period elements C, N, O, and F are 2.5, 3.0, 3.5, and 4.0, respectively. Electronegativity increases across a period (left to right) and decreases down a group. Which of the following lists these four elements in **decreasing** order of electronegativity?

(A) F $>$ N $>$ O $>$ C
(B) O $>$ F $>$ N $>$ C
(C) C $>$ N $>$ O $>$ F
(D) F $>$ O $>$ N $>$ C

Q2. According to the de Broglie relation $\lambda = h/(mv)$, when rewritten for a particle with kinetic energy $KE = \frac{1}{2}mv^2$, we get $\lambda = h/\sqrt{2m \cdot KE}$.

Which of the following particles has the **longest** de Broglie wavelength when all four particles have the *same kinetic energy*?

(A) Proton ($m_p \approx 1.67 \times 10^{-27}$ kg)
(B) Alpha particle ($m_\alpha \approx 6.64 \times 10^{-27}$ kg)
(C) Electron ($m_e \approx 9.11 \times 10^{-31}$ kg)
(D) Neutron ($m_n \approx 1.67 \times 10^{-27}$ kg)

Q3. Lithium (Li) exhibits anomalous behaviour among alkali metals and resembles magnesium (Mg) due to their similar charge density (diagonal relationship). Which of the following properties is **shared by Li and Mg** but not by other alkali metals?

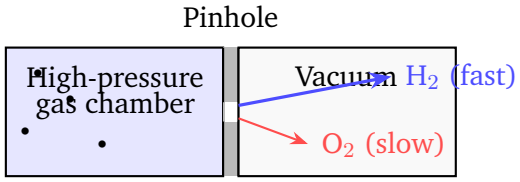
(A) Both Li and Mg react directly with molecular nitrogen (N_2) at room temperature to form their respective nitrides: Li_3N and Mg_3N_2.
(B) Both Li and Mg form hydroxides that are completely dissociated strong bases in dilute aqueous solution.
(C) Both Li and Mg react explosively with water at room temperature, liberating hydrogen.
(D) Both Li and Mg form peroxides (Li_2O_2 and MgO_2) on reacting with excess O_2.

Q4. The electron-withdrawing inductive effect ($-I$) of chlorine substituents stabilises the carboxylate anion and increases the acidity of carboxylic acids. More chlorine atoms $\Rightarrow$ greater inductive withdrawal $\Rightarrow$ stronger acid. Which of the following correctly ranks these acids in **decreasing** order of acid strength?

(A) $CH_3COOH > ClCH_2COOH > Cl_3CCOOH$
(B) $Cl_3CCOOH > ClCH_2COOH > CH_3COOH$
(C) $ClCH_2COOH > Cl_3CCOOH > CH_3COOH$
(D) $CH_3COOH > Cl_3CCOOH > ClCH_2COOH$

Q5. Two gases, H_2 ($M = 2$ g/mol) and O_2 ($M = 32$ g/mol), are allowed to effuse separately through a small pinhole under identical conditions of temperature and pressure, as illustrated below. According to Graham's law, the rate of effusion is inversely proportional to the square root of

molar mass. The ratio of the rate of effusion of H_2 to that of O_2 (i.e. r_{H_2}/r_{O_2}) is:



(A) 2
(B) 8
(C) $\sqrt{2}$
(D) 4

Q6. The bond dissociation enthalpy of the hydrogen halides (H−X) decreases as the halogen atom becomes larger, because orbital overlap between H 1s and halogen valence orbital becomes progressively poorer. Which of the following correctly lists the H−X bond strengths in **decreasing** order?

(A) HF > HCl > HBr > HI
(B) HI > HBr > HCl > HF
(C) HCl > HF > HBr > HI
(D) HF > HI > HCl > HBr

Q7. A chiral organic compound contains **three** independent stereocenters and has no internal plane of symmetry (no meso form possible). The *maximum* possible number of stereoisomers (including all enantiomers and diastereomers) for this compound is:

(A) 4
(B) 8
(C) 6
(D) 16

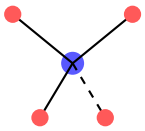
Q8. Which of the following reactions is expected to have the **most positive** standard entropy change (ΔS°)? (Consider the change in the number of moles of gaseous species, Δn_g.)

(A) $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ $[\Delta n_g = -2]$

(B) $C(s) + O_2(g) \rightarrow CO_2(g)$ $[\Delta n_g = 0]$
(C) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $[\Delta n_g = +1]$
(D) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $[\Delta n_g = 0]$

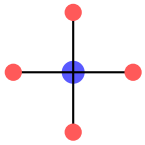
Q9. Among the following 4-coordinate metal complexes, which metal ion **invariably** adopts a **square planar** geometry due to its d^8 configuration and strong crystal-field stabilisation energy (CFSE)?

Tetrahedral



e.g. $[ZnCl_4]^{2-}$

Square Planar



e.g. $[PtCl_4]^{2-}$

(A) Zn^{2+} (d^{10} — tetrahedral in most 4-coordinate complexes)
(B) Ni^{2+} (d^8, weak-field ligands — tetrahedral possible)
(C) Cu^{2+} (d^9 — Jahn–Teller distorted octahedral, not inherently 4-coordinate square planar)
(D) Pt^{2+} (d^8, strong-field metal — always square planar)

Q10. Bromination of toluene with $Br_2/FeBr_3$ proceeds by electrophilic aromatic substitution (EAS). The methyl group is an *ortho/para* activating director. Due to steric hindrance at the *ortho* positions, the **major** product isolated in practice is:

(A) 4-Bromotoluene (para-bromotoluene)
(B) 3-Bromotoluene (meta-bromotoluene)
(C) 2-Bromotoluene (ortho-bromotoluene) as the sole product
(D) 2,4-Dibromotoluene (requires excess Br_2)

***Q11–Q30**: 2 marks each ($-\frac{2}{3}$ for wrong). Choose the **single** correct option.*

Q11. Given the standard reduction potentials: $E^\circ(Zn^{2+}/Zn) = -0.76$ V, $E^\circ(Cu^{2+}/Cu) = +0.34$ V, $E^\circ(Fe^{3+}/Fe^{2+}) = +0.77$ V, and $E^\circ(Ag^+/Ag) = +0.80$ V. For a spontaneous galvanic cell, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Which combination gives the **maximum** standard cell EMF?

(A) Cu^{2+}/Cu (cathode) $\|$ Zn/Zn^{2+} (anode): $E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10$ V

(B) Ag^{+}/Ag (cathode) $\|$ Zn/Zn^{2+} (anode): $E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56$ V

(C) Fe^{3+}/Fe^{2+} (cathode) $\|$ Zn/Zn^{2+} (anode): $E^\circ_{\text{cell}} = 0.77 - (-0.76) = 1.53$ V

(D) Ag^{+}/Ag (cathode) $\|$ Cu/Cu^{2+} (anode): $E^\circ_{\text{cell}} = 0.80 - 0.34 = 0.46$ V

Q12. Acyl derivatives of carboxylic acids differ in their reactivity toward nucleophilic acyl substitution. The reactivity is governed by the stability of the leaving group: a more stable (weaker base) leaving group makes the reaction faster. Which of the following correctly gives the reactivity order (**most reactive** first)?

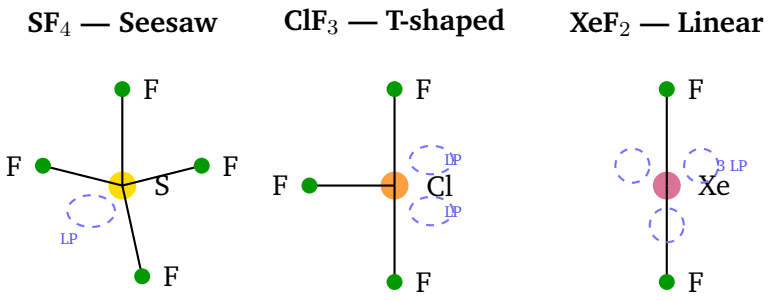
(A) Ester $>$ Acid anhydride $>$ Acid chloride $>$ Amide

(B) Amide $>$ Ester $>$ Acid anhydride $>$ Acid chloride

(C) Acid chloride $>$ Acid anhydride $>$ Ester $>$ Amide

(D) Acid anhydride $>$ Acid chloride $>$ Amide $>$ Ester

Q13. According to VSEPR theory, the molecular geometry of SF_4 is determined by 4 bond pairs and 1 lone pair on sulfur. The lone pair occupies an equatorial position in the trigonal bipyramidal electron-pair geometry, giving a **molecular** geometry that is (see diagram below):



(A) Square planar

(B) Trigonal bipyramidal

(C) Trigonal pyramidal

(D) Seesaw (butterfly)

Q14. Fischer esterification is an acid-catalysed equilibrium reaction between a carboxylic acid and an alcohol to give an ester and water. Which statement correctly describes the **role of the acid catalyst** and the key mechanistic step?

(A) The acid catalyst protonates the carbonyl oxygen of the carboxylic acid, activating the carbonyl carbon toward nucleophilic attack by the alcohol oxygen; subsequent proton transfers and loss of water give the ester.

(B) The acid catalyst deprotonates the alcohol, forming an alkoxide ion which then attacks the carbonyl carbon directly.

(C) The reaction is irreversible; once the ester is formed it cannot revert to the carboxylic acid and alcohol.

(D) The acid catalyst converts the carboxylic acid into a free acylium ion ($RC{\equiv}O^{+}$) which is then trapped by the alcohol.

Q15. 2,4-Dinitrochlorobenzene undergoes nucleophilic aromatic substitution (NAS) with NaOH far more readily than chlorobenzene does. The correct explanation for this enhanced reactivity is:

(A) Chlorobenzene undergoes NAS by an elimination–addition (benzyne) mechanism; dinitrochlorobenzene is simply faster due to a different pathway.

(B) The two nitro groups at the *ortho* and *para* positions relative to Cl stabilise the anionic Meisenheimer complex (addition intermediate) through resonance delocalization of the negative charge, greatly lowering the activation energy.

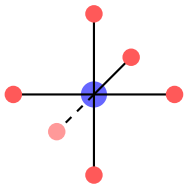
(C) The inductive electron withdrawal by the two nitro groups weakens the C–Cl bond, making Cl^{-} a better leaving group through an SN2-like direct displacement.

(D) NAS requires an acidic medium; the nitro groups lower the pH sufficiently to catalyse the reaction with OH^{-}.

Q16. The Jahn–Teller theorem states that any non-linear molecule with a degenerate electronic ground state will distort to remove the degeneracy. For octahedral complexes, which electronic configuration undergoes the

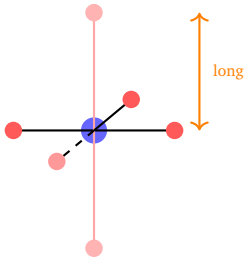
most pronounced Jahn–Teller distortion?

Regular O_h



All 6 bonds equal

JT Elongated



4 short + 2 long

(A) d^6 high-spin octahedral (e.g. Fe^{2+} with weak-field ligands, $(t_{2g})^4(e_g)^2$)
(B) d^5 high-spin octahedral (e.g. Mn^{2+}, $(t_{2g})^3(e_g)^2$, half-filled — non-degenerate)
(C) d^9 octahedral (e.g. Cu^{2+}, $(t_{2g})^6(e_g)^3$ — one hole in e_g, strong degeneracy)
(D) d^3 octahedral (e.g. Cr^{3+}, $(t_{2g})^3$ — non-degenerate ground state)

Q17. For the Haber synthesis: $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $\Delta H = -92$ kJ. Which of the following changes **correctly** shifts the equilibrium to the **right** (favouring NH_3 formation)?

(A) Increasing the temperature (shifts equilibrium left, toward endothermic direction)
(B) Adding an inert gas at constant volume (partial pressures unchanged, no shift occurs)
(C) Decreasing the total pressure (equilibrium shifts left, toward more moles of gas)
(D) Increasing the total pressure at constant temperature (equilibrium shifts right, toward fewer moles of gas: 4 mol $\rightarrow$ 2 mol)

Q18. The mass spectrum of 1-propanol ($CH_3CH_2CH_2OH$, $M = 60$ g/mol) shows a molecular ion and characteristic fragment peaks. The most abundant fragment (base peak) is formed by α-cleavage adjacent to the oxygen. Which of the following correctly identifies the molecular ion peak and base peak?

(A) $M^+ = 60$; base peak at $m/z = 31$ ($CH_2{=}OH^+$, formed by loss of C_2H_5 via α-cleavage)

(B) $M^+ = 59$; base peak at $m/z = 45$ (loss of CH_3)
(C) $M^+ = 62$; base peak at $m/z = 43$ (loss of OH)
(D) $M^+ = 60$; the molecular ion peak is also the base peak (no fragmentation observed)

Q19. Iodine pentafluoride (IF_5) is an interhalogen compound in which iodine has an expanded octet. With 5 bonding pairs and 1 lone pair, the electron-pair geometry is octahedral. The **molecular** geometry of IF_5 is:

(A) Trigonal bipyramidal (5 bond pairs, 0 lone pairs)
(B) Square pyramidal (5 bond pairs, 1 lone pair — lone pair in one octahedral position)
(C) Pentagonal planar (requires 5 electron pairs in the equatorial plane)
(D) T-shaped (3 bond pairs, 2 lone pairs)

Q20. 5.85 g of NaCl (molar mass $= 58.5$ g/mol) is dissolved in 500 g of water. Using $K_b(\text{water}) = 0.512\,^\circ\text{C kg mol}^{-1}$ and van't Hoff factor $i = 2$ (complete dissociation of NaCl into Na^+ and Cl^-), the elevation in boiling point $\Delta T_b = i \cdot K_b \cdot m$ is:

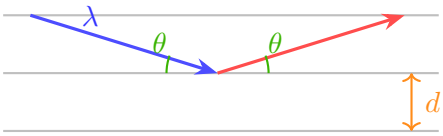
(A) $0.512\,^\circ$C
(B) $0.102\,^\circ$C
(C) $0.205\,^\circ$C
(D) $0.410\,^\circ$C

Q21. Friedel–Crafts reactions with Lewis acid catalysts ($AlCl_3$) are used for alkylation and acylation of aromatic rings. Which of the following statements is **correct**?

(A) Friedel–Crafts alkylation with isopropyl chloride always gives the expected straight-chain product without any carbocation rearrangement.
(B) Friedel–Crafts alkylation of benzene with n-propyl chloride gives n-propylbenzene as the exclusive product.
(C) Friedel–Crafts acylation of benzene with propanoyl chloride (CH_3CH_2COCl/AlC gives a product resulting from rearrangement of the acylium ion.
(D) Friedel–Crafts acylation of benzene with acetyl chloride ($CH_3COCl/AlCl_3$) gives **acetophenone** without any carbocation rearrangement, because

the acylium ion is resonance-stabilised and does not rearrange.

Q22. X-rays of wavelength $\lambda = 1.54$ Å are reflected from crystal planes of spacing $d = 3.08$ Å. Using Bragg's law $2d\sin\theta = n\lambda$ with $n = 1$, what is the glancing angle θ (the angle between the incident beam and the crystal plane surface)?



(A) $\theta \approx 14.5°$
(B) $\theta \approx 30.0°$
(C) $\theta \approx 7.25°$
(D) $\theta \approx 45.0°$

Q23. Phosphorous acid (H_3PO_3) appears to contain three acidic hydrogens from its formula, yet it is in fact a **diprotic** acid ($pK_{a1} = 1.3$, $pK_{a2} = 6.7$; the third proton does not dissociate). The correct explanation is:

(A) One hydrogen atom is permanently expelled as H_2 gas during dissolution, leaving only two ionisable protons.
(B) One hydrogen atom is directly bonded to the phosphorus atom (P – H bond, not P – O – H); only the two O – H groups are ionisable.
(C) All three hydrogen atoms are equivalent but electrostatic repulsion prevents the third from dissociating.
(D) H_3PO_3 is actually a monoprotic acid with only one ionisable proton due to internal hydrogen bonding.

Q24. Styrene oxide (an α-phenyl epoxide) undergoes ring opening with water. Under **acid-catalysed** conditions, the regiochemistry follows an SN1-like pathway. The nucleophile (H_2O) attacks which carbon, and what is the product?

(A) The less substituted ($-CH_2-$) carbon (SN2-like, base-catalysed regiochemistry); product: Ph–CH(epoxide-open)
(B) Styrene oxide does not react with water under acidic conditions.

(C) The more substituted benzylic carbon (Ph–$\overset{+}{C}$H$-$), which bears the partial positive charge; product: Ph–CH(OH)–CH_2OH

(D) The epoxide undergoes **elimination** under acidic conditions to give styrene + H_2O.

Q25. A colloidal sol of $Fe(OH)_3$ is prepared by hydrolysis of $FeCl_3$ in hot water. The particles selectively adsorb Fe^{3+} ions (from the medium) onto their surface, acquiring a characteristic charge. What is the sign of the charge on the $Fe(OH)_3$ sol particles?

(A) Negative (due to selective adsorption of OH^- ions)

(B) Neutral (no net charge on colloidal particles)

(C) Variable — depends entirely on the concentration of $FeCl_3$ used

(D) Positive (due to selective adsorption of Fe^{3+} ions on the particle surface)

Q26. The isotope ^{232}Th has a half-life $t_{1/2} = 1.40 \times 10^{10}$ yr. A sample initially containing N_0 atoms of ^{232}Th is stored for a period $t = 2.80 \times 10^{10}$ yr. The fraction of ^{232}Th atoms remaining (N/N_0) after this time is:

(A) 0.25

(B) 0.50

(C) 0.125

(D) 0.75

Q27. (R)-2-Bromobutane reacts with sodium cyanide (NaCN) in DMSO (a polar aprotic solvent) via a bimolecular nucleophilic substitution (SN2) mechanism. Given that SN2 proceeds with **complete inversion** of configuration (Walden inversion), the product 2-methylbutanenitrile has the configuration:

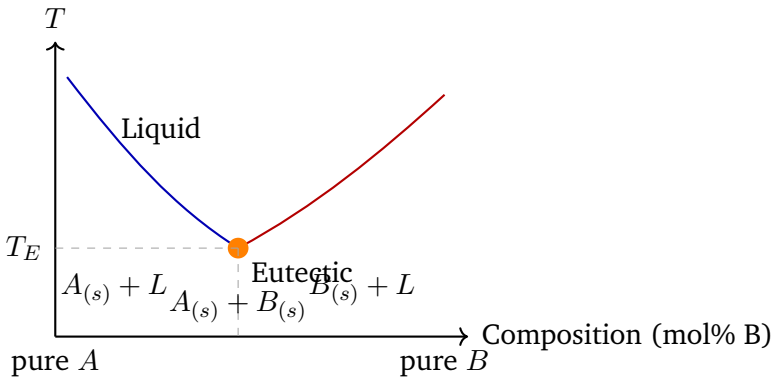
(A) (R)-2-methylbutanenitrile (retention of configuration)

(B) A racemic 50:50 mixture of (R)- and (S)-2-methylbutanenitrile

(C) (S)-2-methylbutanenitrile (complete inversion of configuration at the stereogenic centre)

(D) (R)-pentanenitrile (chain elongation with rearrangement)

Q28. For a two-component ($C = 2$) system studied at constant pressure (isobaric), the reduced Gibbs phase rule gives $F = C - P + 1$. At the **eutectic point** of a simple binary system, three phases coexist simultaneously: solid A + solid B + liquid. How many degrees of freedom F are there at the eutectic point?



(A) $F = 1$ (one degree of freedom — temperature can vary)

(B) $F = 0$ (system is invariant — temperature and composition are both fixed)

(C) $F = 2$ (two degrees of freedom)

(D) $F = 3$ (three degrees of freedom)

Q29. A Lewis acid is a species that **accepts** an electron pair; a Lewis base **donates** an electron pair. In which of the following reactions does $AlCl_3$ function as a **Lewis acid**?

(A) $AlCl_3$ donates a lone pair to BCl_3, forming a dative bond ($AlCl_3$ as Lewis base)

(B) $AlCl_3 + 3\,NaOH \rightarrow Al(OH)_3 + 3\,NaCl$ (simple metathesis, not Lewis acid–base)

(C) $2\,AlCl_3 \rightarrow Al_2Cl_6$ (dimerisation through bridging Cl atoms, mutual Lewis acid–base)

(D) $AlCl_3 + Cl^- \rightarrow AlCl_4^-$ ($AlCl_3$ accepts the electron pair from Cl^-, acting as Lewis acid)

Q30. In the Strecker synthesis, an aldehyde (RCHO) is converted to an α-amino acid in two steps: (1) reaction with NH_3 and HCN to give an α-amino nitrile; (2) hydrolysis of the nitrile group to COOH. When **propanal**

(CH_3CH_2CHO, R = ethyl) is the starting aldehyde, the α-amino acid obtained is:

(A) Alanine [2-aminopropanoic acid; from acetaldehyde, $R = CH_3$]
(B) Valine [2-amino-3-methylbutanoic acid; from isobutyraldehyde]
(C) 2-Aminobutanoic acid [$CH_3CH_2CH(NH_2)COOH$; from propanal, $R = CH_3CH_2$]
(D) Glycine [aminoacetic acid; from formaldehyde, $R = H$]

Section B — Multiple Select Questions (MSQ)

***Q31–Q40**: 2 marks each. **No negative marking.** **One or more** options are correct; full marks only if* all *correct options are selected.*

Q31. Which of the following statements about **entropy** are correct? Select **all** that apply.

(A) Entropy is a **state function**: its change (ΔS) depends only on the initial and final states of the system, not on the path taken.
(B) For a reversible process, $\Delta S_{\text{universe}} = 0$; for any spontaneous (irreversible) process, $\Delta S_{\text{universe}} > 0$ (Second Law of Thermodynamics).
(C) The entropy of a perfect crystal of any pure substance at 0 K is **always positive** (Third Law of Thermodynamics).
(D) The mixing of two different ideal gases at constant temperature and pressure always results in an increase in entropy ($\Delta S_{\text{mix}} = -nR\sum x_i \ln x_i > 0$).

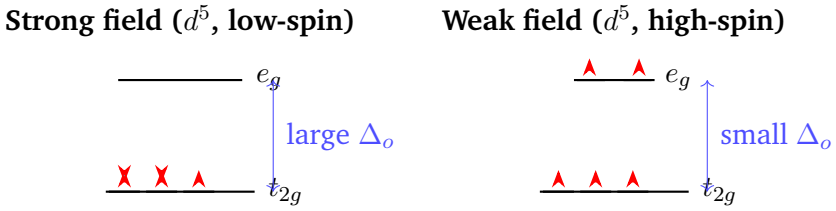
Q32. Which of the following statements about **E2 elimination** are correct? Select **all** that apply.

(A) E2 is a **bimolecular**, concerted reaction that requires a **base** (e.g. KO^{t}Bu or KOH/EtOH) to abstract the β-hydrogen simultaneously as the leaving group departs.
(B) E2 proceeds through a discrete planar **carbocation** intermediate (as in the E1 mechanism), which subsequently loses a proton to give the alkene.

(C) The E2 mechanism requires an **anti-periplanar** arrangement of the β-H and the leaving group (180° dihedral), imposed by orbital requirements of the concerted four-centre transition state.

(D) Under most conditions E2 produces the **more substituted** (Zaitsev) alkene as the major product.

Q33. Which of the following statements about **Crystal Field Theory (CFT)** are correct? Select **all** that apply.



(A) CFT predicts that all transition-metal complexes are **colourless** because the d orbitals in a complex remain degenerate.

(B) **Strong-field** ligands (CO, CN^-, en) cause a large Δ_o splitting, leading to **low-spin** complexes with fewer unpaired electrons.

(C) The colour of a transition-metal complex arises from the **absorption** of visible light; the energy of the absorbed photon equals the crystal-field splitting energy Δ_o.

(D) CFT predicts that $[Fe(CN)_6]^{4-}$ (d^6, CN^- is a strong-field ligand) is a **high-spin** complex with 4 unpaired electrons.

Q34. Which of the following statements about **photochemical reactions** are correct? Select **all** that apply.

(A) Photochemical reactions are initiated by the absorption of a photon ($h\nu$). According to the Grotthuss–Draper law, only the light **absorbed** by a substance can cause a photochemical change.

(B) The **quantum yield** ϕ is defined as the number of molecules reacting per photon absorbed. For chain reactions, $\phi \gg 1$ (e.g. $\phi \approx 10^6$ for H_2/Cl_2 photochlorination).

(C) The reaction $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ is a photochemical **chain reaction** initiated by Cl_2 photolysis and propagated by Cl• radicals.

(D) All photochemical reactions are **endothermic** overall because the light energy absorbed must exceed the activation energy; no energy is released in the products.

Q35. Which of the following statements about **directing effects** in electrophilic aromatic substitution (EAS) are correct? Select **all** that apply.

(A) Groups such as $-$OH, $-$OR, and $-NR_2$ are *ortho/para* directors that **activate** the benzene ring toward EAS (electron donation by resonance: $+M > -I$).

(B) Groups such as $-$COOH, $-$CHO, and $-NO_2$ are *ortho/para* directors that **activate** the ring toward EAS.

(C) Halogens ($-$F, $-$Cl, $-$Br, $-$I) are *ortho/para* directors but **deactivate** the ring (electron withdrawal by induction $>$ donation by resonance overall; ring is less reactive than benzene).

(D) The nitro group ($-NO_2$) is a strong **deactivating** group that directs an incoming electrophile to the **meta** position.

Q36. Which of the following statements about **atomic orbitals and nodal surfaces** are correct? Select **all** that apply.

(A) The **1s** orbital has exactly **one** radial node and no angular nodes.

(B) The number of **radial** nodes $= n - l - 1$; for the $2p$ orbital ($n = 2$, $l = 1$): number of radial nodes $= 2 - 1 - 1 = 0$.

(C) The **3d** orbital ($l = 2$) has exactly **three** angular nodes (nodal surfaces).

(D) The **total** number of nodal surfaces $= n-1$; for the 3s orbital ($n = 3$): total nodes $= 2$ (all radial; angular nodes $= l = 0$).

Q37. Which of the following statements about **VSEPR theory** are correct? Select **all** that apply.

(A) Lone pairs of electrons repel bond pairs more strongly than bond pairs repel each other, causing **compression** of the bond angles below the ideal geometry value.

(B) Water (H_2O) adopts a **bent** molecular geometry: 2 bond pairs and 2 lone pairs around O give a V-shape with $\angle$HOH $\approx 104.5^\circ$.

(C) Ammonia (NH_3) adopts a **trigonal pyramidal** geometry: 3 bond pairs and 1 lone pair around N give $\angle$HNH $\approx 107^\circ$.

(D) Beryllium chloride ($BeCl_2$) has a **bent** molecular geometry because the Be atom has 2 lone pairs in addition to the 2 bond pairs.

Q38. Which of the following statements about **concentration cells** are correct? Select **all** that apply.

(A) In a concentration cell, **both** electrodes are composed of the **same metal** and are immersed in solutions of the same electrolyte but at **different** concentrations.

(B) The EMF of a concentration cell is given by $E = \dfrac{RT}{nF} \ln\left(\dfrac{c_{\text{high}}}{c_{\text{low}}}\right)$, which is positive when $c_{\text{high}} > c_{\text{low}}$ (high-concentration side is the cathode).

(C) A concentration cell can produce a non-zero, spontaneous EMF even when **both** electrode solutions have **identical** ion concentrations.

(D) A concentration cell operates spontaneously until the concentrations of both electrode solutions **equalise**; at that point $\Delta G = 0$ and EMF $= 0$.

Q39. Which of the following statements about **Michael addition** are correct? Select **all** that apply.

(A) Michael addition is a **1,4-conjugate** addition of a nucleophile (the Michael donor) to the β-carbon of an α,β-unsaturated carbonyl compound (the Michael acceptor).

(B) Michael addition typically requires **acidic** conditions; a Brønsted acid catalyst deprotonates the Michael acceptor to activate it.

(C) The Michael donor is typically a **stabilised carbanion** (e.g. malonate anion, acetylacetonate), generated by treatment of the active-methylene compound with a base.

(D) The Michael acceptor is an **electron-deficient** alkene conjugated with an electron-withdrawing group, such as methyl acrylate, acrylonitrile, or methyl vinyl ketone.

Q40. Which of the following statements about the **allotropes of sulfur** are correct? Select **all** that apply.

(A) Rhombic (α-) sulfur at room temperature consists of $\mathbf{S}_4$ ring units.

(B) Rhombic (α-) sulfur is the most thermodynamically **stable** allotrope of sulfur at room temperature and atmospheric pressure.

(C) Monoclinic (β-) sulfur is stable **above** $96\,^{\circ}$C (the rhombic–monoclinic transition temperature) and transforms back to rhombic sulfur on slow cooling below $96\,^{\circ}$C.

(D) **Plastic** (amorphous) sulfur is formed by rapidly quenching molten sulfur into cold water; it is a rubber-like, elastic, amorphous solid composed of long polymeric sulfur chains.

Section C — Numerical Answer Type (NAT)

***Q41–Q50**: 1 mark each. **No negative marking.** Enter the exact numerical value.*

Q41. Carbon dioxide (CO_2, $M = 44$ g/mol) and helium (He, $M = 4$ g/mol) effuse through a small orifice at the same temperature and pressure. The time required for a fixed volume of a gas to effuse is inversely proportional to its rate of effusion, and by Graham's law, the rate of effusion is proportional to $1/\sqrt{M}$. If helium takes time t_{He} to effuse a fixed volume, calculate the ratio $t_{\mathrm{CO_2}}/t_{\mathrm{He}}$ correct to two decimal places.

Q42. Calculate the standard entropy change ΔS° (in $\mathrm{J\,mol^{-1}\,K^{-1}}$, to one decimal place) for the combustion of methane:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$$

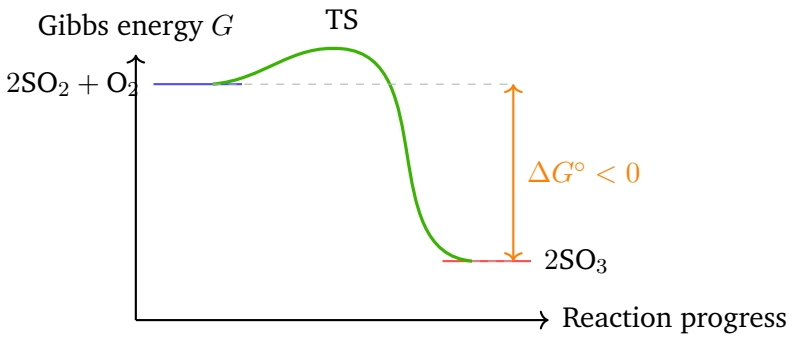
Standard molar entropies ($\mathrm{J\,mol^{-1}\,K^{-1}}$): $S^{\circ}[\mathrm{CH_4}(g)] = 186.3$; $S^{\circ}[\mathrm{O_2}(g)] = 205.1$; $S^{\circ}[\mathrm{CO_2}(g)] = 213.8$; $S^{\circ}[\mathrm{H_2O}(l)] = 69.9$.

Q43. A first-order reaction has rate constant $k_1 = 1.5 \times 10^{-3}\ \mathrm{s^{-1}}$ at $T_1 = 27\,^{\circ}$C (300 K) and activation energy $E_a = 50\,000\ \mathrm{J\,mol^{-1}}$. Using the Arrhenius equation in the form

$$\ln\!\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

calculate the rate constant k_2 (in $\mathrm{s^{-1}}$) at $T_2 = 0\,^{\circ}$C (273 K). ($R = 8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$.) Report your answer to three significant figures.

Q44. For the equilibrium $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, the equilibrium constant $K_c = 280$ at 700 K. Using the relation $K_p = K_c(RT)^{\Delta n_g}$ with $\Delta n_g = 2 - (2+1) = -1$ and $R = 0.0821\ \text{L atm mol}^{-1}\,\text{K}^{-1}$, calculate K_p to two decimal places.



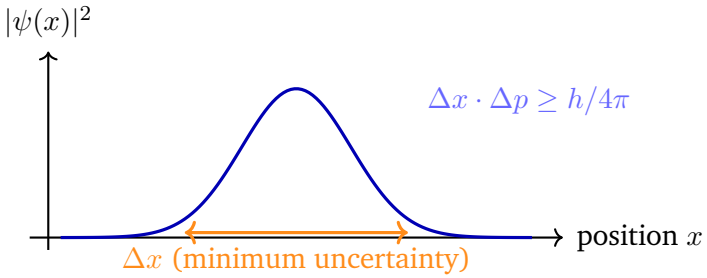
Q45. The limiting molar conductivity of a weak electrolyte cannot be measured directly. Using **Kohlrausch's law of independent migration of ions**, calculate $\lambda_m^\circ(\text{NH}_4\text{OH})$ in $\text{S cm}^2\,\text{mol}^{-1}$, given:

$$\lambda_m^\circ(\text{NH}_4\text{Cl}) = 129.8, \quad \lambda_m^\circ(\text{NaOH}) = 248.1, \quad \lambda_m^\circ(\text{NaCl}) = 126.4 \quad \text{(all in S cm}^2\text{mol}^{-1}$$

Q46. An electron (mass $m_e = 9.11 \times 10^{-31}$ kg) has an uncertainty in velocity $\Delta v = 1.0 \times 10^6\ \text{m s}^{-1}$. Using the Heisenberg uncertainty principle

$$\Delta x \cdot m_e\,\Delta v \geq \frac{h}{4\pi},$$

calculate the **minimum** uncertainty in position Δx_{min} (in m) to three significant figures. ($h = 6.626 \times 10^{-34}$ J s.)



Q47. NaCl crystallises in the rock-salt (FCC-based) structure with $Z = 4$ formula units per unit cell and lattice parameter $a = 5.64\,\text{Å} = 5.64 \times 10^{-8}$ cm. Calculate the density ρ of NaCl (in g cm^{-3}) using $\rho = ZM/(N_A a^3)$.

(Molar mass of NaCl $= 58.44\ \text{g mol}^{-1}$; $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$.) Report to two decimal places.

Q48. 6.0 g of urea [$\text{CO(NH}_2)_2$, molar mass $= 60\ \text{g mol}^{-1}$, non-electrolyte, $i = 1$] is dissolved in 200 g of water ($K_f = 1.86\ ^\circ\text{C kg mol}^{-1}$). Calculate the **depression in freezing point** $\Delta T_f = K_f \cdot m$ (in °C) correct to two decimal places.

Q49. Calculate the **degree of unsaturation** (index of hydrogen deficiency, IHD) for the molecular formula C_9H_{12} (the formula of mesitylene, 1,3,5-trimethylbenzene). Use: IHD $= (2C + 2 - H)/2$.

Q50. Calculate the **spin-only magnetic moment** μ_s (in Bohr magnetons, BM) of the Cr^{3+} ion. Chromium has atomic number 24; Cr^{3+} has a d^3 configuration with all three d electrons unpaired. Use $\mu_s = \sqrt{n(n+2)}$ BM, where n = number of unpaired electrons. Round your answer to two decimal places.

***Q51–Q60**: 2 marks each. **No negative marking.** Enter the exact numerical value.*

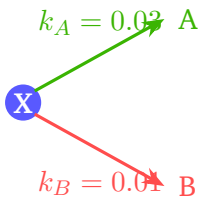
Q51. For the reaction $2\,\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\,\text{H}_2\text{O}(l)$ at $T = 298$ K:

$\Delta H^\circ = -571.6$ kJ (for the balanced equation), $\Delta S^\circ = -326.4\ \text{J K}^{-1}$ (for the l

Using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, calculate ΔG° **per mole of H_2O formed** (in kJ mol^{-1}), correct to one decimal place.

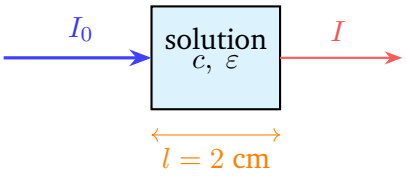
Q52. Reactant X undergoes two simultaneous first-order reactions:

$$X \xrightarrow{k_A} A \quad (k_A = 0.03\ \text{min}^{-1}), \qquad X \xrightarrow{k_B} B \quad (k_B = 0.01\ \text{min}^{-1}).$$



For parallel first-order reactions, the fractional yield of each product is constant and equals $k_i/(k_A + k_B)$. Calculate the percentage of X that is converted to product **A** (the selectivity toward A).

Q53. A solution has molar absorptivity $\varepsilon = 1.5 \times 10^4\ \mathrm{L\,mol^{-1}\,cm^{-1}}$, molar concentration $c = 5.0 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$, and path length $l = 2.00$ cm. Using the Beer–Lambert law $A = \varepsilon c l$ and the relation $\%T = 100 \times 10^{-A}$:



Calculate the **percent transmittance** ($\%T$) of this solution, correct to two decimal places.

Q54. Calculate the **degree of unsaturation** (IHD) for benzaldehyde, which has the molecular formula C_7H_6O. For a compound with formula $C_nH_mO_p$ (no N or halogens), use IHD $= (2n + 2 - m)/2$ (oxygen atoms do not change the IHD formula). Report as an integer.

Q55. The complex $[Fe(H_2O)_6]^{2+}$ contains Fe^{2+} in a d^6 configuration. Since H_2O is a weak-field ligand, the complex is **high-spin**: the electron configuration is $(t_{2g})^4(e_g)^2$, giving **four** unpaired electrons. Calculate the spin-only magnetic moment $\mu_s = \sqrt{n(n+2)}$ BM. Round to two decimal places.

Q56. Calculate the electrode potential E (in V) for the Ag^+/Ag half-cell at 298 K when $[Ag^+] = 1.0 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$. Using the Nernst equation at 298 K:

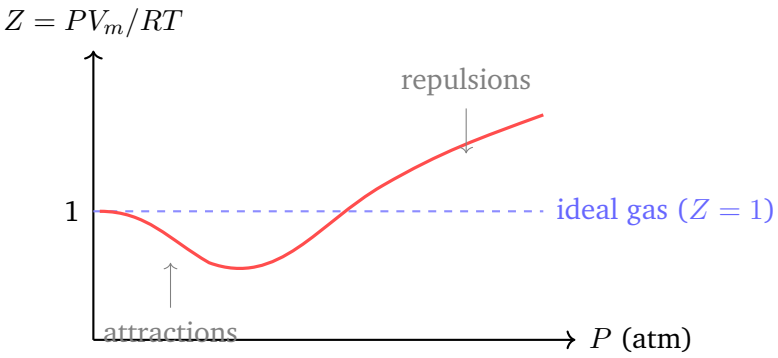
$$E = E^\circ - \frac{0.059}{n} \log\left(\frac{1}{[Ag^+]}\right),$$

with $E^\circ(Ag^+/Ag) = +0.80$ V and $n = 1$. Report to three decimal places.

Q57. For nitrogen gas (N_2), van der Waals constants: $a = 1.39\ \mathrm{L^2\,atm\,mol^{-2}}$, $b = 0.0391\ \mathrm{L\,mol^{-1}}$. At $T = 500$ K and $P = 200$ atm, use the first-order approximation

$$V_m \approx \frac{RT}{P} + b - \frac{a}{RT}$$

to estimate the molar volume, then calculate the compression factor $Z = PV_m/(RT)$. ($R = 0.0821\ \mathrm{L\,atm\,mol^{-1}\,K^{-1}}$.) Report Z to three decimal places.



Q58. Ethyl acetoacetate (ethyl 3-oxobutanoate, EAA) exists as an equilibrium mixture of keto and enol tautomers. In **CCl_4** (a non-polar, non-hydrogen-bonding solvent) at room temperature, the mixture is approximately **49% enol** and **51% keto**. Express the percentage of the **keto** form (as a whole number integer) present in CCl_4 solution.

Q59. Using **Slater's rules**, calculate the effective nuclear charge Z^* experienced by a $4p$ electron in a bromine atom (Br, $Z = 35$). The electron configuration of Br is $[\text{Ar}]\,3d^{10}\,4s^2\,4p^5$. Apply the following shielding contributions to one of the 4p electrons:

- Same shell [$4s^2 4p^4$ (other 4 electrons in 4p) + $4s^2$]: 6 electrons $\times\, 0.35$

$3s^2 3p^6$ (8 electrons in $n-1$ s/p shell): $\times\, 0.85$

$3d^{10}$ (10 electrons in $3d$ group): $\times\, 1.00$

$1s^2 2s^2 2p^6$ (10 electrons, inner core): $\times\, 0.85$

Calculate σ (total shielding) and then $Z^* = Z - \sigma$. Report to two decimal places.

Q60. For the gas-phase decomposition: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,

$$\Delta H^\circ = +88\,\text{kJ mol}^{-1}, \quad \Delta S^\circ = +170\,\text{J mol}^{-1}\text{K}^{-1}.$$

The equilibrium constant $K_p = 1$ when $\Delta G^\circ = 0$, which occurs at the temperature $T = \Delta H^\circ/\Delta S^\circ$. Calculate this temperature in kelvin, rounded to the nearest integer.

Solutions

IIT JAM Chemistry – Sample Paper 3

Section A Solutions — MCQ

Solution

Concept — Pauling Electronegativity:
Electronegativity increases across a period (left to right) and decreases down a group in the periodic table. The Pauling values for the second-period elements are directly given: C = 2.5, N = 3.0, O = 3.5, F = 4.0.

Step 1 — Arranging in decreasing order:
F (4.0) $>$ O (3.5) $>$ N (3.0) $>$ C (2.5). This corresponds to option (D).

Final Answer: F $>$ O $>$ N $>$ C $\Rightarrow$ **(D)**

Why other options are wrong:

Q1.
- (A): Places N above O — incorrect; O (3.5) $>$ N (3.0).
- (B): Places O above F — incorrect; F (4.0) $>$ O (3.5).
- (C): Reverses the order entirely (increasing, not decreasing).

Answer: (D) ← *Go back to Q1*

Solution

Concept — de Broglie Wavelength at Fixed Kinetic Energy:
From $\lambda = h/\sqrt{2m \cdot KE}$, at the same kinetic energy, $\lambda \propto 1/\sqrt{m}$. The particle with the *smallest* mass has the *longest* wavelength.

Step 1 — Compare masses:

Q2.
- Electron: 9.11×10^{-31} kg (smallest by far)
- Proton & Neutron: $\approx 1.67 \times 10^{-27}$ kg
- Alpha particle: 6.64×10^{-27} kg (largest)

Step 2 — Longest λ:
Since $m_e \ll m_p = m_n \ll m_\alpha$, the electron has the largest λ.

Final Answer: Electron has longest de Broglie wavelength $\Rightarrow$ **(C)**

Why other options are wrong:

- (A): Proton is $\sim 1836\times$ heavier than electron — much shorter λ.
- (B): Alpha particle is the heaviest — shortest λ.
- (D): Neutron has same mass as proton — shorter λ than electron.

Answer: (C) ← *Go back to Q2*

Solution

Concept — Diagonal Relationship (Li and Mg):
Li and Mg have similar charge-to-size ratios (charge density), giving them similar chemical behaviours despite being in different groups and periods.

Step 1 — Identifying the shared property:
Both Li and Mg react directly with N_2 gas at room temperature:

$$4\,\text{Li} + \text{N}_2 \rightarrow 2\,\text{Li}_3\text{N}$$

$$3\,\text{Mg} + \text{N}_2 \rightarrow \text{Mg}_3\text{N}_2$$

Other alkali metals (Na, K, Rb, Cs) do **not** react with N_2 under ordinary conditions.

Final Answer: Both form nitrides with $N_2 \Rightarrow$ **(A)**

Why other options are wrong:

Q3.

- (B): LiOH and $Mg(OH)_2$ are *weak* bases (sparingly soluble), not strong bases like NaOH/KOH.
- (C): Li reacts gently with water; Mg reacts only with steam; neither reacts explosively.
- (D): Li forms Li_2O (normal oxide) with limited O_2, and Mg forms MgO; peroxides are not typical products.

Answer: (A) ← *Go back to Q3*

Solution

Concept — Inductive Effect and Acid Strength:
Electron-withdrawing groups ($-I$ effect) stabilise the carboxylate anion by dispersing the negative charge, increasing acid strength. More chlorine atoms $\Rightarrow$ stronger $-I$ effect $\Rightarrow$ stronger acid.

Step 1 — pK_a values:

Q4.

- CH_3COOH: $pK_a \approx 4.76$ (no Cl, weakest acid)
- $ClCH_2COOH$: $pK_a \approx 2.86$ (one Cl)
- Cl_3CCOOH: $pK_a \approx 0.65$ (three Cl, strongest acid)

Decreasing pK_a means increasing acid strength.

Final Answer: $Cl_3CCOOH > ClCH_2COOH > CH_3COOH \Rightarrow$ **(B)**

Why other options are wrong:

- (A): Reverses the order — CH_3COOH is the weakest, not the strongest.
- (C): Places monochloroacetate above trichloroacetate — incorrect.
- (D): Places acetic acid above trichloroacetate — incorrect.

Answer: (B) ← *Go back to Q4*

Solution

Concept — Graham's Law of Effusion:
$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$, where r is the rate of effusion and M is molar mass.

Step 1 — Apply the formula:

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

Final Answer: $r(H_2)/r(O_2) = 4 \Rightarrow$ **(D)**

Why other options are wrong:

Q5.
- (A): $2 = \sqrt{4}$; this would be the ratio for $M_2/M_1 = 4$ — not the case here.
- (B): $8 = \sqrt{64}$; incorrect ratio.
- (C): $\sqrt{2}$ corresponds to $M_2/M_1 = 2$ — not applicable here.

Answer: (D) ← *Go back to Q5*

Solution

Concept — H–X Bond Strength in Group 17:
Bond dissociation enthalpy decreases as the halogen becomes larger and heavier, because the orbital overlap between the small H 1s orbital and the increasingly large halogen valence orbital decreases. HF has the smallest F atom $\Rightarrow$ best overlap $\Rightarrow$ strongest bond.

Step 1 — Bond energies (approximate):
HF $\approx$ 569, HCl $\approx$ 432, HBr $\approx$ 366, HI $\approx$ 298 kJ/mol.

Final Answer: HF $>$ HCl $>$ HBr $>$ HI $\Rightarrow$ **(A)**

Why other options are wrong:

Q6.
- (B): Completely reverses the correct trend.
- (C): Places HCl above HF — incorrect; HF is the strongest.
- (D): Illogical ordering; places HI above HCl.

Answer: (A) ← *Go back to Q6*

Solution

Concept — Maximum Stereoisomers from n Stereocenters:
For n independent, non-equivalent stereocenters with no meso forms, the maximum number of stereoisomers is 2^n.

Step 1 — Apply the formula:
With $n = 3$ stereocenters and no meso forms possible:

$$\text{max stereoisomers} = 2^3 = 8$$

This includes 4 pairs of enantiomers (i.e., 4 diastereomers each with its mirror image).

Final Answer: Maximum 8 stereoisomers $\Rightarrow$ **(B)**

Why other options are wrong:

Q7.

- (A): $4 = 2^2$ — would apply to only 2 stereocenters.
- (C): 6 is not a power of 2; not valid here.
- (D): $16 = 2^4$ — would apply to 4 stereocenters.

Answer: (B) *← Go back to Q7*

Solution

Concept — Entropy Change and Δn_g:
The most positive ΔS° generally corresponds to the largest increase in the number of moles of gas (Δn_g), since gaseous species have far higher entropy than liquids or solids.

Step 1 — Evaluate each option:

Q8.

- (A) $N_2 + 3H_2 \rightarrow 2NH_3$: $\Delta n_g = 2 - 4 = -2$ (large decrease in gas, $\Delta S^\circ < 0$)
- (B) C(s) + O_2(g) $\rightarrow$ CO_2(g): $\Delta n_g = 0$ (nearly zero ΔS° for gases)
- (C) $CaCO_3$(s) $\rightarrow$ CaO(s) + CO_2(g): $\Delta n_g = +1$ (creates 1 mol gas from solids, most positive)
- (D) H_2(g) + Cl_2(g) $\rightarrow$ 2HCl(g): $\Delta n_g = 0$ (no change in moles of gas)

Final Answer: $CaCO_3 \rightarrow CaO + CO_2$ has the most positive ΔS° $\Rightarrow$ **(C)**

Why other options are wrong:

- (A): $\Delta n_g = -2$; entropy decreases.
- (B): Converts a solid into gas but Δn_g(gas) = 0; modest entropy change.
- (D): $\Delta n_g = 0$; small entropy change.

Answer: (C) ← *Go back to Q8*

Solution

Concept — Square Planar Geometry in d^8 Complexes:
Heavy metal d^8 ions (Pd^{2+}, Pt^{2+}, Au^{3+}, Rh^{+}) *always* adopt square planar geometry regardless of ligand field strength. This is because the very large crystal-field splitting energy (CFSE) for 4d and 5d metals makes the square planar configuration strongly preferred over tetrahedral.

Step 1 — Analyse each ion:

Q9.

- Zn^{2+} (d^{10}): No CFSE; prefers tetrahedral geometry.
- Ni^{2+} (d^8, 3d): May be tetrahedral with weak-field ligands.
- Cu^{2+} (d^9): Octahedral with Jahn–Teller distortion; not inherently 4-coordinate square planar.
- Pt^{2+} (d^8, 5d): Always square planar due to enormous CFSE from 5d metal.

Final Answer: Pt^{2+} invariably adopts square planar geometry $\Rightarrow$ **(D)**

Why other options are wrong:

- (A): d^{10} has zero CFSE; Zn prefers tetrahedral.
- (B): 3d Ni^{2+} can be tetrahedral with weak-field ligands.
- (C): Cu^{2+} is d^9, not d^8; favours octahedral geometry.

Answer: (D) ← *Go back to Q9*

Solution

Concept — EAS Bromination of Toluene (Major Product):
The methyl group is an *ortho/para* activating director. In practice, *para*-bromotoluene is the major isolated product because the two *ortho* positions suffer significant steric hindrance from the adjacent methyl group, disfavouring *ortho* attack.

Step 1 — Predict orientation:
Methyl directs to *ortho* and *para*. *Para* is sterically more accessible:

$$\text{Toluene} + Br_2/FeBr_3 \rightarrow \textit{para}\text{-bromotoluene (major)} + \textit{ortho}\text{-bromotoluene (minor)}$$

Final Answer: 4-Bromotoluene (para) is the major product $\Rightarrow$ **(A)**

Why other options are wrong:

Q10.

- (B): Meta product — methyl is an *o/p*-director, so meta is strongly dis-

favoured.

- (C): Ortho is a minor product due to steric hindrance; not the exclusive product.
- (D): 2,4-Dibromotoluene requires excess Br_2 and is not the initial major product.

Answer: (A) ← *Go back to Q10*

Solution

Concept — Standard Cell EMF:

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. To maximise EMF, choose the highest E° cathode and the lowest E° anode.

Step 1 — Calculate all options:

Q11.

- (A) $Cu^{2+}/Cu \parallel Zn$: $0.34 - (-0.76) = 1.10$ V
- (B) $Ag^{+}/Ag \parallel Zn$: $0.80 - (-0.76) = 1.56$ V **(maximum)**
- (C) $Fe^{3+}/Fe^{2+} \parallel Zn$: $0.77 - (-0.76) = 1.53$ V
- (D) $Ag^{+}/Ag \parallel Cu$: $0.80 - 0.34 = 0.46$ V

Final Answer: Ag^{+}/Ag cathode with Zn anode gives maximum 1.56 V $\Rightarrow$ **(B)**

Why other options are wrong:

- (A): 1.10 V $<$ 1.56 V.
- (C): 1.53 V $<$ 1.56 V.
- (D): Only 0.46 V; Cu anode raises the anode potential.

Answer: (B) ← *Go back to Q11*

Solution

Concept — Reactivity of Acyl Derivatives:

Reactivity in nucleophilic acyl substitution is governed by the basicity (stability) of the leaving group: weaker base $\equiv$ better leaving group $\equiv$ faster reaction.

Step 1 — Rank leaving groups by basicity:

Q12.

- Cl^- (weakest base, best LG) $\Rightarrow$ Acid chloride: most reactive
- $RCOO^-$ (moderate) $\Rightarrow$ Acid anhydride: second
- RO^- (more basic) $\Rightarrow$ Ester: third
- NH_2^- (strongest base, worst LG) $\Rightarrow$ Amide: least reactive

Final Answer: Acid chloride > Anhydride > Ester > Amide ⇒ **(C)**

Why other options are wrong:

- (A): Reverses ester and acid chloride positions; wrong.
- (B): Places amide first — amide is the least reactive.
- (D): Places anhydride above acid chloride — incorrect order.

Answer: (C) ← *Go back to Q12*

Solution

Concept — VSEPR Geometry of SF_4:

SF_4: S has 6 valence electrons; 4 are used in S–F bonds, leaving 1 lone pair. Total electron pairs = 5 ⇒ trigonal bipyramidal electron geometry. The lone pair occupies an *equatorial* position (to minimise repulsions with three 90° bond pairs). The resulting *molecular* geometry (positions of atoms only) is seesaw (butterfly).

Step 1 — Assign geometry:

Trigonal bipyramidal electron pairs with one equatorial lone pair:

Q13.

- 2 axial F atoms (top and bottom)
- 2 equatorial F atoms (left and right)
- 1 equatorial lone pair (at the "missing" equatorial position)

This gives the characteristic **seesaw (butterfly)** shape.

Final Answer: SF_4 has seesaw (butterfly) molecular geometry ⇒ **(D)**

Why other options are wrong:

- (A): Square planar requires 4 bond pairs + 2 lone pairs (octahedral EP geometry).
- (B): Trigonal bipyramidal requires 5 bond pairs + 0 lone pairs.
- (C): Trigonal pyramidal requires 3 bond pairs + 1 lone pair (tetrahedral EP geometry), e.g., NH_3.

Answer: (D) ← *Go back to Q13*

Solution

Concept — Fischer Esterification Mechanism:

Fischer esterification proceeds via acid catalysis. The key step is protonation of the carbonyl oxygen of the carboxylic acid, which increases the electrophilicity of the carbonyl carbon, enabling nucleophilic attack by the lone pair of the alcohol

oxygen.

Step 1 — Mechanism outline:

Q14.

1. H^+ protonates C=O of RCOOH $\rightarrow$ resonance-stabilised oxocarbenium ion.
2. Alcohol O attacks the activated carbonyl C (nucleophilic addition).
3. Proton transfers; water is lost.
4. Deprotonation gives the ester product.

The reaction is an equilibrium (reversible).

Final Answer: Acid protonates carbonyl O; alcohol attacks activated C $\Rightarrow$ **(A)**

Why other options are wrong:

- (B): Acid catalyst does not deprotonate the alcohol; alkoxide is a base-catalysis mechanism.
- (C): Fischer esterification is reversible; an equilibrium exists.
- (D): Acylium ions ($RC{\equiv}O^+$) are intermediates in Friedel–Crafts acylation, not Fischer esterification.

Answer: (A) ← *Go back to Q14*

Solution

Concept — Nucleophilic Aromatic Substitution (NAS) and Meisenheimer Complex:

NAS proceeds by an addition–elimination mechanism. The rate-determining step is the formation of the Meisenheimer complex (an anionic σ-complex). Electron-withdrawing groups at the *ortho* and *para* positions stabilise this negatively charged intermediate by resonance.

Step 1 — Effect of two nitro groups:

In 2,4-dinitrochlorobenzene, the nitro groups at positions 2 and 4 (relative to Cl) are *ortho* and *para* to Cl. When OH^- attacks the ipso carbon, the resulting carbanion (Meisenheimer complex) is stabilised by resonance delocalization onto both nitro groups:

$$\text{Cl(with two } NO_2) + OH^- \rightarrow [\text{Meisenheimer complex}] \xrightarrow{-Cl^-} \text{phenol product}$$

This greatly lowers the activation energy relative to unsubstituted chlorobenzene.

Final Answer: Nitro groups stabilise Meisenheimer complex by resonance $\Rightarrow$ **(B)**

Why other options are wrong:

Q15.

- (A): Benzyne mechanism is for unactivated aryl halides under harsh condi-

tions; dinitrochlorobenzene reacts by addition–elimination, not benzyne.
- (C): Inductive weakening of C–Cl bond is a minor effect; resonance stabilisation of the intermediate is the dominant explanation.
- (D): NAS does not require acidic medium; it is accelerated by electron-withdrawing groups.

Answer: (B) ← *Go back to Q15*

Solution

Concept — Jahn–Teller Distortion:
The Jahn–Teller theorem applies when the ground-state electronic configuration is *degenerate*. For octahedral complexes, asymmetric occupation of the e_g level causes the most pronounced distortion. The d^9 configuration has $(t_{2g})^6(e_g)^3$: three electrons in two e_g orbitals — one orbital has 2 electrons, the other has 1. This is a degenerate e_g ground state ⇒ strong Jahn–Teller distortion (typically elongation along z-axis).

Step 1 — Analyse each configuration:

Q16.
- d^6 high-spin: $(t_{2g})^4(e_g)^2$ — e_g^2 is degenerate but distortion is mild.
- d^5 high-spin: $(t_{2g})^3(e_g)^2$ — half-filled; non-degenerate; no JT distortion.
- d^9: $(t_{2g})^6(e_g)^3$ — one hole in e_g; most pronounced JT distortion (Cu^{2+} classic example).
- d^3: $(t_{2g})^3$ — non-degenerate; no JT distortion.

Final Answer: d^9 (Cu^{2+}) shows most pronounced Jahn–Teller distortion ⇒ **(C)**

Why other options are wrong:

- (A): d^6 high-spin has e_g^2 degeneracy but distortion is weaker than d^9.
- (B): d^5 high-spin is non-degenerate (half-filled); no JT distortion.
- (D): d^3 has a non-degenerate t_{2g}^3 ground state; no JT distortion.

Answer: (C) ← *Go back to Q16*

Solution

Concept — Le Châtelier's Principle (Haber Process):
For $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$: the reaction converts 4 mol of gas into 2 mol. Increasing total pressure favours the side with fewer moles of gas (right side), producing more NH_3.

Step 1 — Evaluate each change:

Q17.

- (A): Increasing T shifts equilibrium LEFT (reaction is exothermic, $\Delta H = -92$ kJ).
- (B): Adding inert gas at constant volume: partial pressures unchanged, no shift.
- (C): Decreasing pressure shifts LEFT (toward 4 mol gas side).
- (D): Increasing total pressure $\Rightarrow$ equilibrium shifts RIGHT (toward 2 mol gas) $\Rightarrow$ more NH_3.

Final Answer: Increasing total pressure shifts equilibrium right $\Rightarrow$ **(D)**

Why other options are wrong:

- (A): Higher T favours reverse (endothermic) direction.
- (B): Inert gas at constant volume has no effect on partial pressures.
- (C): Decreasing pressure shifts left, reducing NH_3 yield.

Answer: (D) *← Go back to Q17*

Solution

Concept — Mass Spectrometry of 1-Propanol (α-Cleavage):
1-Propanol: $CH_3CH_2CH_2OH$; MW = 60 g/mol. The molecular ion appears at $m/z = 60$. The most characteristic fragmentation is α-cleavage: breaking the C–C bond adjacent (α) to the oxygen. Loss of C_2H_5 (29 mass units) from the α-carbon gives the resonance-stabilised oxocarbenium ion $CH_2{=}OH^+$ at $m/z = 31$.

Step 1 — Identify the α-cleavage:

$$\underset{\underset{||}{}}{CH_3CH_2CH_2OH} \xrightarrow{\alpha\text{-cleavage}} CH_3CH_2\bullet + \overset{+}{C}H_2OH$$

m/z of $CH_2{=}OH^+$ = 12 + 2 + 16 + 1 = 31 (base peak)

Final Answer: $M^+ = 60$; base peak at $m/z = 31$ $\Rightarrow$ **(A)**

Why other options are wrong:

Q18.

- (B): $M^+ = 59$ is wrong; MW of 1-propanol is 60. $m/z = 45$ corresponds to loss of CH_3 from 2-propanol.
- (C): $M^+ = 62$ is wrong; 1-propanol is C_3H_8O, MW = 60.
- (D): 1-propanol does fragment; the molecular ion is not the base peak.

Answer: (A) *← Go back to Q18*

Solution

Concept — VSEPR Geometry of IF_5:

IF_5: I has 7 valence electrons; 5 are used in I–F bonds, leaving 1 lone pair. Total electron pairs = 6 $\Rightarrow$ octahedral electron-pair geometry. One octahedral position is occupied by the lone pair, giving 5 I–F bonds in a square pyramidal arrangement.

Step 1 — Assign geometry:

Octahedral EP geometry with 1 lone pair $\Rightarrow$ **square pyramidal** molecular geometry: 4 F atoms in the base plane, 1 F atom at the apex, and 1 lone pair at the remaining octahedral position.

Final Answer: IF_5 has square pyramidal geometry $\Rightarrow$ **(B)**

Why other options are wrong:

Q19.

- (A): Trigonal bipyramidal has 5 bond pairs, 0 lone pairs (e.g., PCl_5).
- (C): Pentagonal planar is not a standard VSEPR geometry for this combination.
- (D): T-shaped has 3 bond pairs + 2 lone pairs in trigonal bipyramidal EP geometry (e.g., ClF_3).

Answer: (B) ← *Go back to Q19*

Solution

Concept — Boiling Point Elevation:

$\Delta T_b = i \cdot K_b \cdot m$, where m is molality (mol solute per kg solvent).

Step 1 — Calculate molality:

Moles of NaCl $= 5.85/58.5 = 0.100$ mol

Mass of water $= 500$ g $= 0.500$ kg

$m = 0.100/0.500 = 0.200$ mol/kg

Step 2 — Calculate ΔT_b:

$\Delta T_b = i \cdot K_b \cdot m = 2 \times 0.512 \times 0.200 = 0.205\,^\circ$C

Final Answer: $\Delta T_b = 0.205\,^\circ$C $\Rightarrow$ **(C)**

Why other options are wrong:

Q20.

- (A): 0.512 ignores the van't Hoff factor $i = 2$.
- (B): 0.102 uses $i = 1$ and $m = 0.200$; forgets factor of 2.
- (D): 0.410 is double the correct answer; error in calculation.

Answer: (C) ← *Go back to Q20*

Solution

Concept — Friedel–Crafts Acylation vs. Alkylation:
Key difference: the acylium ion ($RC{\equiv}O^+ \leftrightarrow R^+{-}C{=}O$) is resonance-stabilised and *does not undergo rearrangement*. Alkylations via carbocations CAN rearrange.

Step 1 — Evaluate option (D):
Acetyl chloride (CH_3COCl) with $AlCl_3$ generates the resonance-stabilised acetylium ion ($CH_3C{\equiv}O^+ \leftrightarrow {}^+CH_3C{=}O$). It attacks benzene cleanly to give **acetophenone** (methyl phenyl ketone) without rearrangement.

Final Answer: FC acylation gives acetophenone without rearrangement $\Rightarrow$ **(D)**

Why other options are wrong:

Q21.

- (A): Isopropyl carbocation *can* rearrange; alkylation products include rearranged species.
- (B): n-Propyl chloride $\rightarrow$ secondary carbocation rearrangement; isopropylbenzene (not n-propylbenzene) is obtained.
- (C): Acylium ions do *not* rearrange; propanoyl chloride gives propiophenone cleanly.

Answer: (D) ← *Go back to Q21*

Solution

Concept — Bragg's Law:
$2d\sin\theta = n\lambda$. With $n = 1$, $\lambda = 1.54$ Å, $d = 3.08$ Å:

Step 1 — Solve for $\sin\theta$:

$$\sin\theta = \frac{n\lambda}{2d} = \frac{1 \times 1.54}{2 \times 3.08} = \frac{1.54}{6.16} = 0.250$$

Step 2 — Find θ:

$$\theta = \arcsin(0.250) \approx 14.5^\circ$$

Final Answer: $\theta \approx 14.5^\circ \Rightarrow$ **(A)**

Why other options are wrong:

Q22.

- (B): $\theta = 30^\circ$ would require $\sin\theta = 0.500$, which would need $\lambda/2d = 0.5$ (i.e., $\lambda = d$, not the case here).
- (C): $\theta = 7.25^\circ$ corresponds to $n = 2$ using half the wavelength.
- (D): $\theta = 45^\circ$ corresponds to $\sin\theta = 0.707$; impossible with these values.

Answer: (A) ← *Go back to Q22*

Solution

Concept — Structure of H_3PO_3 (Phosphorous Acid):
Despite having the formula H_3PO_3, only two of the three hydrogen atoms are O–H (ionisable). The third hydrogen is directly bonded to the phosphorus atom as a P–H bond, which is *not* acidic because P–H bonds do not ionise under normal conditions.

Step 1 — Structural formula:

Q23. $H-P(=O)(OH)_2$: phosphorus has a direct P–H bond, one P=O, and two P–O–H groups.

Only the two O–H groups release protons: $pK_{a1} = 1.3$, $pK_{a2} = 6.7$.

Final Answer: One H is P-bonded (not ionisable); only two O–H protons dissociate $\Rightarrow$ **(B)**

Why other options are wrong:

- (A): H_2 gas is not expelled; this is not a redox dissolution.
- (C): The three H atoms are not equivalent; one is P–H, two are O–H.
- (D): H_3PO_3 is diprotic, not monoprotic.

Answer: (B) ← *Go back to Q23*

Solution

Concept — Acid-Catalysed Epoxide Ring Opening (SN1-like):
Under acid catalysis, the epoxide oxygen is protonated first, generating an oxocarbenium-like species. The nucleophile then attacks the *more substituted* (more carbocation-like) carbon. For styrene oxide, the benzylic carbon (Ph–CH) is stabilised by benzylic resonance, making it the site of nucleophilic attack.

Step 1 — Regiochemistry:

Protonation of oxygen $\rightarrow$ partial positive charge at benzylic C (Ph–$\overset{\delta+}{C}$H–CH_2). H_2O attacks the benzylic C:

$$\text{Ph–CH–CH}_2 + \text{H}^+ \rightarrow \text{Ph–}\overset{+}{\text{C}}\text{H–CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{Ph–CH(OH)–CH}_2\text{OH}$$

Final Answer: Product is Ph–CH(OH)–CH_2OH (1-phenyl-1,2-ethanediol) $\Rightarrow$ **(C)**

Why other options are wrong:

Q24.

- (A): Attack at less substituted C is the *base-catalysed* (SN2) regiochemistry, not acid-catalysed.
- (B): Styrene oxide does react with water under acidic conditions.

- (D): Elimination to give styrene does not occur under mild acid-catalysed ring-opening conditions.

Answer: (C) ← *Go back to Q24*

Solution

Concept — Charge on $Fe(OH)_3$ Colloid:
Colloidal particles acquire charge by selective adsorption of ions from the dispersion medium (Helmholtz double layer). $Fe(OH)_3$ sol is prepared by hydrolysis of $FeCl_3$ in excess $FeCl_3$ solution. The sol particles selectively adsorb the common Fe^{3+} ions from the medium (Paneth–Fajans rule: ions that are part of the crystal lattice of the solid are preferentially adsorbed).

Step 1 — Determine charge:
$Fe(OH)_3$ particles adsorb Fe^{3+} cations $\Rightarrow$ the particles carry a **positive** charge.

Final Answer: $Fe(OH)_3$ sol is positively charged $\Rightarrow$ **(D)**

Why other options are wrong:

Q25.

- (A): OH^- adsorption would occur in excess NaOH; not the case here (excess $FeCl_3$).
- (B): Colloidal particles in this preparation are not neutral.
- (C): The charge is consistently positive (not variable) due to selective Fe^{3+} adsorption.

Answer: (D) ← *Go back to Q25*

Solution

Concept — Radioactive Decay (Half-Life):
After each half-life, the fraction remaining is multiplied by $\frac{1}{2}$. After n half-lives: $N/N_0 = (1/2)^n$.

Step 1 — Number of half-lives:
$t = 2.80 \times 10^{10}$ yr, $t_{1/2} = 1.40 \times 10^{10}$ yr

$$n = \frac{t}{t_{1/2}} = \frac{2.80 \times 10^{10}}{1.40 \times 10^{10}} = 2 \text{ half-lives}$$

Step 2 — Fraction remaining:

$$\frac{N}{N_0} = \left(\frac{1}{2}\right)^2 = \frac{1}{4} = 0.25$$

Final Answer: 0.25 (25%) of ^{232}Th remains $\Rightarrow$ **(A)**

Why other options are wrong:

Q26.

- (B): 0.50 = $(1/2)^1$ — only 1 half-life elapsed.
- (C): 0.125 = $(1/2)^3$ — 3 half-lives; t would be 4.20×10^{10} yr.
- (D): 0.75 would imply decay of only 25%; this is not a standard half-life fraction.

Answer: (A) ← *Go back to Q26*

Solution

Concept — SN2 Walden Inversion:
SN2 mechanism proceeds with *complete inversion* of configuration at the stereocentre (backside attack). (R)-substrate always gives (S)-product and vice versa.

Step 1 — Reaction:
(R)-2-Bromobutane + CN^- (in DMSO, polar aprotic) $\rightarrow$ SN2 product
Backside attack of CN^- at the stereogenic C $\Rightarrow$ complete inversion $\Rightarrow$ (S)-2-methylbutanenitrile.

Step 2 — Note on CN^-:
CN^- attacks via carbon, extending the chain by one C. The substituent priority order changes, but the spatial arrangement inverts.

Final Answer: (S)-2-methylbutanenitrile (complete inversion) $\Rightarrow$ **(C)**

Why other options are wrong:

Q27.

- (A): Retention of configuration is characteristic of SN1 (racemisation) or SNi; SN2 always inverts.
- (B): Racemisation occurs in SN1; the polar aprotic solvent (DMSO) and primary-like substrate favour SN2.
- (D): CN^- does not cause rearrangement; product is 2-methylbutanenitrile, not pentanenitrile.

Answer: (C) ← *Go back to Q27*

Solution

Concept — Gibbs Phase Rule at the Eutectic Point:
Reduced phase rule (constant pressure): $F = C - P + 1$.

Step 1 — Apply at eutectic:

Q28.

- $C = 2$ (two components: A and B)
- $P = 3$ (three phases coexist: solid A + solid B + liquid)

$$F = 2 - 3 + 1 = 0$$

Zero degrees of freedom: the system is **invariant**. Both temperature and composition are uniquely fixed at the eutectic point.

Final Answer: $F = 0$ (invariant system) $\Rightarrow$ **(B)**

Why other options are wrong:

- (A): $F = 1$ would mean temperature can vary; that contradicts the eutectic being a fixed point.
- (C): $F = 2$ would require $P = 1$; not possible with 3 coexisting phases.
- (D): $F = 3$ would require $P = 0$; physically impossible.

Answer: (B) *← Go back to Q28*

Solution

Concept — Lewis Acid–Base Theory:
A Lewis acid *accepts* an electron pair; a Lewis base *donates* an electron pair. $AlCl_3$ has an empty p orbital on Al (6 valence electrons around Al); it is an electron-pair *acceptor* (Lewis acid).

Step 1 — Identify the Lewis acid–base reaction:
$AlCl_3 + Cl^- \rightarrow AlCl_4^-$:
Cl^- donates a lone pair to the empty orbital of $AlCl_3$. $AlCl_3$ accepts the electron pair $\Rightarrow$ $AlCl_3$ acts as a **Lewis acid**.

Final Answer: $AlCl_3 + Cl^- \rightarrow AlCl_4^-$ demonstrates $AlCl_3$ as Lewis acid $\Rightarrow$ **(D)**

Why other options are wrong:

Q29.

- (A): $AlCl_3$ cannot donate a lone pair to BCl_3 (both are Lewis acids); the premise is wrong.
- (B): $AlCl_3$ + 3NaOH is simple metathesis (acid–base in Arrhenius sense), not a Lewis acid–base interaction.
- (C): Al_2Cl_6 dimerisation does involve $AlCl_3$ as Lewis acid (accepting lone pair from bridging Cl), but the question shows $AlCl_3$ acting as both donor and acceptor; option (D) more cleanly illustrates $AlCl_3$ as Lewis acid.

Answer: (D) *← Go back to Q29*

Q30.

Solution

Concept — Strecker Synthesis:

Strecker synthesis converts an aldehyde (RCHO) to an α-amino acid via two steps:

1. RCHO + NH_3 + HCN $\rightarrow$ R–CH(NH_2)–CN (α-aminonitrile)
2. R–CH(NH_2)–CN + H_2O/H^+ $\rightarrow$ R–CH(NH_2)–COOH (α-amino acid)

Step 1 — Apply to propanal:

Propanal: CH_3CH_2CHO (R = ethyl, CH_3CH_2-)

Product: CH_3CH_2–CH(NH_2)–COOH = **2-aminobutanoic acid**

Final Answer: 2-Aminobutanoic acid from propanal $\Rightarrow$ **(C)**

Why other options are wrong:

- (A): Alanine comes from acetaldehyde ($R = CH_3$), not propanal.
- (B): Valine comes from isobutyraldehyde ($R = (CH_3)_2CH-$).
- (D): Glycine comes from formaldehyde ($R = H$).

Answer: (C) ← *Go back to Q30*

Section B Solutions — MSQ

Q31.

Solution

Concept — Entropy Fundamentals:

Statement (A) — CORRECT: Entropy is a **state function**. $\Delta S = S_{\text{final}} - S_{\text{initial}}$, independent of path. This is a fundamental thermodynamic property.

Statement (B) — CORRECT: Second Law of Thermodynamics: for a reversible process $\Delta S_{\text{universe}} = 0$; for any spontaneous (irreversible) process $\Delta S_{\text{universe}} > 0$.

Statement (C) — INCORRECT: The Third Law states that the entropy of a perfect crystal of a pure substance at 0 K is **zero** ($S = 0$), not positive.

Statement (D) — CORRECT: Mixing two different ideal gases at constant T and P always increases entropy: $\Delta S_{\text{mix}} = -nR\sum x_i \ln x_i > 0$ (since $x_i < 1 \Rightarrow \ln x_i < 0$). This is the entropy of mixing.

Final Answer: Correct statements: A, B, D $\Rightarrow$ **(ABD)**

Answer: (ABD) ← *Go back to Q31*

Q32.

Solution

Concept — E2 Elimination Mechanism:

Statement (A) — CORRECT: E2 is bimolecular and concerted: the base abstracts a β-H simultaneously as the leaving group departs and the double bond forms. Strong bulky bases like KO^{t}Bu favour E2 over SN2.

Statement (B) — INCORRECT: E2 does *not* proceed through a carbocation intermediate. A discrete carbocation intermediate is the hallmark of the **E1** mechanism. In E2, all bonds break and form in a single concerted step.

Statement (C) — CORRECT: E2 strictly requires an **anti-periplanar** (180° dihedral) arrangement between the β-H and the leaving group. This is an orbital requirement for the concerted four-centre transition state (antiperiplanar arrangement allows the σ electrons to flow into the π system).

Statement (D) — CORRECT: Zaitsev's rule: E2 predominantly forms the **more substituted** (thermodynamically more stable) alkene under most conditions (unless very bulky base).

Final Answer: Correct statements: A, C, D $\Rightarrow$ **(ACD)**

Answer: (ACD) ← *Go back to Q32*

Q33.

Solution

Concept — Crystal Field Theory:

Statement (A) — INCORRECT: CFT predicts that ligands *split* the d orbitals into sets of different energies (t_{2g} and e_g in octahedral field). This splitting removes the degeneracy and causes absorption of visible light, making complexes **coloured**, not colourless.

Statement (B) — CORRECT: Strong-field ligands (CO, CN^-, en) cause a large Δ_o. When $\Delta_o >$ pairing energy, electrons pair up in the lower-energy t_{2g} orbitals $\Rightarrow$ **low-spin** complex with fewer unpaired electrons.

Statement (C) — CORRECT: The colour of transition-metal complexes arises from absorption of visible light. The energy of the absorbed photon $h\nu$ equals Δ_o (the crystal-field splitting energy). The complementary colour is what is observed.

Statement (D) — INCORRECT: $[Fe(CN)_6]^{4-}$ is a d^6 complex with CN^- (a *strong*-field ligand). Strong field $\Rightarrow$ large $\Delta_o \Rightarrow$ **low-spin**: all 6 electrons are in t_{2g} giving $(t_{2g})^6(e_g)^0$ with **0** unpaired electrons, not 4.

Final Answer: Correct statements: B, C $\Rightarrow$ **(BC)**

Answer: (BC) ← *Go back to Q33*

Q34.

Solution

Concept — Photochemical Reactions:

Statement (A) — CORRECT: Grotthuss–Draper law: only radiation that is *absorbed* by a system can cause photochemical change. Light that passes through without absorption has no chemical effect.

Statement (B) — CORRECT: Quantum yield ϕ = (molecules reacted)/(photons absorbed). For chain reactions like H_2/Cl_2 photochlorination, one photon initiates a chain of thousands of steps, giving $\phi \gg 1$ (up to $\sim 10^6$).

Statement (C) — CORRECT: $H_2 + Cl_2 \rightarrow 2HCl$ is a photochemical chain reaction. Initiation: $Cl_2 \xrightarrow{h\nu} 2Cl\bullet$. Propagation: $Cl\bullet + H_2 \rightarrow HCl + H\bullet$; $H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$. Termination: radical combination.

Statement (D) — INCORRECT: Photochemical reactions are *not* necessarily endothermic overall. For example, $H_2 + Cl_2 \rightarrow 2HCl$ is *exothermic* ($\Delta H < 0$) even though initiated photochemically. Light provides activation energy (initiation), but the overall reaction can release energy.

Final Answer: Correct statements: A, B, C $\Rightarrow$ **(ABC)**

Answer: (ABC) ← *Go back to Q34*

Q35.

Solution

Concept — Directing Effects in EAS:

Statement (A) — CORRECT: $-OH$, $-OR$, $-NR_2$ donate electrons by resonance ($+M$) to the ring, *activating* it (making it more reactive than benzene) and directing electrophiles to *ortho/para* positions.

Statement (B) — INCORRECT: $-COOH$, $-CHO$, and $-NO_2$ are electron-withdrawing groups that **deactivate** the ring. Moreover, $-COOH$ and $-CHO$ are *meta*-directors (not *ortho/para*). $-NO_2$ is also a meta-director and deactivating.

Statement (C) — CORRECT: Halogens are *ortho/para* directors (donate lone pairs by resonance at *o/p*), but they **deactivate** the ring overall because their inductive

electron withdrawal ($-I$) exceeds their resonance donation ($+M$). The ring is less reactive than benzene.

Statement (D) — CORRECT: $-NO_2$ is a *strong deactivating* group and a *meta*-director. Resonance withdrawal makes *ortho/para* positions electron-poor; the meta position retains more electron density $\Rightarrow$ electrophile attacks meta.

Final Answer: Correct statements: A, C, D $\Rightarrow$ **(ACD)**

Answer: (ACD) ← *Go back to Q35*

Q36.

Solution

Concept — Atomic Orbitals and Nodes:
Radial nodes $= n - l - 1$; angular nodes $= l$; total nodes $= n - 1$.

Statement (A) — INCORRECT: The 1s orbital ($n = 1$, $l = 0$): radial nodes $= 1 - 0 - 1 = \mathbf{0}$ (not one). Angular nodes $= 0$. Total nodes $= 0$.

Statement (B) — CORRECT: For 2p ($n = 2$, $l = 1$): radial nodes $= 2 - 1 - 1 = \mathbf{0}$. The 2p orbital has one angular nodal plane ($l = 1$) but *zero* radial nodes. The statement correctly identifies 0 radial nodes.

Statement (C) — INCORRECT: The 3d orbital ($n = 3$, $l = 2$): angular nodes $= l = \mathbf{2}$ (not 3). Radial nodes $= 3 - 2 - 1 = 0$.

Statement (D) — CORRECT: For 3s ($n = 3$, $l = 0$): total nodes $= n - 1 = \mathbf{2}$; angular nodes $= l = 0$; radial nodes $= 2$. All nodal surfaces are radial (spherical shells). Statement is correct.

Final Answer: Correct statements: B, D $\Rightarrow$ **(BD)**

Answer: (BD) ← *Go back to Q36*

Q37.

Solution

Concept — VSEPR Theory:

Statement (A) — CORRECT: Lone pair–bond pair repulsion $>$ bond pair–bond pair repulsion. This compresses bond angles below the ideal tetrahedral/trigonal planar values. Example: NH_3 has $107° < 109.5°$.

Statement (B) — CORRECT: H_2O: O has 2 bond pairs + 2 lone pairs (tetrahedral EP geometry). The two lone pairs compress the H–O–H angle to $104.5° < 109.5°$. Molecular geometry is **bent** (V-shaped).

Statement (C) — CORRECT: NH_3: N has 3 bond pairs + 1 lone pair (tetrahedral EP geometry). The one lone pair compresses H–N–H to $107°$. Molecular geometry is **trigonal pyramidal**.

Statement (D) — INCORRECT: $BeCl_2$ has only 2 bond pairs and *no lone pairs* on Be (Be has 2 valence electrons, both used in bonds). EP geometry = linear (2 electron pairs); molecular geometry is **linear** ($180°$), *not bent*.

Final Answer: Correct statements: A, B, C $\Rightarrow$ **(ABC)**

Answer: (ABC) ← *Go back to Q37*

Q38.

Solution

Concept — Concentration Cells:

Statement (A) — CORRECT: A concentration cell uses the same metal/electrode material in both half-cells, with solutions of *different* concentrations of the same electrolyte. The EMF arises solely from the concentration difference.

Statement (B) — CORRECT: EMF $= \dfrac{RT}{nF}\ln\left(\dfrac{c_{\text{high}}}{c_{\text{low}}}\right)$. When $c_{\text{high}} > c_{\text{low}}$, ln > 0 $\Rightarrow$ EMF > 0 (spontaneous). The higher-concentration electrode is the cathode (reduction occurs there, reducing the concentration).

Statement (C) — INCORRECT: If both solutions have *identical* concentrations, $c_{\text{high}}/c_{\text{low}} = 1$, $\ln(1) = 0$, so EMF $= 0$. No spontaneous driving force.

Statement (D) — CORRECT: The cell operates until concentrations equalise: at that point $\ln(c_{\text{high}}/c_{\text{low}}) = \ln(1) = 0 \Rightarrow$ EMF $= 0$, $\Delta G = 0$.

Final Answer: Correct statements: A, B, D $\Rightarrow$ **(ABD)**

Answer: (ABD) ← *Go back to Q38*

Q39.

Solution

Concept — Michael Addition:

Statement (A) — CORRECT: Michael addition is a **1,4-conjugate addition**. The nucleophile (Michael donor) attacks the β-carbon (C-4) of the α,β-unsaturated carbonyl system (Michael acceptor). The initial adduct is an enolate that is protonated to give the 1,4-addition product.

Statement (B) — INCORRECT: Michael addition typically requires **basic** conditions (not acidic). A base generates the stabilised carbanion (Michael donor) by deprotonating the active-methylene compound. Acid conditions are used in different reactions.

Statement (C) — CORRECT: The Michael donor is a **stabilised carbanion**, such as the malonate anion (generated from diethyl malonate + base) or the acetylacetonate anion. Stabilisation arises from delocalization over two electron-withdrawing groups.

Statement (D) — CORRECT: The Michael acceptor is an **electron-deficient alkene** conjugated with an EWG: examples include methyl acrylate ($H_2C{=}CHCO_2Me$), acrylonitrile ($H_2C{=}CHCN$), and methyl vinyl ketone ($H_2C{=}CHCOCH_3$). The EWG activates the β-carbon toward nucleophilic attack.

Final Answer: Correct statements: A, C, D $\Rightarrow$ **(ACD)**

Answer: (ACD) ← *Go back to Q39*

Q40.

Solution

Concept — Allotropes of Sulfur:

Statement (A) — INCORRECT: Rhombic and monoclinic sulfur both consist of $\mathbf{S_8}$ crown-shaped rings (cyclooctasulfur), *not* S_4 units. The two allotropes differ in how the S_8 rings pack in the crystal lattice.

Statement (B) — CORRECT: Rhombic (α-) sulfur is the most thermodynamically **stable** allotrope at room temperature and atmospheric pressure. It has the lowest Gibbs energy under ambient conditions.

Statement (C) — CORRECT: Monoclinic (β-) sulfur is thermodynamically stable **above** $96\,^\circ$C (the transition temperature). On slow cooling below $96\,^\circ$C, it reverts to rhombic sulfur.

Statement (D) — CORRECT: Plastic (amorphous) sulfur is produced by rapidly quenching molten sulfur ($> 180\,^\circ$C, where S_8 rings are broken) into cold water. The resulting solid is an amorphous, rubber-like, elastic material composed of long polymeric sulfur chains (S_n).

Final Answer: Correct statements: B, C, D $\Rightarrow$ **(BCD)**

Answer: (BCD) ← *Go back to Q40*

Section C Solutions — NAT

Q41.

Solution

Concept — Graham's Law (Effusion Time Ratio):

Rate of effusion $\propto 1/\sqrt{M}$. Since rate = volume/time, time $\propto \sqrt{M}$.

$$\frac{t_{CO_2}}{t_{He}} = \sqrt{\frac{M_{CO_2}}{M_{He}}}$$

Calculation:

$$\frac{t_{CO_2}}{t_{He}} = \sqrt{\frac{44}{4}} = \sqrt{11} = 3.3166\ldots \approx \mathbf{3.32}$$

$$\boxed{3.32}$$

Answer: (3.32) ← *Go back to Q41*

Q42.

Solution

Concept — Standard Entropy Change (ΔS°):

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

Reaction: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Calculation:

$$\Delta S^\circ = [S^\circ(CO_2) + 2S^\circ(H_2O)] - [S^\circ(CH_4) + 2S^\circ(O_2)]$$

$$= [213.8 + 2 \times 69.9] - [186.3 + 2 \times 205.1]$$

$$= [213.8 + 139.8] - [186.3 + 410.2]$$

$$= 353.6 - 596.5$$

$$= -242.9 \text{ J mol}^{-1}\text{K}^{-1}$$

The large negative ΔS° reflects the conversion of gaseous reactants to liquid water (large decrease in entropy).

$$\boxed{-242.9 \text{ J mol}^{-1}\text{K}^{-1}}$$

Answer: (-242.9) ← Go back to Q42

Q43.

Solution

Concept — Arrhenius Equation:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given: $k_1 = 1.5 \times 10^{-3}$ s^{-1}, $T_1 = 300$ K, $T_2 = 273$ K, $E_a = 50\,000$ J mol^{-1}, $R = 8.314$ J mol^{-1} K^{-1}.

Step 1 — Compute the exponent:

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{1}{273} - \frac{1}{300} = 0.003663 - 0.003333 = 3.30 \times 10^{-4}\ \text{K}^{-1}$$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{50000}{8.314} \times 3.30 \times 10^{-4} = -6013.0 \times 3.30 \times 10^{-4} = -1.984$$

Step 2 — Solve for k_2:

$$k_2 = k_1 \cdot e^{-1.984} = 1.5 \times 10^{-3} \times 0.1374 = 2.06 \times 10^{-4}\ \text{s}^{-1}$$

$$\boxed{k_2 = 2.06 \times 10^{-4}\ \text{s}^{-1}}$$

Answer: (2.06e-4) ← Go back to Q43

Q44.

Solution

Concept — Relationship Between K_p and K_c:

$$K_p = K_c \cdot (RT)^{\Delta n_g}$$

Reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
$\Delta n_g = 2 - (2 + 1) = -1$

Calculation:

$$RT = 0.0821 \times 700 = 57.47\ \text{L atm mol}^{-1}$$

$$K_p = K_c \cdot (RT)^{-1} = \frac{280}{57.47} = 4.872 \approx \mathbf{4.87}$$

$$\boxed{K_p = 4.87}$$

Answer: (4.87) ← *Go back to Q44*

Q45.

Solution

Concept — Kohlrausch's Law:

The limiting molar conductivity of NH_4OH cannot be measured directly (weak electrolyte). Using Kohlrausch's law:

$$\lambda_m^\circ(NH_4OH) = \lambda_m^\circ(NH_4Cl) + \lambda_m^\circ(NaOH) - \lambda_m^\circ(NaCl)$$

Rationale: NH_4^+ from NH_4Cl, OH^- from NaOH, and subtract Na^+ + Cl^- (from NaCl):

$$\lambda^\circ(NH_4^+)+\lambda^\circ(OH^-) = [\lambda^\circ(NH_4^+)+\lambda^\circ(Cl^-)]+[\lambda^\circ(Na^+)+\lambda^\circ(OH^-)]-[\lambda^\circ(Na^+)+\lambda^\circ(Cl^-)]$$

Calculation:

$$= 129.8 + 248.1 - 126.4 = 251.5 \text{ S cm}^2\text{mol}^{-1}$$

$$\boxed{\lambda_m^\circ(NH_4OH) = 251.5 \text{ S cm}^2\text{mol}^{-1}}$$

Answer: (251.5) ← *Go back to Q45*

Q46.

Solution

Concept — Heisenberg Uncertainty Principle:

$$\Delta x_{\text{min}} = \frac{h}{4\pi \cdot m_e \cdot \Delta v}$$

Given: $h = 6.626 \times 10^{-34}$ J s, $m_e = 9.11 \times 10^{-31}$ kg, $\Delta v = 1.0 \times 10^6$ m s^{-1}.

Calculation:

$$\Delta x_{\text{min}} = \frac{6.626 \times 10^{-34}}{4\pi \times 9.11 \times 10^{-31} \times 1.0 \times 10^6}$$
$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14159 \times 9.11 \times 10^{-25}}$$
$$= \frac{6.626 \times 10^{-34}}{1.1446 \times 10^{-23}}$$
$$= 5.79 \times 10^{-11} \text{ m}$$

This is approximately 0.579 Å — comparable to atomic dimensions.

$$\boxed{\Delta x_{\text{min}} = 5.79 \times 10^{-11} \text{ m}}$$

Answer: (5.79e-11) ← Go back to Q46

Q47.

Solution

Concept — Density of NaCl Crystal:

$$\rho = \frac{ZM}{N_A \cdot a^3}$$

where $Z = 4$ (FCC unit cell), $M = 58.44$ g mol^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}, $a = 5.64 \times 10^{-8}$ cm.

Step 1 — Volume of unit cell:

$$a^3 = (5.64 \times 10^{-8})^3 = (5.64)^3 \times 10^{-24} = 179.4 \times 10^{-24} \text{ cm}^3 = 1.794 \times 10^{-22} \text{ cm}^3$$

Step 2 — Denominator:

$$N_A \cdot a^3 = 6.022 \times 10^{23} \times 1.794 \times 10^{-22} = 108.0 \text{ cm}^3\text{mol}^{-1}$$

Step 3 — Density:

$$\rho = \frac{4 \times 58.44}{108.0} = \frac{233.8}{108.0} = 2.164 \approx \mathbf{2.16} \text{ g cm}^{-3}$$

$$\boxed{\rho = 2.16 \text{ g cm}^{-3}}$$

Answer: (2.16) ← Go back to Q47

Q48.

Solution

Concept — Freezing Point Depression:

$$\Delta T_f = K_f \cdot m \quad (i = 1 \text{ for non-electrolyte urea})$$

Step 1 — Calculate molality:

Moles of urea $= 6.0/60 = 0.10$ mol

Mass of solvent $= 200$ g $= 0.200$ kg

$m = 0.10/0.200 = 0.50$ mol kg^{-1}

Step 2 — Calculate ΔT_f:

$$\Delta T_f = 1.86 \times 0.50 = 0.93\,^\circ\text{C}$$

$$\boxed{\Delta T_f = 0.93\,^\circ\text{C}}$$

Answer: (0.93) ← *Go back to Q48*

Q49.

Solution

Concept — Index of Hydrogen Deficiency (IHD):

$$\text{IHD} = \frac{2C + 2 - H}{2}$$

For C_9H_{12} (mesitylene):

$$\text{IHD} = \frac{2(9) + 2 - 12}{2} = \frac{18 + 2 - 12}{2} = \frac{8}{2} = 4$$

Interpretation: Mesitylene (1,3,5-trimethylbenzene) has a benzene ring (IHD = 4): 3 double bonds + 1 ring $= 4$. This is consistent.

$$\boxed{\text{IHD} = 4}$$

Answer: (4) ← *Go back to Q49*

Q50.

Solution

Concept — Spin-Only Magnetic Moment:

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

where n = number of unpaired electrons.

Cr^{3+} configuration: Cr (Z = 24) is [Ar]$3d^5 4s^1$ in ground state. Cr^{3+} loses 3 electrons: [Ar]$3d^3$. All 3 d-electrons are unpaired (Hund's rule): $n = 3$.

Calculation:

$$\mu_s = \sqrt{3(3+2)} = \sqrt{3 \times 5} = \sqrt{15} = 3.873 \approx \mathbf{3.87}\ \text{BM}$$

$$\boxed{\mu_s = 3.87 \text{ BM}}$$

Answer: (3.87) ← *Go back to Q50*

***Q51–Q60**: 2 marks each. **No negative marking.** Full solutions below.*

Q51.

Solution

Concept — Gibbs Free Energy (ΔG°) per mole of H_2O:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Given (for the balanced equation producing 2 mol H_2O):
$\Delta H^\circ = -571.6$ kJ, $\Delta S^\circ = -326.4$ J K^{-1} $= -0.3264$ kJ K^{-1}, $T = 298$ K.

Step 1 — ΔG° for balanced equation:

$$\Delta G^\circ = -571.6 - 298 \times (-0.3264) = -571.6 + 97.27 = -474.33 \text{ kJ}$$

Step 2 — Per mole of H_2O:

$$\Delta G^\circ_{\text{per mol}} = \frac{-474.33}{2} = -237.17 \approx \mathbf{-237.2} \text{ kJ mol}^{-1}$$

$$\boxed{\Delta G^\circ = -237.2 \text{ kJ mol}^{-1} \text{ of } H_2O}$$

Answer: (-237.2) ← *Go back to Q51*

Q52.

Solution

Concept — Selectivity in Parallel First-Order Reactions:
For parallel reactions $X \xrightarrow{k_A} A$ and $X \xrightarrow{k_B} B$, the fractional yield of A is constant:

$$\text{Selectivity toward A} = \frac{k_A}{k_A + k_B} \times 100\%$$

Calculation:

$$\%\text{ to A} = \frac{0.03}{0.03 + 0.01} \times 100 = \frac{0.03}{0.04} \times 100 = 0.75 \times 100 = 75\%$$

The selectivity is independent of time and initial concentration: no matter how long the reaction proceeds, 75% of the converted X always forms A.

$$\boxed{75\%}$$

Answer: (75) ← *Go back to Q52*

Q53.

Solution

Concept — Beer–Lambert Law and Percent Transmittance:

$$A = \varepsilon c l, \qquad \%T = 100 \times 10^{-A}$$

Step 1 — Calculate absorbance:

$$A = \varepsilon c l = (1.5 \times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}) \times (5.0 \times 10^{-5} \text{ mol L}^{-1}) \times (2.00 \text{ cm})$$

$$A = 1.5 \times 10^4 \times 5.0 \times 10^{-5} \times 2.00 = 1.5$$

Step 2 — Calculate %T:

$$\%T = 100 \times 10^{-1.5} = 100 \times 0.031623 = 3.162 \approx \mathbf{3.16}\%$$

Only 3.16% of the incident light is transmitted; the solution absorbs 96.84%.

$$\boxed{\%T = 3.16\%}$$

Answer: (3.16) ← *Go back to Q53*

Q54.

Solution

Concept — IHD for C_7H_6O (Benzaldehyde):

$$\text{IHD} = \frac{2C + 2 - H}{2}$$

(Oxygen atoms do not appear in the IHD formula for C/H/O compounds.)

Calculation:

$$\text{IHD} = \frac{2(7) + 2 - 6}{2} = \frac{14 + 2 - 6}{2} = \frac{10}{2} = 5$$

Interpretation: Benzaldehyde = benzene ring (IHD = 4: 3 double bonds + 1 ring) + aldehyde C=O (IHD = 1) = IHD of 5. Consistent.

$$\boxed{\text{IHD} = 5}$$

Answer: (5) ← *Go back to Q54*

Q55.

Solution

Concept — Spin-Only Magnetic Moment of $[Fe(H_2O)_6]^{2+}$:
Fe^{2+} is d^6. H_2O is a **weak-field** ligand ⇒ **high-spin** complex.

Step 1 — Electron configuration (high-spin d^6):
$(t_{2g})^4(e_g)^2$: using Hund's rule within e_g (2 electrons, both unpaired), and t_{2g} has 4 electrons: 3 unpaired + 1 paired ⇒ 4 unpaired total ($n = 4$).

Step 2 — Calculate μ_s:

$$\mu_s = \sqrt{n(n+2)} = \sqrt{4 \times 6} = \sqrt{24} = 4.899 \approx \mathbf{4.90}\ \text{BM}$$

$$\boxed{\mu_s = 4.90\ \text{BM}}$$

Answer: (4.90) ← *Go back to Q55*

Q56.

Solution

Concept — Nernst Equation for Ag^+/Ag:

$$E = E^\circ - \frac{0.059}{n} \log\left(\frac{1}{[Ag^+]}\right)$$

Given: $E^\circ = +0.80$ V, $n = 1$, $[Ag^+] = 1.0 \times 10^{-3}$ mol L^{-1}.

Calculation:

$$\log\left(\frac{1}{[Ag^+]}\right) = \log\left(\frac{1}{10^{-3}}\right) = \log(10^3) = 3$$

$$E = 0.80 - \frac{0.059}{1} \times 3 = 0.80 - 0.177 = 0.623\ \text{V}$$

The electrode potential decreases from 0.80 V to 0.623 V due to the lower Ag^+ concentration.

$$\boxed{E = 0.623\ \text{V}}$$

Answer: (0.623) ← Go back to Q56

Q57.

Solution

Concept — van der Waals Gas and Compression Factor Z:

$$V_m \approx \frac{RT}{P} + b - \frac{a}{RT}$$

$$Z = \frac{PV_m}{RT}$$

Given (N_2): $a = 1.39$ L^2 atm mol^{-2}, $b = 0.0391$ L mol^{-1}, $T = 500$ K, $P = 200$ atm, $R = 0.0821$ L atm mol^{-1} K^{-1}.

Step 1 — Calculate each term:

$$\frac{RT}{P} = \frac{0.0821 \times 500}{200} = \frac{41.05}{200} = 0.20525 \text{ L mol}^{-1}$$

$$b = 0.0391 \text{ L mol}^{-1}$$

$$\frac{a}{RT} = \frac{1.39}{41.05} = 0.03386 \text{ L mol}^{-1}$$

Step 2 — Molar volume:

$$V_m = 0.20525 + 0.0391 - 0.03386 = 0.21049 \text{ L mol}^{-1}$$

Step 3 — Compression factor:

$$Z = \frac{PV_m}{RT} = \frac{200 \times 0.21049}{41.05} = \frac{42.098}{41.05} = 1.0255 \approx \mathbf{1.026}$$

$Z > 1$ at high pressure confirms repulsive interactions dominate.

$$\boxed{Z = 1.026}$$

Answer: (1.026) ← Go back to Q57

Q58.

Solution

Concept — Keto-Enol Tautomerism of Ethyl Acetoacetate (EAA):

Ethyl acetoacetate (EAA) exists as an equilibrium mixture of keto and enol forms. The enol is stabilised by intramolecular hydrogen bonding and conjugation (six-membered ring with H-bond). In polar solvents, the keto form dominates; in non-polar solvents (like CCl_4), the enol form is more favoured due to intramolecular H-bonding.

Given data: In CCl_4: approximately 49% enol and 51% keto.

Result: The keto form constitutes **51%** of EAA in CCl_4 solution.

$$\boxed{51\%}$$

Answer: (51) ← *Go back to Q58*

Solution

Concept — Slater's Rules for Effective Nuclear Charge (Z^*):
$Z^* = Z - \sigma$, where σ is the total shielding constant.

For a 4p electron in Br ($Z = 35$), configuration: [Ar]$3d^{10}4s^24p^5$:

Q59.

Group	Electrons	Shielding constant	Contribution
Same shell [$4s^2$, $4p^4$ (other)]	6	0.35	$6 \times 0.35 = 2.10$
$n-1$ s/p: [$3s^23p^6$]	8	0.85	$8 \times 0.85 = 6.80$
$n-1$ d: [$3d^{10}$]	10	1.00	$10 \times 1.00 = 10.00$
Inner core: [$1s^22s^22p^6$]	10	0.85	$10 \times 0.85 = 8.50$

Total shielding:

$$\sigma = 2.10 + 6.80 + 10.00 + 8.50 = 27.40$$

Effective nuclear charge:

$$Z^* = 35 - 27.40 = 7.60$$

$$\boxed{Z^* = 7.60}$$

Answer: (7.60) ← *Go back to Q59*

Q60.

Solution

Concept — Temperature at Which $K_p = 1$ (i.e., $\Delta G^\circ = 0$):
At equilibrium with $K_p = 1$: $\Delta G^\circ = -RT \ln K_p = 0$.
Setting $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0$:

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Given: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
$\Delta H^\circ = +88\,000$ J mol^{-1}, $\Delta S^\circ = +170$ J mol^{-1} K^{-1}.

Calculation:

$$T = \frac{88\,000}{170} = 517.6 \approx \mathbf{518}\ \text{K}$$

At 518 K, $\Delta G^\circ = 0$ and $K_p = 1$. Above this temperature, $T\Delta S^\circ > \Delta H^\circ \Rightarrow \Delta G^\circ < 0$ $\Rightarrow$ decomposition is spontaneous.

$$\boxed{T = 518\ \text{K}}$$

Answer: (518) ← *Go back to Q60*

Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	D	2	C	3	A	4	B	5	D
6	A	7	B	8	C	9	D	10	A
11	B	12	C	13	D	14	A	15	B
16	C	17	D	18	A	19	B	20	C
21	D	22	A	23	B	24	C	25	D
26	A	27	C	28	B	29	D	30	C
31	ABD	32	ACD	33	BC	34	ABC	35	ACD
36	BD	37	ABC	38	ABD	39	ACD	40	BCD
41	3.32	42	-242.9	43	2.06e-4	44	4.87	45	251.5
46	5.79e-11	47	2.16	48	0.93	49	4	50	3.87
51	-237.2	52	75	53	3.16	54	5	55	4.90
56	0.623	57	1.026	58	51	59	7.60	60	518