KEAM Chemistry

Sample Paper – 4

Duration: 36 Minutes **Maximum Marks: 120**

Instructions

- This paper contains **30** Multiple Choice Questions (Single Correct Answer), modelled on the Chemistry portion of **KEAM** entrance.
- Each correct answer carries **+4 marks**. There is **a penalty of** -1 **mark** for each incorrect answer. Unattempted questions carry no penalty.
- Only **one** option is correct. Choose carefully.
- Syllabus level: **Class 11 & 12 (NCERT / Kerala State Board) — Physical, Inorganic and Organic Chemistry.**
- Use of mobile phones, personal calculators, log tables, or any electronic gadgets is strictly prohibited inside the examination hall.

Chemistry Questions

Q1. Which of the following statements **correctly distinguishes molality from molarity** with respect to the effect of temperature on their values?

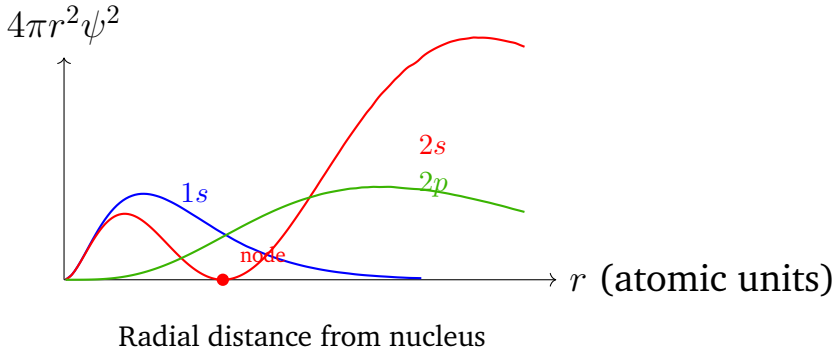
(A) Molarity is temperature-independent because it is based on the mass of the solvent, which does not change with temperature.

(B) Both molarity and molality change with temperature, since both definitions involve a volume measurement.

(C) Molality is temperature-independent because it is defined as moles of solute per kilogram of **solvent** (a mass ratio); molarity changes with temperature because it involves the **volume of solution**, which expands or contracts with temperature.

(D) Normality is the only concentration unit that is truly temperature-independent.

Q2. The figure below shows the radial probability distribution curves $4\pi r^2\psi^2$ versus r for three atomic orbitals of hydrogen ($1s$, $2s$, and $2p$). Based on these curves, which statement is **correct**?



Radial distance from nucleus

(A) The $1s$ orbital has two peaks in its radial distribution curve, indicating two shells of maximum electron density.

(B) The $2p$ orbital (for $n = 2$, $l = 1$) has one radial node where the curve crosses zero at a finite, non-zero value of r.

(C) All three orbitals shown ($1s$, $2s$, and $2p$) possess at least one radial node.

(D) The $2s$ orbital has exactly **one radial node** (the curve passes through zero at a finite r, marked in the figure), while both the $1s$ orbital and the $2p$ orbital ($n = 2$) have **zero radial nodes**.

Q3. Using **VSEPR theory**, the correct molecular geometries of **ClF_3** and **IF_5** are, respectively:

(A) Trigonal planar and pentagonal planar

(B) Trigonal pyramidal and square planar

(C) **T-shaped** (two lone pairs occupy equatorial positions of trigonal bipyramidal arrangement) and **square pyramidal** (one lone pair occupies one vertex of octahedral arrangement)

(D) Trigonal bipyramidal and octahedral

Q4. For the predominant resonance structure of **N_2O** (nitrous oxide) written as : $N{\equiv}N^+{-}O:^-$ (terminal N forms a triple bond with central N^+, which forms a single bond with O^-), the formal charges on the **terminal N**, **central N**, and **O** are respectively:

(A) $0,\ +1,\ -1$

(B) $+1,\ 0,\ -1$

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

(D) $0,\ 0,\ 0$

Q5. Among the hydrides **CH_4**, **NH_3**, **PH_3**, and **H_2S**, which compound has the **highest boiling point**, and what is the primary reason?

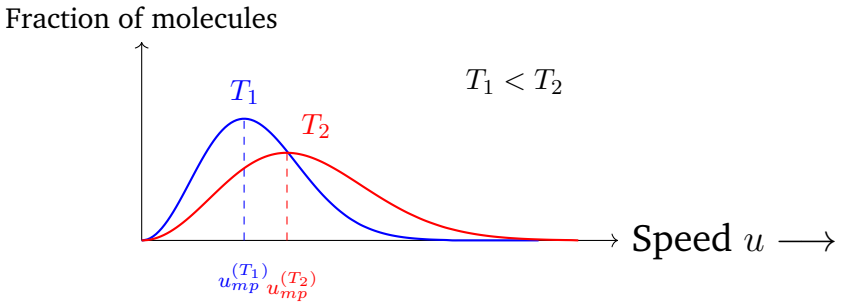
(A) CH_4, because it has the highest molar mass among the second-period hydrides listed.

(B) **NH_3**, due to strong **intermolecular hydrogen bonding** (N–H$\cdots$N); nitrogen is highly electronegative and small, making H-bonds especially strong and numerous.

(C) PH_3, because the large, polarisable phosphorus atom creates stronger London dispersion forces.

(D) H_2S, because sulfur is larger and has a more polarisable electron cloud than nitrogen, overcoming the lack of H-bonding.

Q6. The figure below shows **Maxwell–Boltzmann speed distribution** curves for an ideal gas at two temperatures T_1 and T_2 ($T_1 < T_2$). Based on the curves, which statement is **correct**?



(A) At higher temperature, the fraction of molecules at the most probable speed *increases*.

(B) The total area under the speed distribution curve *decreases* as temperature increases.

(C) At higher temperature T_2, the distribution curve is **broader and flatter**, and the most probable speed u_{mp} shifts to a **higher value** compared to T_1.

(D) The most probable speed u_{mp} is completely independent of temperature.

Q7. **Kirchhoff's equation** describes how the enthalpy change ΔH of a chemical reaction varies with temperature. If $\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})$, which of the following statements is **correct**?

(A) ΔH increases with temperature when ΔC_p is negative.

(B) ΔH is always independent of temperature for reactions involving ideal gases.

(C) ΔH decreases with temperature when ΔC_p is positive.

(D) From $\dfrac{d(\Delta H)}{dT} = \Delta C_p$: if $\Delta C_p > 0$, ΔH **increases with temperature**; if $\Delta C_p < 0$, ΔH decreases with temperature; only if $\Delta C_p = 0$ is ΔH temperature-independent.

Q8. For the **isothermal reversible expansion** of n moles of an ideal gas from volume V_1 to V_2 (where $V_2 > V_1$) at temperature T, the work done *on* the system (IUPAC sign convention) is:

(A) $W = -nRT \ln\left(\dfrac{V_2}{V_1}\right) = -nRT \ln\left(\dfrac{P_1}{P_2}\right)$, which is **negative** for expansion (system does work on surroundings).

(B) $W = +nRT \ln\left(\dfrac{V_2}{V_1}\right)$, which is positive for expansion.

(C) $W = -P_{\text{ext}}(V_2 - V_1)$, which is the correct expression for isothermal reversible expansion.

(D) $W = 0$, since temperature is constant in an isothermal process.

Q9. For a weak monobasic acid HA dissolved in water at concentration C mol/L, if α is the **degree of dissociation** and K_a is the acid dissociation constant, the approximate expression (valid when $\alpha \ll 1$, i.e. Ostwald's dilution law) is:

(A) $\alpha = K_a \,/\, C$

(B) $\alpha = K_a \cdot C$

(C) $\alpha = \sqrt{K_a \,/\, C}$

(D) $\alpha = \sqrt{K_a \cdot C}$

Q10. For the sparingly soluble salt **CaF_2**, the solubility equilibrium is:

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + 2\,\mathrm{F^-(aq)}$$

If the molar solubility of CaF_2 is s mol/L, then the solubility product K_{sp} equals:

(A) $K_{sp} = s^2$

(B) $K_{sp} = 4s^3$

(C) $K_{sp} = s^3$

(D) $K_{sp} = 2s^3$

Q11. According to the **electrochemical theory of corrosion**, the rusting of iron in the presence of moisture and oxygen proceeds as a **galvanic cell** process. Which of the following descriptions is **correct**?

(A) Iron acts as the *cathode* and is oxidised; oxygen is reduced at the anode.

(B) Corrosion is a purely chemical (non-electrochemical) process involving no electron transfer.

(C) The entire surface of an iron object corrodes uniformly, regardless of impurities or mechanical stress.

(D) Iron acts as the **anode** ($\mathrm{Fe \rightarrow Fe^{2+} + 2e^-}$, oxidation); electrons flow to the cathodic region where O_2 is reduced; moisture/saline water acts as the electrolyte; and the product $Fe(OH)_3/Fe_2O_3 \cdot xH_2O$ (rust) forms.

Q12. **Kohlrausch's law of independent migration of ions** states that, at infinite dilution, the molar conductivity Λ_m^∞ of any electrolyte:

(A) Is equal to the **sum** of the limiting molar ionic conductances of its constituent ions: $\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$, where $\nu_\pm$ are stoichiometric

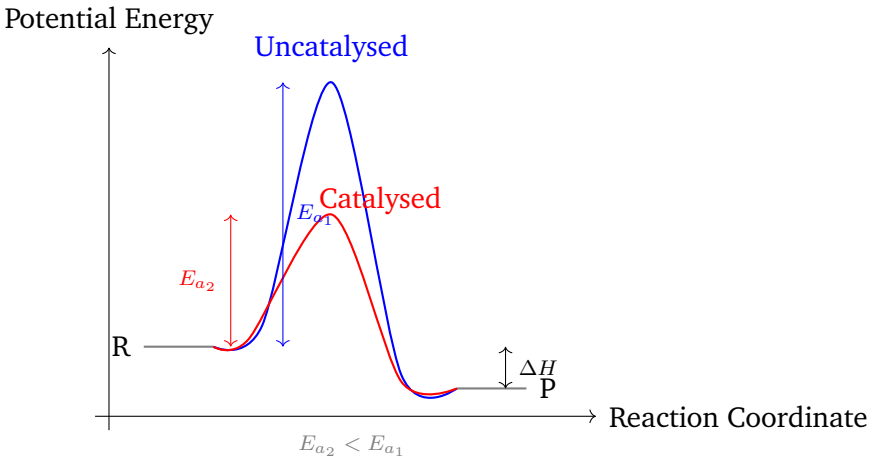
numbers. This also allows indirect determination of Λ_m^∞ for weak electrolytes.

(B) Is equal to the *product* of the limiting molar ionic conductances of its ions.

(C) Depends on the concentration of the electrolyte even at infinite dilution.

(D) Cannot be used to estimate Λ_m^∞ for weak electrolytes like acetic acid.

Q13. The energy profile diagram below shows the potential energy versus reaction coordinate for both the **uncatalysed** (blue) and **catalysed** (red) pathways of the same reaction. Based on the diagram, which statement is **correct**?



(A) A catalyst *increases* the activation energy of the forward reaction, allowing more molecules to react.

(B) A catalyst lowers the ΔH (enthalpy change) of the reaction by stabilising the products.

(C) A catalyst provides an alternative reaction pathway with a **lower activation energy** ($E_{a_2} < E_{a_1}$), while the overall ΔH of the reaction (difference in energy of reactants and products) remains **unchanged**.

(D) Addition of a catalyst significantly increases the equilibrium constant K_c of the reaction.

Q14. The acid-catalysed hydrolysis of ethyl acetate in aqueous solution:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

is experimentally found to obey **first-order kinetics** (rate $= k'[\text{ester}]$) even though two reactants are involved. This is because:

(A) The reaction is inherently zero-order; the rate does not depend on any concentration.

(B) Water is the solvent and is present in enormous excess ($[H_2O] \approx 55.5\,\text{mol}\,L^{-1}$); its concentration remains essentially **constant**, making it a **pseudo first-order** reaction with $k' = k[H_2O]$.

(C) The reaction is truly second-order but only the ester concentration appears in the rate law by convention.

(D) The acid catalyst is consumed during the reaction, making the order undefined.

Q15. Acetic acid (CH_3COOH) when dissolved in **benzene** undergoes **dimerisation** through hydrogen bonding:

$$2\,CH_3COOH(\text{benzene}) \rightleftharpoons (CH_3COOH)_2(\text{benzene})$$

If dimerisation is **essentially complete**, the van't Hoff factor i for acetic acid in benzene is approximately:

(A) $i = 2$ (association doubles the particle count)

(B) $i = 1$ (no change in number of particles)

(C) $i = 1.5$ (partial dimerisation assumed)

(D) $i = 0.5$ (two moles of monomer associate to form one mole of dimer, halving the number of solute particles in solution)

Q16. According to **Henry's law**, $p = K_H \cdot x$ (where K_H is Henry's constant, x is the mole fraction of dissolved gas, and p is the partial pressure of the gas). If the partial pressure of CO_2 above a carbonated drink is **doubled** at constant temperature, its molar solubility in the drink will:

(A) Remain unchanged (Henry's law does not apply to CO_2).

(B) Decrease by half (inverse relationship).

(C) **Double**, because $x = p/K_H$; doubling p at constant K_H directly doubles the mole fraction x of dissolved CO_2.

(D) Increase four-fold (quadratic relationship with pressure).

Q17. The term **"inert pair effect"**, observed prominently in heavier p-block elements (Groups 13–15), refers to:

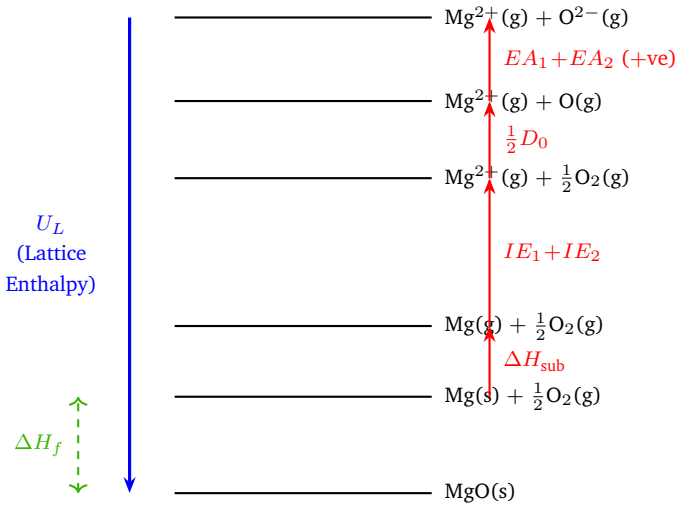
(A) The reluctance of the outermost ns^2 electron pair to participate in bond formation, due to poor shielding by filled $(n-1)d$ and $(n-2)f$ electrons; heavier elements preferentially adopt the $(n-2)$ **oxidation state** (e.g., Tl^{+} is more stable than Tl^{3+}; Pb^{2+} more stable than Pb^{4+}; Bi^{3+} more stable than Bi^{5+}).

(B) The tendency of heavier p-block elements to form more stable higher oxidation states ($+4$, $+5$) than lighter members.

(C) Greater covalent bonding tendency in heavier p-block elements due to increased polarisability.

(D) Higher electronegativity of heavier p-block elements causing them to be less reactive with non-metals.

Q18. The **Born–Haber cycle** for formation of **MgO(s)** from its elements is shown below (energy levels connected by arrows). Based on the cycle, which statement is **correct**?



(A) The second electron affinity (EA_2) of oxygen ($O^{-} \rightarrow O^{2-}$) is strongly exothermic because O^{2-} is a very stable species.

(B) The enormous **exothermic lattice enthalpy** of MgO (Mg^{2+} and O^{2-} are small, doubly charged ions) more than compensates for the **en-**

dothermic second electron affinity ($EA_2 \approx +798\,\mathrm{kJ\,mol^{-1}}$) and other endothermic steps, making ΔH_f of MgO negative.

(C) The formation of Mg^{2+} from gaseous Mg requires only a single ionisation energy.

(D) The Born–Haber cycle cannot be applied to ionic compounds that contain multiply charged ions.

Q19. Which of the following statements about the **structures and properties of nitrogen oxides** (NO, NO_2, N_2O_5) is **correct**?

(A) NO is a diamagnetic molecule with no unpaired electrons ($\sigma^2\pi^4$ electronic configuration).

(B) NO_2 is a linear molecule with bond angle 180° (similar to CO_2).

(C) N_2O_5 contains only N=O double bonds; there is no N−O−N bridging oxygen.

(D) NO has **one unpaired electron** (11 electrons total, paramagnetic odd-electron species); NO_2 also has **one unpaired electron** (17 electrons, paramagnetic, bent shape $\approx 134^\circ$); and N_2O_5 contains a **N−O−N bridging oxygen** in its covalent structure $O_2N{-}O{-}NO_2$.

Q20. Silicones are important synthetic polymers. Which statement **correctly describes their structure and properties**?

(A) Silicones have a carbon–carbon backbone (−C−C−) similar to polyethylene.

(B) Silicones are ionic compounds that dissolve freely in water.

(C) Silicones possess a **Si−O−Si (siloxane) backbone** with organic groups (e.g., $-CH_3$, $-C_6H_5$) covalently bonded to each Si atom; they are **water-repellent, thermally stable** (up to $\approx 250^\circ$C), chemically inert, and used as lubricants, sealants, waterproofing agents, and in medical prosthetics/implants.

(D) Silicones are allotropic forms of silicon dioxide (SiO_2), differing only in crystal structure.

Q21. Due to **lanthanide contraction**, which pair of 4d and 5d transition elements (from the same group) shows **remarkably similar atomic and ionic radii** and, as a consequence, nearly identical chemical properties?

(A) **Zr (Group 4, 4d) and Hf (Group 4, 5d)**: lanthanide contraction causes Hf to have almost the same atomic radius ($\approx$159 pm) as Zr ($\approx$160 pm), making them the most chemically similar pair in the periodic table and extremely difficult to separate.

(B) Ti (3d, Group 4) and Zr (4d, Group 4) show near-identical properties due to lanthanide contraction.

(C) La and Ac show chemical similarity because of lanthanide contraction in the 5d series.

(D) Fe (3d) and Ru (4d) show near-identical properties because of actinide contraction.

Q22. The **chelate effect** refers to the greater thermodynamic stability of metal complexes formed by polydentate (chelating) ligands compared to analogous complexes of equivalent monodentate ligands. The **primary reason** for this extra stability is:

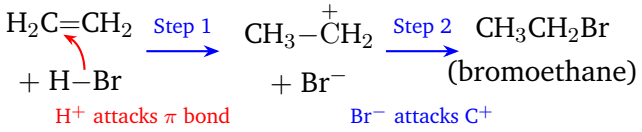
(A) Each individual metal–chelate bond is inherently much stronger than the corresponding metal–monodentate bond.

(B) A **favourable entropy increase** ($\Delta S > 0$): replacement of several monodentate ligands by one polydentate ligand releases more free molecules into solution, increasing the number of independent species and hence the entropy of the system, making $\Delta G = \Delta H - T\Delta S$ more negative.

(C) Chelate rings reduce the overall size of the complex, preventing its dissociation.

(D) The chelate effect is purely an enthalpic stabilisation; the entropy contribution is negligible.

Q23. The schematic diagram below shows the **mechanism of electrophilic addition of HBr to ethene**. Based on the diagram, which statement **correctly describes** this mechanism?



(A) The addition of HBr to ethene proceeds by a *free-radical* mechanism initiated by UV light or peroxides.

(B) The first step of the mechanism involves nucleophilic attack of Br^- directly on the π bond.

(C) The carbocation intermediate $CH_3CH_2^+$ formed in Step 1 is a *nucleophile* that attacks Br^-.

(D) The mechanism involves **electrophilic attack of H^+ (from HBr) on the π electrons of ethene** to form a carbocation intermediate (Step 1, slow), followed by **nucleophilic attack of Br^-** on the carbocation to give bromoethane (Step 2, fast).

Q24. An organic compound containing **only C, H, and O** is burned completely. Combustion of **0.50 g** of the compound yields **0.733 g of CO_2** and **0.300 g of H_2O**. The **empirical formula** of the compound is:

(A) $C_2H_4O_2$

(B) C_2H_2O

(C) CH_2O $[\,C : H : O = 0.0167 : 0.0333 : 0.0167 = 1 : 2 : 1\,]$

(D) CH_4O

Q25. **DDT** (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was one of the first synthetic insecticides. Which of the following statements about DDT is **correct**?

(A) DDT is a **persistent organochlorine pesticide**: it is non-biodegradable, **lipophilic** (accumulates in fatty tissues), and undergoes **biomagnification** up the food chain; once used widely against malaria-carrying mosquitoes, it is now banned in most countries under the Stockholm Convention on persistent organic pollutants (POPs) due to ecotoxicity and human health concerns.

(B) DDT is a biodegradable carbamate insecticide that decomposes rapidly in soil and water.

(C) DDT acts as a systemic fungicide used to protect crop plants from fungal infections.

(D) DDT is an organophosphate compound that inhibits the enzyme acetylcholinesterase in insects.

Q26. The **iodoform test** (I_2 / NaOH) gives a characteristic yellow precipitate of iodoform (CHI_3) with compounds that contain the **CH_3CO-** group or the **$CH_3CH(OH)-$** group. Which of the following pairs both give a **positive iodoform test**?

(A) Propanal (CH_3CH_2CHO) and 1-propanol ($CH_3CH_2CH_2OH$)

(B) **Acetaldehyde (CH_3CHO) and ethanol (C_2H_5OH)**: acetaldehyde has the CH_3CO- unit; ethanol is oxidised in situ to acetaldehyde under the basic conditions and then gives CHI_3.

(C) Benzaldehyde (C_6H_5CHO) and phenol (C_6H_5OH)

(D) Pentan-3-one ($CH_3CH_2COCH_2CH_3$) and cyclohexanol

Q27. Both **Clemmensen reduction** and **Wolff–Kishner reduction** convert the carbonyl group (C=O) in aldehydes or ketones directly to a methylene group ($-CH_2-$). Which statement **correctly distinguishes** the two methods?

(A) Clemmensen reduction uses NH_2NH_2 and KOH; Wolff–Kishner reduction uses Zn-Hg amalgam and conc. HCl.

(B) Both reductions use acidic conditions (Zn-Hg/HCl) and convert ketones to secondary alcohols.

(C) Wolff–Kishner uses Zn-Hg/conc. HCl (acidic medium); Clemmensen uses NH_2NH_2/KOH (basic medium).

(D) **Clemmensen reduction** uses **Zn-Hg amalgam / conc. HCl** (**acidic medium**; not suitable for acid-sensitive substrates); **Wolff–Kishner reduction** uses **NH_2NH_2 / KOH, high temperature** (**basic medium**; not suitable for base-sensitive substrates); both give $-CH_2-$ from

C=O.

Q28. **Fischer esterification** is the acid-catalysed reaction of a carboxylic acid with an alcohol:

$$\mathrm{RCOOH} + \mathrm{R'OH} \underset{\Delta}{\overset{H^+}{\rightleftharpoons}} \mathrm{RCOOR'} + \mathrm{H_2O}$$

Which of the following statements about this reaction is **correct**?

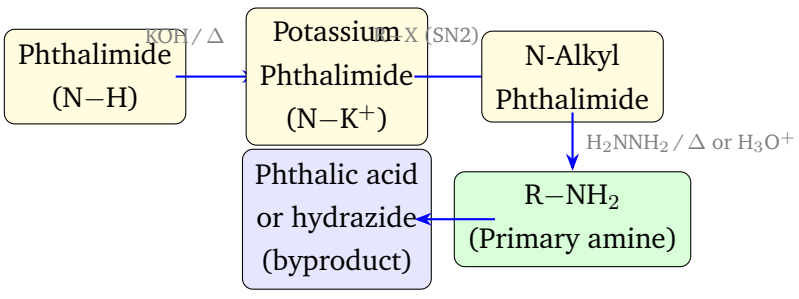
(A) Fischer esterification is an irreversible reaction that proceeds to $>$ 99% completion under all conditions.

(B) The mechanism involves nucleophilic attack of the *carboxylic acid oxygen* on the protonated alcohol carbon.

(C) Fischer esterification is a **reversible equilibrium reaction**; yield of ester is maximised by removing water (e.g., using molecular sieves, azeotropic distillation) or using a large excess of one reactant; the mechanism proceeds by **nucleophilic addition of the alcohol oxygen to the protonated carbonyl carbon** of the acid, followed by elimination of water.

(D) Fischer esterification occurs only with primary alcohols; secondary and tertiary alcohols are completely unreactive.

Q29. The **Gabriel phthalimide synthesis** for preparing primary amines is shown schematically below. Based on the diagram, which statement about this synthesis is **correct**?



(A) Gabriel synthesis **exclusively produces primary amines**: phthalimide has only one N−H bond, so only a single N-alkylation is possible; **secondary and tertiary amines cannot be prepared** by this route.

(B) Gabriel synthesis can produce secondary and tertiary amines by successive alkylation steps.

(C) The final hydrolysis step requires H_2/Pd as a catalyst to release the primary amine.

(D) Aryl halides (ArX) readily undergo Gabriel synthesis via the SN2 mechanism.

Q30. Which of the following **correctly defines** both the **saponification number** and the **iodine value** of fats and oils?

(A) Saponification number measures the degree of unsaturation; iodine value indicates the average molecular mass of the fatty acid chains.

(B) **Saponification number**: the number of **milligrams of KOH** required to saponify completely **1 gram of fat/oil** (inversely related to the average molar mass of constituent fatty acids — fats with shorter chains have higher saponification numbers). **Iodine value**: the number of **grams of I_2 absorbed per 100 grams of fat/oil** (measures the degree of unsaturation — higher iodine value indicates more C=C double bonds, i.e. more unsaturated fat or oil).

(C) A high iodine value indicates that the fat is highly *saturated* and free from double bonds.

(D) Saponification number directly equals the total number of ester linkages in one molecule of the fat.

Solutions

Sol 1.

Solution

Concept — Concentration units: Molarity (M) = moles of solute / volume of solution in litres. Volume changes with temperature (thermal expansion), so molarity is *temperature-dependent*. Molality (m) = moles of solute / mass of solvent in kilograms. Mass does not vary with temperature, so molality is *temperature-independent*.

Step 1 — Key distinction:

- Molarity involves volume of *solution* $\Rightarrow$ changes with temperature.
- Molality involves mass of *solvent* $\Rightarrow$ independent of temperature.

Why other options are wrong:

- Option A: Incorrectly claims molarity is temperature-independent; molarity involves volume, not mass.
- Option B: Incorrect; molality is mass-based and does *not* change with temperature.
- Option D: Normality is also volume-based (equivalents per litre) and is temperature-dependent.

Final Answer: Molality is temperature-independent (mass-based); molarity is not (volume-based). $\Rightarrow$ C

Answer: (C) Go Back to Q 1

Sol 2.

Solution

Concept — Radial nodes: The number of radial nodes for an orbital with quantum numbers n (principal) and l (azimuthal) is given by $(n - l - 1)$.

- $1s$: $n = 1$, $l = 0 \Rightarrow$ radial nodes $= 1 - 0 - 1 = 0$
- $2s$: $n = 2$, $l = 0 \Rightarrow$ radial nodes $= 2 - 0 - 1 = 1$
- $2p$: $n = 2$, $l = 1 \Rightarrow$ radial nodes $= 2 - 1 - 1 = 0$

Step 1 — Reading the diagram: The $2s$ curve crosses zero at one finite value of r (the node marked in the figure), confirming exactly one radial node. The $1s$ curve starts at zero (at $r = 0$) and increases to a single peak then decays smoothly

— no crossing, zero radial nodes. The $2p$ curve is zero only at the origin ($r = 0$) due to the centrifugal barrier ($\propto r^l$), has one broad hump, and zero radial nodes.

Why other options are wrong:

- Option A: $1s$ has a single peak; not two.
- Option B: $2p$ has zero radial nodes ($n - l - 1 = 0$); the curve does not cross zero at any non-zero r.
- Option C: $1s$ and $2p$ both have zero radial nodes; the statement "all three have at least one" is false.

Final Answer: $2s$ has 1 radial node; $1s$ and $2p$ ($n = 2$) each have 0 radial nodes. $\Rightarrow$ D

Answer: (D) Go Back to Q 2

Sol 3.

Solution

Concept — VSEPR theory: The shape is determined by the number of electron pairs (bonding + lone) around the central atom. Lone pairs exert greater repulsion than bonding pairs.

Step 1 — ClF_3 (electron pairs around Cl): Cl: 7 valence electrons; 3 used in bonding with F; 2 lone pairs remain. Total: 5 electron pairs (trigonal bipyramidal geometry). Lone pairs preferentially occupy equatorial positions (less repulsion). With 3 F and 2 LP: **T-shaped** (bond angle $\approx 87.5°$).

Step 2 — IF_5 (electron pairs around I): I: 7 valence electrons; 5 used in bonding with F; 1 lone pair. Total: 6 electron pairs (octahedral geometry). One LP occupies one apex position. With 5 F and 1 LP: **square pyramidal**.

Why other options are wrong:

- Option A: Trigonal planar requires 3 bonds and 0 LP; pentagonal planar is not a VSEPR shape for these.
- Option B: Trigonal pyramidal (e.g., NH_3, with 3 bonds + 1 LP) does not match ClF_3 (2 LP).
- Option D: Trigonal bipyramidal (5 bonds, 0 LP) and octahedral (6 bonds, 0 LP) ignore the lone pairs.

Final Answer: ClF_3 is T-shaped; IF_5 is square pyramidal. $\Rightarrow$ C

Answer: (C) Go Back to Q 3

Sol 4.

Solution

Concept — Formal charge: $\mathrm{FC} = V_e - N_e - \frac{1}{2}B_e$, where V_e = valence electrons of the free atom, N_e = non-bonding electrons on the atom, B_e = bonding electrons shared by the atom.

Step 1 — Structure :N≡N$^+$−O:$^-$:

Atom	V_e	N_e	B_e (half) $\Rightarrow$ FC
Terminal N (≡N, with one lone pair)	5	2	$6/2 = 3 \Rightarrow 5 - 2 - 3 = \mathbf{0}$
Central N (≡N$^+$−, no lone pairs)	5	0	$8/2 = 4 \Rightarrow 5 - 0 - 4 = \mathbf{+1}$
O (−O:$^-$, three lone pairs)	6	6	$2/2 = 1 \Rightarrow 6 - 6 - 1 = \mathbf{-1}$

Why other options are wrong:

- Option B: Assigns $+1$ to terminal N and 0 to central N — incorrect allocation of bonds.
- Option C: Assigns -1 to terminal N — terminal N has 2 non-bonding electrons and forms triple bond.
- Option D: Zero formal charges on all atoms would require a different (less stable) Lewis structure.

Final Answer: Terminal N: 0; central N: $+1$; O: -1. $\Rightarrow$ A

Answer: (A) Go Back to Q 4

Sol 5.

Solution

Concept — Intermolecular forces and boiling point: Stronger intermolecular forces require more energy to overcome $\Rightarrow$ higher boiling point. Hydrogen bonding (X−H$\cdots$X, X = N, O, F) is significantly stronger than dipole–dipole or London dispersion forces.

Step 1 — Comparison of boiling points:

- CH_4 (bp $= -161.5°$C): non-polar; only weak London dispersion forces.
- **NH_3** (bp $= -33.4°$C): **strong N−H$\cdots$N hydrogen bonds**. N is highly electronegative ($\chi = 3.0$) and the molecule is small $\Rightarrow$ effective H-bonding.
- PH_3 (bp $= -87.7°$C): P is large and less electronegative; H-bonding is negligible.
- H_2S (bp $= -60.3°$C): S is large with polarisable electrons; slightly stronger London forces than PH_3, but no H-bonding.

$NH_3 > H_2S > PH_3 > CH_4$ in boiling point.

Why other options are wrong:

- A: CH_4 has only London forces and has the *lowest* boiling point in this series.
- C: PH_3 cannot form effective H-bonds; its bp is below H_2S.
- D: H_2S has higher bp than PH_3 but far lower than NH_3.

Final Answer: NH_3 has the highest boiling point due to intermolecular hydrogen bonding. $\Rightarrow$ B

Answer: (B) Go Back to Q 5

Sol 6.

Solution

Concept — Maxwell–Boltzmann distribution: The speed distribution function is $f(u) \propto u^2 e^{-mu^2/2k_BT}$. The most probable speed $u_{mp} = \sqrt{2RT/M}$. As T increases: (1) u_{mp} increases; (2) the curve shifts right and flattens (broader); (3) the total area under the curve remains 1 (constant number of molecules).

Step 1 — Analysis of the diagram: The T_2 curve (red) has its peak at a higher speed than T_1 (blue): $u_{mp}^{(T_2)} > u_{mp}^{(T_1)}$. The T_2 curve is broader (wider) with a lower peak height; T_1 is narrower with a taller peak.

Why other options are wrong:

- Option A: The peak height (fraction at u_{mp}) *decreases* at higher T; the curve flattens.
- Option B: Area under both curves is always 1 (normalisation condition); it does not decrease.
- Option D: $u_{mp} = \sqrt{2RT/M}$ explicitly shows that u_{mp} increases with T.

Final Answer: Higher T_2: broader, flatter curve; u_{mp} shifts to higher values. $\Rightarrow$ C

Answer: (C) Go Back to Q 6

Sol 7.

Solution

Concept — Kirchhoff's equation: $\dfrac{d(\Delta H)}{dT} = \Delta C_p$.

Integrating: $\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_p(T_2 - T_1)$.

Step 1 — Analysis:

- If $\Delta C_p > 0$: $\dfrac{d(\Delta H)}{dT} > 0 \Rightarrow \Delta H$ **increases** with temperature.
- If $\Delta C_p < 0$: $\dfrac{d(\Delta H)}{dT} < 0 \Rightarrow \Delta H$ **decreases** with temperature.
- If $\Delta C_p = 0$: ΔH is temperature-independent.

Why other options are wrong:

- Option A: When $\Delta C_p < 0$, ΔH decreases (not increases) with T.
- Option B: ΔH is temperature-independent only if $\Delta C_p = 0$, not generally.
- Option C: ΔH decreases when $\Delta C_p < 0$ (not positive).

Final Answer: Kirchhoff's equation: $\Delta C_p > 0 \Rightarrow \Delta H$ increases with temperature. $\Rightarrow$ D

Answer: (D) Go Back to Q 7

Sol 8.

Solution

Concept — Work in isothermal reversible expansion: For a reversible process, the external pressure equals the gas pressure at each infinitesimal step. Work done *on* system: $W = -\int_{V_1}^{V_2} P_{\text{gas}}\, dV$.

Step 1 — Derivation:

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V}\, dV = -nRT\left[\ln V\right]_{V_1}^{V_2} = -nRT \ln \frac{V_2}{V_1}$$

For an isothermal process with ideal gas: $P_1V_1 = P_2V_2 \Rightarrow V_2/V_1 = P_1/P_2$. So $W = -nRT \ln(P_1/P_2)$.

For **expansion** ($V_2 > V_1$, $P_2 < P_1$): $\ln(V_2/V_1) > 0 \Rightarrow W < 0$ (system does work on surroundings).

Why other options are wrong:

- Option B: Has the wrong sign (positive); this would mean work is done *on*

the system during expansion, which is incorrect.

- Option C: $W = -P_{\text{ext}}\Delta V$ applies to *irreversible* expansion at constant external pressure.
- Option D: $W \neq 0$; "isothermal" means constant temperature (not zero work). For isothermal expansion, $\Delta U = 0$, so $q = -W \neq 0$.

Final Answer: $W = -nRT\ln(V_2/V_1)$, negative for expansion. $\Rightarrow$ A

Answer: (A) Go Back to Q 8

Sol 9.

Solution

Concept — Weak acid equilibrium: HA $\rightleftharpoons$ H^+ + A^-. At initial concentration C and degree of dissociation α: $[H^+] = [A^-] = C\alpha$; $[HA] = C(1-\alpha)$.

Step 1 — Deriving the expression:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

When $\alpha \ll 1$: $(1-\alpha) \approx 1$, so $K_a \approx C\alpha^2$.

$$\alpha^2 = \frac{K_a}{C} \quad \Rightarrow \quad \boxed{\alpha = \sqrt{\frac{K_a}{C}}}$$

This is **Ostwald's dilution law**: the degree of dissociation of a weak electrolyte is inversely proportional to the square root of concentration.

Why other options are wrong:

- Option A: $\alpha = K_a/C$ would imply $K_a = C\alpha$ (not $C\alpha^2$); dimensionally incorrect.
- Option B: $\alpha = K_aC$ would give $\alpha > 1$ for large C — physically impossible.
- Option D: $\alpha = \sqrt{K_aC}$ would mean $K_a = \alpha^2/C^2 \cdot C = \alpha^2/C$ — wrong sign of dependence.

Final Answer: $\alpha = \sqrt{K_a/C}$ (Ostwald's dilution law, for $\alpha \ll 1$). $\Rightarrow$ C

Answer: (C) Go Back to Q 9

Sol 10.

Solution

Concept — Solubility product: K_{sp} = product of ionic concentrations raised to their stoichiometric powers at equilibrium.

Step 1 — CaF_2 dissociation:

$$\mathrm{CaF_2(s)} \rightleftharpoons \mathrm{Ca^{2+}(aq)} + 2\,\mathrm{F^-(aq)}$$

If molar solubility $= s$: $[\mathrm{Ca^{2+}}] = s$ and $[\mathrm{F^-}] = 2s$ (two moles of F^- per formula unit).

$$K_{sp} = [\mathrm{Ca^{2+}}][\mathrm{F^-}]^2 = (s)(2s)^2 = s \times 4s^2 = 4s^3$$

Why other options are wrong:

- Option A: s^2 applies to a 1:1 electrolyte like AgCl ($[\mathrm{Ag^+}][\mathrm{Cl^-}] = s^2$).
- Option C: s^3 omits the stoichiometric factor from $[\mathrm{F^-}]^2 = (2s)^2 = 4s^2$, not s^2.
- Option D: $2s^3$ is also wrong; the correct factor from $(2s)^2$ is 4, not 2.

Final Answer: $K_{sp}(\mathrm{CaF_2}) = (s)(2s)^2 = 4s^3$. $\Rightarrow$ B

Answer: (B) Go Back to Q 10

Sol 11.

Solution

Concept — Electrochemical theory of corrosion: Corrosion of iron operates as an electrochemical (galvanic) cell. Grain boundaries, impurities (e.g., cementite Fe_3C), and regions of mechanical stress create localised potential differences.

Step 1 — Half-reactions:

- **Anodic region** (oxidation, iron corrodes): $\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\mathrm{e^-}$, $E^\circ = -0.44\,\mathrm{V}$.
- **Cathodic region** (reduction, O_2 consumed): $\mathrm{O_2(g)} + 2\mathrm{H_2O(l)} + 4\mathrm{e^-} \rightarrow 4\mathrm{OH^-(aq)}$, $E^\circ = +0.40\,\mathrm{V}$.
- Fe^{2+} further oxidised and hydrated: $4\mathrm{Fe^{2+}} + \mathrm{O_2} + 8\mathrm{OH^-} + 4x\mathrm{H_2O} \rightarrow 2\mathrm{Fe_2O_3}\cdot x\mathrm{H_2O}$ (rust).
- Moisture and dissolved electrolytes (CO_2, NaCl) act as the electrolyte.

Why other options are wrong:

- Option A: Iron is the *anode* (oxidised), not cathode; oxidation and reduction occur at different sites.
- Option B: Corrosion is fundamentally an electrochemical (redox) process.
- Option C: Corrosion occurs preferentially at pits, scratches, grain boundaries and stressed regions — not uniformly.

Final Answer: Iron = anode (Fe $\rightarrow$ Fe^{2+}); O_2 reduced at cathode; moisture = electrolyte. $\Rightarrow$ $\boxed{D}$

Answer: (D) Go Back to Q 11

Sol 12.

Solution

Concept — Kohlrausch's law of independent migration: At infinite dilution, interionic interactions become negligible, and each ion migrates independently in the electric field with its own characteristic limiting molar conductance λ^∞.

Step 1 — Statement of law:

$$\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$$

where ν_+ and ν_- are the stoichiometric numbers of cations and anions.

Important application: Allows calculation of Λ_m^∞ for *weak electrolytes* (e.g., CH_3COOH) that cannot be measured directly by extrapolation, using data from strong electrolytes:

$$\Lambda_m^\infty(CH_3COOH) = \Lambda_m^\infty(HCl) + \Lambda_m^\infty(CH_3COONa) - \Lambda_m^\infty(NaCl)$$

Why other options are wrong:

- Option B: Ionic conductances are *added*, not multiplied.
- Option C: At *infinite* dilution, ions are infinitely far apart; Λ_m^∞ is a constant, not concentration-dependent.
- Option D: Kohlrausch's law specifically enables calculation of Λ_m^∞ for weak electrolytes indirectly.

Final Answer: $\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$ (sum of limiting ionic conductances). $\Rightarrow$ $\boxed{A}$

Answer: (A) Go Back to Q 12

Sol 13.

Solution

Concept — Catalysis and energy profile: A catalyst provides an alternative reaction pathway that passes through transition state(s) of lower energy. It does not alter the energy levels of the reactants (R) or products (P), so $\Delta H = H(\mathrm{P}) - H(\mathrm{R})$ is the same for both pathways.

Step 1 — Reading the diagram: Both blue (uncatalysed) and red (catalysed) curves originate from the same reactant level and terminate at the same product level. The catalysed pathway passes through a lower-energy transition state ($E_{a_2} < E_{a_1}$). The ΔH (vertical gap between R and P levels) is identical for both.

Why other options are wrong:

- Option A: A catalyst *lowers* activation energy; this is its defining property.
- Option B: ΔH depends only on the energy difference between reactants and products — both curves have the same R and P levels.
- Option D: The equilibrium constant $K_c = e^{-\Delta G^\circ/RT}$, which depends on ΔG° (state function). A catalyst does not change ΔG°, so K_c is unchanged.

Final Answer: Catalyst lowers E_a ($E_{a_2} < E_{a_1}$); ΔH of reaction is unchanged. $\Rightarrow$ C

Answer: (C) Go Back to Q 13

Sol 14.

Solution

Concept — Pseudo first-order reactions: When one reactant is in great excess (typically the solvent), its concentration is virtually constant throughout the reaction. The reaction then appears to be of lower order — it is called *pseudo first-order*.

Step 1 — Analysis: True rate law: rate $= k[\text{ester}][\mathrm{H_2O}]$ (second-order overall).

$[\mathrm{H_2O}]$ in water as solvent $\approx 55.5\,\mathrm{mol\,L^{-1}}$, which is essentially **constant** compared to ester concentration ($\ll 1\,\mathrm{mol\,L^{-1}}$). Therefore:

$$\text{rate} = k'[\text{ester}], \quad k' = k[\mathrm{H_2O}] = \text{constant}$$

This is a **pseudo first-order** reaction with effective (pseudo) rate constant k'.

Why other options are wrong:

- Option A: Rate clearly depends on ester concentration; zero-order would mean constant rate regardless of [ester].
- Option C: The reaction *is* truly second-order, but appears first-order due to the constant $[H_2O]$.
- Option D: H^+ is a catalyst; it is not consumed (it is regenerated), so it cannot make the order "undefined."

Final Answer: Pseudo first-order reaction; $[H_2O] \approx$ const. gives effective first-order. $\Rightarrow$ B

Answer: (B) Go Back to Q 14

Sol 15.

Solution

Concept — Van't Hoff factor for association: When solute particles *associate*, the number of particles in solution decreases; the van't Hoff factor $i < 1$. For n moles of monomer $\rightarrow$ 1 mole of n-mer: $i = 1/n$.

Step 1 — Complete dimerisation:

$$2\,CH_3COOH \rightarrow (CH_3COOH)_2$$

Start with 1 mol monomer; after complete dimerisation: $\frac{1}{2}$ mol dimer.

$$i = \frac{\text{moles of particles in solution after association}}{\text{moles of solute initially dissolved}} = \frac{1/2}{1} = 0.5$$

Physical consequence: colligative properties (e.g., depression of freezing point) are halved compared to a non-associating solute of the same molality.

Why other options are wrong:

- Option A: $i = 2$ corresponds to complete *dissociation* into 2 ions (e.g., NaCl in water); here particles decrease.
- Option B: $i = 1$ means no change in particle count; applies to non-electrolytes like glucose in water.
- Option C: $i = 1.5$ would correspond to 50% dimerisation (partial); question specifies complete dimerisation.

Final Answer: Complete dimerisation $\Rightarrow i = 0.5$. $\Rightarrow$ D

Answer: (D) Go Back to Q 15

Sol 16.

Solution

Concept — Henry's law: $p = K_H \cdot x$, where K_H is Henry's law constant (specific to the gas-liquid system at a given temperature), x is the mole fraction of dissolved gas, and p is the partial pressure of the gas above the liquid.

Step 1 — Effect of doubling pressure: Rearranging: $x = p/K_H$.

If $p \to 2p$ (pressure doubled), K_H remains constant (temperature unchanged):

$$x_{\text{new}} = \frac{2p}{K_H} = 2 \cdot \frac{p}{K_H} = 2x$$

The molar solubility doubles. This is a **linear relationship** between pressure and solubility.

Why other options are wrong:

- Option A: Henry's law explicitly predicts proportional variation of solubility with pressure.
- Option B: Solubility decreasing with pressure would require $K_H < 0$, which is physically impossible.
- Option D: The relationship is linear ($x \propto p$), not quadratic ($x \propto p^2$).

Final Answer: Molar solubility doubles when pressure doubles (Henry's law is linear). $\Rightarrow$ C

Answer: (C) Go Back to Q 16

Sol 17.

Solution

Concept — Inert pair effect: Moving down a group in the p-block, the ns^2 electrons are increasingly poorly shielded by the filled $(n-1)d$ and $(n-2)f$ subshells (which are poor shielders). The increased effective nuclear charge on the ns^2 pair makes those electrons more tightly held and less available for bonding. This "inert pair" leads to a preference for the $(n-2)$ oxidation state (using only the np electrons for bonding).

Step 1 — Examples:

- Group 13: Ga^{3+} (stable) $\to$ In^{3+} (stable) $\to$ **Tl^{+} more stable than Tl^{3+}**.
- Group 14: Ge^{4+}, Sn^{4+} (stable) $\to$ **Pb^{2+} more stable than Pb^{4+}**.
- Group 15: As^{5+}, Sb^{5+} (stable) $\to$ **Bi^{3+} more stable than Bi^{5+}**.

Why other options are wrong:

- Option B: Inert pair effect causes preference for *lower* oxidation states; directly opposite to higher oxidation states.
- Option C: Covalent character is related to ionic potential (Fajan's rules), not to inert pair effect.
- Option D: Electronegativity generally *decreases* down the p-block group; this is not the basis of the inert pair effect.

Final Answer: Inert pair effect: ns^2 reluctant to bond; heavier elements prefer $(n-2)$ oxidation state. $\Rightarrow$ A

Answer: (A) Go Back to Q 17

Sol 18.

Solution

Concept — Born–Haber cycle: Uses Hess's law to relate the lattice enthalpy of an ionic solid to measurable thermodynamic quantities (sublimation, ionisation, bond dissociation, electron affinity, and heat of formation).

Step 1 — Key energy values for MgO formation:

- $\Delta H_{\text{sub}}(\text{Mg}) = +148\,\text{kJ/mol}$ (endothermic)
- $IE_1 + IE_2 = +738 + 1451 = +2189\,\text{kJ/mol}$ (highly endothermic)
- $\frac{1}{2}D_0(\text{O}_2) = +249\,\text{kJ/mol}$ (endothermic)
- $EA_1(\text{O}) = -141\,\text{kJ/mol}$ (exothermic); $EA_2(\text{O}^-) = +798\,\text{kJ/mol}$ (strongly **endothermic**)
- Net EA = $-141 + 798 = +657\,\text{kJ/mol}$ (endothermic overall)
- $U_L(\text{MgO}) \approx -3791\,\text{kJ/mol}$ (enormously exothermic — Mg^{2+} and O^{2-} are both doubly charged and small)

$\Delta H_f = +148+2189+249+657-3791 \approx -548$ (varies by data source, experimental $\approx -601\,\text{kJ/mol}$). The immense lattice enthalpy drives the reaction.

Why other options are wrong:

- Option A: $EA_2(\text{O}^- \to \text{O}^{2-})$ is *endothermic* ($+798\,\text{kJ/mol}$); adding a second electron to an already negative ion requires external energy.
- Option C: Forming Mg^{2+} requires *two* successive ionisation steps (IE_1 and IE_2).
- Option D: Born–Haber cycles are especially useful for multiply charged ions (MgO, CaO, Al_2O_3).

Final Answer: Huge exothermic lattice enthalpy of MgO compensates for endothermic EA_2 and other steps. $\Rightarrow$ B

Answer: (B) Go Back to Q 18

Sol 19.

Solution

Concept — Structures of nitrogen oxides:

Step 1 — Key structural facts:

- **NO**: Total electrons $= 7 + 8 = 15$ (odd). Electronic configuration: $\sigma_{1s}^2\sigma_{1s}^{*2}\sigma_{2s}^2\sigma_{2s}^{*2}\sigma_{2p}^2\pi_{2p}^4\pi_{2p}^{*1}$. **One unpaired electron** $\Rightarrow$ paramagnetic, radical species.
- **NO_2**: Total electrons $= 7 + 16 = 23$ (odd). Bent molecule, $\angle ONO \approx 134^\circ$. **One unpaired electron** on N $\Rightarrow$ paramagnetic; dimerises to N_2O_4 (diamagnetic) by sharing that electron.
- **N_2O_5**: Molecular formula $O_2N{-}O{-}NO_2$; contains a **bridging oxygen** in the $N{-}O{-}N$ link. In solid state it exists as ionic $[NO_2^+][NO_3^-]$.

Why other options are wrong:

- Option A: NO has one unpaired electron; it is *paramagnetic*, not diamagnetic. Bond order = 2.5.
- Option B: NO_2 is *bent* (one lone electron on N pushes the two O atoms apart to $\approx 134^\circ$); it is not linear.
- Option C: N_2O_5 has an $N{-}O{-}N$ bridging oxygen in addition to the $N{=}O$ bonds.

Final Answer: NO and NO_2 both have one unpaired electron; N_2O_5 has $N{-}O{-}N$ bridge. $\Rightarrow$ D

Answer: (D) Go Back to Q 19

Sol 20.

Solution

Concept — Silicones (polyorganosiloxanes): Silicones are semi-inorganic polymers with an alternating Si−O backbone (the siloxane linkage) and organic groups covalently bonded to each Si.

Step 1 — Structure: General formula $[R_2SiO]_n$ (where R = $-CH_3$, $-C_6H_5$, etc.). The chain consists of $-$Si$-$O$-$Si$-$O$-$ units, not C−C units.

Step 2 — Properties and uses:

- **Hydrophobic**: organic groups point outward $\Rightarrow$ water-repellent.
- **Thermally stable**: Si−O bond energy ≈ 375 kJ/mol; stable from -90°C to $+250^\circ$C.
- Chemically inert, non-toxic, low surface tension.
- **Uses**: greases/lubricants, sealants for doors/windows, waterproofing textiles, electrical insulation, medical implants/prosthetics, cosmetics.

Why other options are wrong:

- Option A: Backbone is Si−O−Si, not C−C; that would make it an organic polymer.
- Option B: Silicones are *covalent* and hydrophobic; they are practically insoluble in water.
- Option D: SiO_2 (quartz/silica) is a covalent network solid; silicones contain organic groups on Si and have very different properties.

Final Answer: Silicones: Si−O−Si backbone, organic groups on Si; water-repellent, thermally stable. $\Rightarrow$ C

Answer: (C) Go Back to Q 20

Sol 21.

Solution

Concept — Lanthanide contraction and 4d/5d similarity: The 14 lanthanide elements (Ce to Lu) involve filling of $4f$ orbitals, which are poor shielders of nuclear charge. This causes a steady decrease in atomic radius across the lanthanide series (lanthanide contraction). As a result, 5d-series elements have atomic radii almost *equal* to their 4d congeners.

Step 1 — Zr vs. Hf (Group 4):

Element	Atomic radius	Ionic radius (M^{4+})
Zr ($4d^2 5s^2$)	≈ 160 pm	≈ 72 pm
Hf ($5d^2 6s^2$)	≈ 159 pm	≈ 71 pm

The similarity in size causes nearly identical chemistry: same coordination chemistry, same minerals (hafnon and zircon), and extreme difficulty of separation.

Why other options are wrong:

- Option B: Ti (3d) and Zr (4d) *do not* show near-identical radii; lanthanide contraction does not affect 3d elements.
- Option C: La and Ac are the first members of lanthanide and actinide series respectively; their similarity is due to both being Group 3, not due to lanthanide contraction.
- Option D: Fe (3d) and Ru (4d) comparison involves normal periodic trends, not lanthanide contraction; actinide contraction affects 6d vs 5d.

Final Answer: Zr and Hf show near-identical radii due to lanthanide contraction. $\Rightarrow$ A

Answer: (A) Go Back to Q 21

Sol 22.

Solution

Concept — Chelate effect: Polydentate ligands form more stable complexes than an equivalent number of monodentate ligands. The *thermodynamic* origin is primarily entropic.

Step 1 — Thermodynamic analysis: Consider: $[\mathrm{M(NH_3)_4}]^{n+} + 2\,\mathrm{en} \rightarrow [\mathrm{M(en)_2}]^{n+} + 4\,\mathrm{NH_3}$

- Left side: 1 complex + 2 en = 3 species.
- Right side: 1 complex + 4 NH_3 = 5 species.
- $\Delta n = +2$ species liberated into solution.
- $\Delta S > 0$ (entropy increases); $T\Delta S$ contribution makes $\Delta G = \Delta H - T\Delta S$ more negative.

The enthalpies of individual M−N bonds (en vs. NH_3) are very similar; the extra stability comes almost entirely from the favourable $T\Delta S$ term.

Why other options are wrong:

- Option A: Individual M−en bonds are not appreciably stronger than M−NH_3 bonds; calorimetric studies confirm ΔH contributions are small.
- Option C: Chelate ring formation does not necessarily reduce complex size or steric strain.
- Option D: Entropy is the *dominant* contribution to the chelate effect; the enthalpy term is often similar or even slightly less favourable.

Final Answer: Chelate effect driven primarily by favourable entropy increase ($\Delta S > 0$). $\Rightarrow$ B

Answer: (B) Go Back to Q 22

Sol 23.

Solution

Concept — Electrophilic addition mechanism: In electrophilic addition to alkenes, the electron-rich π bond acts as a Lewis base (nucleophile) and is attacked first by an electrophile (Lewis acid/H^+). A carbocation intermediate forms, which is then attacked by a nucleophile.

Step 1 — Mechanism of HBr + ethene:

(a) **Step 1 (rate-determining, slow):** H^+ (electrophile, from dissociation of H−Br) attacks the π electrons of ethene. The π bond breaks; H bonds to one carbon, creating the ethyl carbocation:

$$H_2C{=}CH_2 + H^+ \rightarrow CH_3{-}\overset{+}{C}H_2$$

(b) **Step 2 (fast):** Br^- (nucleophile) attacks the electron-deficient carbon of the carbocation:

$$CH_3{-}\overset{+}{C}H_2 + Br^- \rightarrow CH_3CH_2Br\ (\text{bromoethane})$$

This is an **AdE2** (electrophilic addition, bimolecular) mechanism.

Why other options are wrong:

- Option A: Free-radical mechanism (AdR) requires homolytic initiation by UV or peroxides; this is the ionic (AdE) mechanism.
- Option B: Br^- attacks the *carbocation* in step 2, not the π bond directly.
- Option C: A carbocation is *electrophilic* (electron-deficient Lewis acid), not nucleophilic.

Final Answer: H^+ attacks π bond (electrophilic, step 1) $\rightarrow$ carbocation $\rightarrow$ Br^- attacks (nucleophilic, step 2). $\Rightarrow$ D

Answer: (D) Go Back to Q 23

Sol 24.

Solution

Concept — Combustion analysis: All carbon in the organic compound is converted to CO_2; all hydrogen to H_2O. Oxygen content is determined by subtraction.

Step 1 — Moles of C (from CO_2):

$$n(CO_2) = \frac{0.733\,\text{g}}{44\,\text{g mol}^{-1}} = 0.01666\,\text{mol} \quad \Rightarrow \quad n(C) = 0.01666\,\text{mol}, \quad m(C) = 0.2000\,\text{g}$$

Step 2 — Moles of H (from H_2O):

$$n(H_2O) = \frac{0.300\,\text{g}}{18\,\text{g mol}^{-1}} = 0.01667\,\text{mol} \quad \Rightarrow \quad n(H) = 2\times0.01667 = 0.03333\,\text{mol}, \quad m(H) = 0.0333$$

Step 3 — Mass and moles of O:

$$m(O) = 0.50 - 0.2000 - 0.0333 = 0.2667\,\text{g} \quad \Rightarrow \quad n(O) = \frac{0.2667}{16} = 0.01667\,\text{mol}$$

Step 4 — Molar ratio:

$$C : H : O = 0.01666 : 0.03333 : 0.01667 = 1 : 2 : 1 \quad \Rightarrow \quad \text{Empirical formula: } \mathbf{CH_2O}$$

Why other options are wrong:

- Options A, B, D: Lead to C:H:O ratios inconsistent with the combustion data.

Final Answer: Empirical formula = CH_2O (C:H:O = 1:2:1). $\Rightarrow$ C

Answer: (C) Go Back to Q 24

Sol 25.

Solution

Concept — DDT (organochlorine pesticide): DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane; mol. formula $C_{14}H_9Cl_5$.

Step 1 — Key properties and environmental concerns:

- **Non-biodegradable (persistent)**: resists microbial degradation; half-life in soil $\approx$ 2–15 years.
- **Lipophilic**: highly soluble in lipids; accumulates in fatty tissues of organisms (bioaccumulation).
- **Biomagnification**: concentration amplifies at each trophic level (plankton $\rightarrow$ small fish $\rightarrow$ large fish $\rightarrow$ birds/humans); up to $10^7\times$ concentration at top of food chain.
- **Ecotoxicity**: causes eggshell thinning in raptors (DDE metabolite inhibits Ca^{2+} transport); population crashes observed in bald eagles, peregrine falcons.
- **Historical use**: $> 4 \times 10^6$ tonnes produced 1940s–70s; crucial in reducing malaria mortality.
- **Current status**: banned/restricted under Stockholm Convention (2001); limited use for disease-vector control in some countries under WHO supervision.

Why other options are wrong:

- Option B: DDT is notoriously persistent (POP = persistent organic pollutant); the opposite of biodegradable.
- Option C: DDT is an insecticide (neurotoxin disrupting Na^+ channels in insects), not a fungicide.
- Option D: DDT is an organochlorine; organophosphates (like malathion, parathion) inhibit acetylcholinesterase.

Final Answer: DDT: persistent organochlorine insecticide; bioaccumulates; biomagnifies; now widely banned. $\Rightarrow$ A

Answer: (A) Go Back to Q 25

Sol 26.

Solution

Concept — Iodoform test: Under I_2/NaOH conditions, compounds with the structural unit **CH_3CO-** (methyl ketones and acetaldehyde) or **$CH_3CH(OH)-$** (which is oxidised in situ to CH_3CO-) undergo successive α-iodination followed by base-promoted cleavage to give CHI_3 (yellow) and a carboxylate.

Step 1 — Analysis of each pair:

- **Option A**: CH_3CH_2CHO (propanal) — the methyl group is β to the C=O, not α; *no CH_3CO-* motif; **negative**. $CH_3CH_2CH_2OH$ (1-propanol) — oxidises to propanal (a non-methyl ketone); **negative**.
- **Option B**: CH_3CHO (acetaldehyde) — has **CH_3CO-** group; **positive** CHI_3. C_2H_5OH (ethanol, CH_3CH_2OH) — is a **$CH_3CH(OH)-$** compound (has CH_3 on carbinol C); *oxidised in situ to CH_3CHO* under the basic conditions; **positive**. **Both give iodoform.**
- **Option C**: C_6H_5CHO (benzaldehyde) — has C_6H_5CO-, not CH_3CO-; **negative**. C_6H_5OH (phenol) — no CH_3CO- or CH_3CHOH motif; **negative**.
- **Option D**: $CH_3CH_2COCH_2CH_3$ (pentan-3-one) — no CH_3 directly on C=O carbon; **negative**. Cyclohexanol — the OH-bearing C has no adjacent CH_3; **negative**.

Final Answer: Acetaldehyde and ethanol both give positive iodoform test. $\Rightarrow$ B

Answer: (B) Go Back to Q 26

Sol 27.

Solution

Concept — Deoxygenation of C=O group: Two classical methods convert aldehyde/ketone C=O directly to $-CH_2-$:

Step 1 — Comparison:

Feature	Clemmensen	Wolff–Kishner
Reagents	Zn-Hg amalgam + conc. HCl	NH_2NH_2 + KOH/NaOH
Medium	**Acidic**	**Basic** (alkaline)
Temperature	Reflux	High temperature ($\approx 200^\circ$C)
Avoid when	Acid-sensitive substrates	Base-sensitive substrates
Result	C=O $\rightarrow$ CH_2	C=O $\rightarrow$ CH_2

Why other options are wrong:

- Option A: Reverses the reagents completely.
- Option B: Wolff–Kishner uses *basic* conditions (KOH), not acidic; neither converts C=O to alcohol.
- Option C: Swaps the conditions (acidic/basic) between the two methods.

Final Answer: Clemmensen = Zn-Hg/HCl (acidic); Wolff–Kishner = NH_2NH_2/KOH (basic). $\Rightarrow$ D

Answer: (D) Go Back to Q 27

Sol 28.

Solution

Concept — Fischer esterification mechanism and equilibrium: Acid-catalysed esterification is a reversible (equilibrium) reaction. The acid protonates the carbonyl group, activating it toward nucleophilic attack by the alcohol.

Step 1 — Mechanism overview:

(a) Protonation of C=O oxygen of RCOOH by H^+ $\rightarrow$ resonance-stabilised oxocarbenium ion.
(b) Nucleophilic attack by the oxygen of R′OH on the activated carbonyl C $\rightarrow$ tetrahedral intermediate.
(c) Proton transfers within the tetrahedral intermediate.
(d) Elimination of H_2O (as a leaving group) from the protonated tetrahedral intermediate.
(e) Deprotonation gives the ester RCOOR′; H^+ is regenerated (catalyst not consumed).

Step 2 — Equilibrium nature and Le Chatelier shifts: $K_c \approx 4$ for many esterifications. Yield is maximised by: (a) removing H_2O (azeotropic distillation, molecular sieves, $CaCl_2$); (b) using excess alcohol or acid.

Why other options are wrong:

- Option A: The reaction is reversible; reverse reaction (hydrolysis of ester) regenerates acid and alcohol.
- Option B: The *alcohol* oxygen attacks the *acid carbonyl*; not the acid oxygen attacking the alcohol.
- Option D: Secondary and tertiary alcohols can undergo Fischer esterification, though more slowly due to steric hindrance.

Final Answer: Reversible equilibrium; alcohol O attacks protonated carbonyl C; yield improved by removing H_2O. $\Rightarrow$ C

Answer: (C) Go Back to Q 28

Sol 29.

Solution

Concept — Gabriel synthesis: A two-step route from alkyl halides to *primary amines only*, using phthalimide as the nitrogen source.

Step 1 — Three-stage mechanism:

(a) **Deprotonation:** Phthalimide (slightly acidic N−H, $pK_a \approx 8.3$) + KOH $\rightarrow$ potassium phthalimide (K^+ salt; the phthalimide anion is a strong, unhindered nitrogen nucleophile).

(b) **N-alkylation (SN2):** Potassium phthalimide + R−X (primary or secondary aliphatic alkyl halide) $\rightarrow$ N-alkylphthalimide. (Aryl halides are unreactive in SN2.)

(c) **Hydrolysis:** N-alkylphthalimide + H_2NNH_2 (hydrazine, Ing–Manske modification) or aq. H_3O^+/OH^- $\rightarrow$ R−NH_2 (primary amine) + phthalic hydrazide or phthalic acid.

Why only primary amines: Phthalimide has exactly *one* N−H bond. After the first (and only possible) N-alkylation, the nitrogen no longer has any N−H bond or free lone pair available for further alkylation. The product is *exclusively* a primary amine.

Why other options are wrong:

- Option B: After the single N-alkylation, no further alkylation is possible; secondary/tertiary amines cannot form.
- Option C: The hydrolysis uses hydrazine (H_2NNH_2) or acid/base, *not* H_2/Pd (hydrogenation catalyst).
- Option D: Aryl halides are poor electrophiles for SN2 reactions (no back-side attack possible at sp^2 C).

Final Answer: Gabriel synthesis gives exclusively primary amines (one N−H $\Rightarrow$ one alkylation only). $\Rightarrow$ A

Answer: (A) Go Back to Q 29

Sol 30.

Solution

Concept — Analytical indices for fats and oils: Saponification number and iodine value are two standard chemical indices used to characterise the nature of lipids (fats and oils).

Step 1 — Saponification number (SN): Definition: The number of milligrams of KOH required to saponify (hydrolyse all ester bonds + neutralise free fatty acids in) 1 gram of fat/oil.

Significance: $\mathrm{SN} \propto 1/\bar{M}_{\text{fat}}$. Fats with short-chain fatty acids have lower molar mass and higher SN (more moles per gram). Example: coconut oil (short chains, SN ≈ 250) vs. lard (longer chains, SN ≈ 194).

Step 2 — Iodine value (IV): Definition: The number of grams of I_2 (or ICl, IBr in Wijs'/Hanus method) absorbed per 100 grams of fat/oil.

Significance: Each C=C double bond absorbs one molecule of I_2 (addition across the double bond). High IV = highly unsaturated (e.g., linseed oil, IV ≈ 180); low IV = saturated fat (e.g., coconut oil, IV ≈ 10).

Why other options are wrong:

- Option A: Reverses the roles: SN $\leftrightarrow$ IV (SN measures chain length; IV measures unsaturation).
- Option C: High IV means highly *unsaturated* (more C=C bonds absorb more I_2); NOT saturated.
- Option D: SN is a *mass-based analytical number* (mg KOH per g fat), not a count of ester linkages per molecule.

Final Answer: SN = mg KOH / g fat (inversely related to chain length); IV = g I_2 / 100 g fat (measures unsaturation). $\Rightarrow$ B

Answer: (B) Go Back to Q 30

Answer Key

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	C	2	D	3	C	4	A	5	B
6	C	7	D	8	A	9	C	10	B
11	D	12	A	13	C	14	B	15	D
16	C	17	A	18	B	19	D	20	C
21	A	22	B	23	D	24	C	25	A
26	B	27	D	28	C	29	A	30	B