Chemistry

HSC Board Exam February–March 2027 – Practice Paper No. 2

Model Answer Paper

Time: 3 hours **Max. Marks: 70**

Model answers show one correct method; any other correct method gets full marks.

SECTION A – Q.1 Select and write the correct answer for the following multiple choice type of questions. **[10]**

(i) Which of the following ionic solids shows both Schottky and Frenkel defects?

(A) NaCl (B) KCl

(C) AgBr (D) ZnS

Answer (1 mark)

(C) AgBr

AgBr shows Schottky defect (like NaCl and KCl) and also Frenkel defect (like ZnS), because the small Ag^+ ion can move into interstitial sites.

(ii) The aqueous solution of which of the following salts has pH greater than 7?

(A) NaCl (B) NH_4Cl

(C) CH_3COONa (D) KNO_3

Answer (1 mark)

(C) CH_3COONa

It is a salt of a weak acid and a strong base. The acetate ion hydrolyses: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$, so the solution is basic.

(iii) For which of the following reactions is $\Delta H = \Delta U$?

(A) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (B) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

(C) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ (D) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Answer (1 mark)

(B) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$\Delta H = \Delta U + \Delta n_g RT$; here $\Delta n_g = 2 - 2 = 0$, so $\Delta H = \Delta U$. (In A $\Delta n_g = -2$, in C and D $\Delta n_g = +1$.)

(iv) For a cell reaction involving two electrons (n = 2), $E°_{cell} = 0.296$ V at 298 K. The equilibrium constant of the cell reaction is _____.

(A) 10^5 (B) 10^{10}

(C) 10^{-10} (D) 10^{20}

Answer (1 mark)

(B) 10^{10}

$\log K = nE°_{cell}/0.0592 = (2 \times 0.296)/0.0592 = 10$, so $K = 10^{10}$.

(v) According to the Arrhenius equation, the slope of the straight line obtained by plotting $\log_{10} k$ against 1/T is _____.

(A) $-E_a/R$ (B) $-E_a/2.303R$

(C) $E_a/2.303R$ (D) $-2.303R/E_a$

Answer (1 mark)
(B) $-E_a/2.303R$
$\log_{10} k = \log_{10} A - (E_a/2.303R)(1/T)$, which is of the form $y = c + mx$ with slope $m = -E_a/2.303R$.

(vi) The hybridisation of xenon in XeF_4 is _____.

(A) sp^3 (B) sp^3d

(C) sp^3d^2 (D) sp^3d^3

Answer (1 mark)
(C) sp^3d^2
Xe has 4 bond pairs and 2 lone pairs (6 electron pairs), so it is sp^3d^2 hybridised and the molecule is square planar.

(vii) Which of the following complexes can exist as cis and trans (geometric) isomers?

(A) $[Cr(NH_3)_6]^{3+}$ (B) $[Cr(NH_3)_5Cl]^{2+}$

(C) $[Cr(NH_3)_4Cl_2]^{+}$ (D) $[Cr(en)_3]^{3+}$

Answer (1 mark)
(C) $[Cr(NH_3)_4Cl_2]^{+}$
It is an octahedral MA_4B_2 complex: the two Cl^- ligands can be adjacent (cis) or opposite (trans). MA_6, MA_5B and $M(AA)_3$ complexes have no cis–trans isomers.

(viii) Which of the following alcohols gives turbidity immediately with Lucas reagent at room temperature?

(A) Butan-1-ol (B) Butan-2-ol

(C) 2-Methylpropan-1-ol (D) 2-Methylpropan-2-ol

Answer (1 mark)
(D) 2-Methylpropan-2-ol
It is a tertiary alcohol; tertiary alcohols react with conc. $HCl/ZnCl_2$ fastest and the insoluble alkyl chloride makes the solution turbid at once.

(ix) Benzenediazonium chloride is converted into chlorobenzene by treating it with _____.

(A) CuCl/HCl (B) H_3PO_2

(C) KI (D) warm water

Answer (1 mark)
(A) CuCl/HCl
This is the Sandmeyer reaction: $C_6H_5N_2^+Cl^- \xrightarrow{(CuCl/HCl)} C_6H_5Cl + N_2$. ($H_3PO_2$ gives benzene, KI gives iodobenzene and warm water gives phenol.)

(x) The α-helix (secondary structure) of a protein is stabilised mainly by _____.

(A) peptide bonds (B) hydrogen bonds

(C) disulfide bonds (D) glycosidic bonds

Answer (1 mark)
(B) hydrogen bonds
The C=O group of one amino acid is hydrogen bonded to the N–H group of the fourth amino acid along the chain.

SECTION A – Q.2 Answer the following questions. **[8]**

(i) What is the van't Hoff factor (i) of $K_4[Fe(CN)_6]$ in a dilute aqueous solution, assuming complete dissociation?

Answer (1 mark)
i = 5, because $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$ gives five ions per formula unit.

(ii) What is the slope of the straight line obtained by plotting $[A]_t$ against t for a zero order reaction?

Answer (1 mark)
Slope = −k. (Integrated rate law: $[A]_t = -kt + [A]_0$.)

(iii) Scandium (Z = 21) is regarded as a transition element. Give reason.

Answer (1 mark)
Its atom has an incompletely filled d subshell in the ground state: Sc = [Ar] $3d^1\ 4s^2$.

(iv) Write the IUPAC name of $CH_3–CH(CH_3)–CH(Cl)–CH_3$.

Answer (1 mark)
2-Chloro-3-methylbutane (both directions give locants 2,3; chloro comes first alphabetically, so it gets the lower number).

(v) Write the IUPAC name of $CH_3–CO–CH_2–CH(CH_3)–CH_3$.

Answer (1 mark)
4-Methylpentan-2-one

(vi) Name the catalyst used in the manufacture of high density polythene (HDP).

Answer (1 mark)
Ziegler–Natta catalyst (triethylaluminium with titanium tetrachloride), at 333–343 K and 6–7 atm.

(vii) What is meant by zero waste technology (ZWT)?

Answer (1 mark)
A chemical process in which the waste is zero or minimum, and the waste of one system is used as raw material for another (e.g. bottom ash of a thermal power station used for making bricks and cement).

(viii) Write the relation between the standard Gibbs energy change (ΔG°) of a reaction and its equilibrium constant (K).

Answer (1 mark)
$\Delta G^\circ = -RT \ln K = -2.303\ RT \log_{10} K$

SECTION B Attempt any EIGHT of the following questions. (Q.3 to Q.14) **[16]**

Q.3 Tungsten, used for bulb filaments, crystallises in a body-centred cubic (bcc) lattice with unit cell edge length 316 pm. Calculate (a) the radius of a tungsten atom and (b) the distance between the centres of two nearest neighbouring atoms. ($\sqrt{3} = 1.732$)

Answer (2 marks)

Given: bcc, a = 316 pm

In bcc, the atoms touch along the body diagonal: $\sqrt{3}\,a = 4r$

(a) $r = \sqrt{3}\,a/4 = (1.732 \times 316)/4 = 547.3/4 = 136.8$ pm

(b) Nearest neighbour distance = $2r = \sqrt{3}\,a/2 = 2 \times 136.8 = 273.7$ pm

Ans: (a) $r \approx 136.8$ pm (b) $d \approx 273.7$ pm

Marking: Relation $\sqrt{3}\,a = 4r$ for bcc – ½ mark · r = 136.8 pm – 1 mark · Nearest neighbour distance 2r = 273.7 pm – ½ mark

Examiner tip: In bcc the atoms touch along the body diagonal ($\sqrt{3}\,a$), not along the face diagonal ($\sqrt{2}\,a$, which is for fcc). Answers 136.8–137 pm and 273.6–274 pm are accepted.

Q.4 The vapour pressure of pure water at a certain temperature is 3.20 kPa. When 4.8 g of a non-volatile non-electrolyte is dissolved in 72 g of water, the vapour pressure falls to 3.168 kPa. Calculate the molar mass of the solute. (Treat the solution as dilute.)

Answer (2 marks)

Given: $P_1^\circ = 3.20$ kPa, $P_1 = 3.168$ kPa, $W_2 = 4.8$ g, $W_1 = 72$ g, $M_1 = 18$ g mol^{-1}

Relative lowering of vapour pressure = $(P_1^\circ - P_1)/P_1^\circ = (3.20 - 3.168)/3.20 = 0.032/3.20 = 0.010$

For a dilute solution, $(P_1^\circ - P_1)/P_1^\circ = x_2 = (W_2\,M_1)/(M_2\,W_1)$

$M_2 = (W_2\,M_1)/(W_1 \times 0.010) = (4.8 \times 18)/(72 \times 0.010) = 86.4/0.72 = 120$ g mol^{-1}

Ans: Molar mass of the solute = 120 g mol^{-1}

Marking: Relative lowering = 0.010 – ½ mark · Formula $(P_1^\circ - P_1)/P_1^\circ = W_2M_1/(M_2W_1)$ – ½ mark · M_2 = 120 g mol^{-1} – 1 mark

Examiner tip: The relative lowering has no unit; use the ratio $(P_1^\circ - P_1)/P_1^\circ$, not the lowering 0.032 kPa itself.

Q.5 A laboratory assistant prepares a buffer solution that is 0.15 M in acetic acid and 0.30 M in sodium acetate. Calculate the pH of the buffer. (pK_a of acetic acid = 4.74; log 2 = 0.3010)

Answer (2 marks)

This is an acidic buffer (weak acid + its salt with a strong base).

Henderson–Hasselbalch equation: $pH = pK_a + \log_{10}([\text{salt}]/[\text{acid}])$

$pH = 4.74 + \log(0.30/0.15) = 4.74 + \log 2$

$= 4.74 + 0.3010 = 5.041$

Ans: pH ≈ 5.04

Marking: Henderson–Hasselbalch equation – ½ mark · Correct substitution [salt]/[acid] = 2 – ½ mark · pH = 5.04 – 1 mark

Examiner tip: Put the salt concentration in the numerator. Writing [acid]/[salt] gives 4.44 and loses the answer mark.

Q.6 For the reaction $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$, $\Delta H = -566.0$ kJ at 298 K. Calculate ΔU for the reaction at 298 K. ($R = 8.314$ J K^{-1} mol^{-1})

Answer (2 marks)

$\Delta H = \Delta U + \Delta n_g RT$, so $\Delta U = \Delta H - \Delta n_g RT$

Δn_g = (moles of gaseous products) − (moles of gaseous reactants) = 2 − 3 = −1 mol

$\Delta n_g RT = -1 \times 8.314 \times 298 = -2478$ J = −2.478 kJ

$\Delta U = -566.0 - (-2.478) = -566.0 + 2.478 = -563.5$ kJ

Ans: $\Delta U = -563.5$ kJ

Marking: $\Delta n_g = -1$ – ½ mark · Formula $\Delta U = \Delta H - \Delta n_g RT$ – ½ mark · $\Delta U = -563.5$ kJ – 1 mark

Examiner tip: Convert $\Delta n_g RT$ from J to kJ before subtracting. Count only gaseous species in Δn_g.

Q.7 A cycle-parts workshop electroplates a steel handlebar with nickel from a nickel(II) sulfate bath. How long (in minutes) must a steady current of 1.93 A be passed to deposit 1.174 g of nickel? (Ni = 58.7 g mol^{-1}; F = 96500 C mol^{-1})

Answer (2 marks)

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$: 2 mol of electrons (2 F) deposit 1 mol (58.7 g) of Ni.

Moles of Ni = 1.174/58.7 = 0.020 mol, so moles of electrons = 2 × 0.020 = 0.040 mol

Q = 0.040 × 96500 = 3860 C

t = Q/I = 3860/1.93 = 2000 s = 2000/60 = 33.3 min

Ans: t ≈ 33.3 minutes (2000 s)

Marking: Electrode reaction / 2 F per mol Ni – ½ mark · Q = 3860 C – ½ mark · t = 2000 s = 33.3 min – 1 mark

Examiner tip: Nickel(II) needs two electrons per ion (n = 2); using n = 1 halves the time. Convert seconds to minutes as asked.

Q.8 For the reaction A + B → products, the following initial rate data were obtained at 300 K:

Experiment	[A]/mol dm^{-3}	[B]/mol dm^{-3}	Initial rate/mol dm^{-3} s^{-1}
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	8.0×10^{-4}
3	0.10	0.20	2.0×10^{-4}

Find the order with respect to A and B, write the rate law and calculate the rate constant.

Answer (2 marks)

Let rate = $k[A]^x[B]^y$

Expt 2 ÷ Expt 1: $(8.0 \times 10^{-4})/(2.0 \times 10^{-4}) = (0.20/0.10)^x \rightarrow 4 = 2^x \rightarrow x = 2$

Expt 3 ÷ Expt 1: $(2.0 \times 10^{-4})/(2.0 \times 10^{-4}) = (0.20/0.10)^y \rightarrow 1 = 2^y \rightarrow y = 0$

Rate law: rate = $k[A]^2$ (second order in A, zero order in B; overall order 2)

$k = \text{rate}/[A]^2 = (2.0 \times 10^{-4})/(0.10)^2 = 2.0 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}

Marking: Order with respect to A = 2 – ½ mark · Order with respect to B = 0 – ½ mark · Rate law rate = $k[A]^2$ – ½ mark · k = 2.0×10^{-2} dm^3 mol^{-1} s^{-1} with unit – ½ mark

Examiner tip: Compare two experiments in which only one concentration changes. The unit of k depends on the overall order (here 2).

Q.9 Write balanced chemical equations for:

(a) Ozone is passed through an aqueous solution of potassium iodide.

(b) Copper is heated with concentrated sulfuric acid.

Answer (2 marks)

(a) $2KI(aq) + H_2O(l) + O_3(g) \rightarrow 2KOH(aq) + I_2(s) + O_2(g)$

(ozone oxidises iodide ions to iodine)

(b) $Cu + 2H_2SO_4\,(conc.) \xrightarrow{(heat)} CuSO_4 + SO_2\uparrow + 2H_2O$

(hot conc. H_2SO_4 acts as an oxidising agent)

Marking: (a) Balanced equation with I_2 – 1 mark · (b) Balanced equation with SO_2 – 1 mark

Examiner tip: Copper does not give H_2 with sulfuric acid; the hot concentrated acid is reduced to SO_2.

Q.10 For the complex $[Cr(en)_2(NH_3)Cl]SO_4$ (en = ethylenediamine), write:

(a) the oxidation state of chromium

(b) the coordination number of chromium

(c) whether the complex is cationic, anionic or neutral

(d) whether it is homoleptic or heteroleptic.

Answer (2 marks)

The complex ion is $[Cr(en)_2(NH_3)Cl]^{2+}$ (balanced by SO_4^{2-}).

(a) $x + 2(0) + 0 + (-1) = +2 \rightarrow x = +3$. Oxidation state of Cr = +3

(b) en is bidentate: $2 \times 2 = 4$, plus NH_3 (1) and Cl^- (1). Coordination number = 6

(c) Cationic complex (the coordination sphere carries a +2 charge)

(d) Heteroleptic (three different kinds of ligands: en, NH_3 and Cl^-)

Marking: (a) +3 – ½ mark · (b) 6 – ½ mark · (c) Cationic – ½ mark · (d) Heteroleptic – ½ mark

Examiner tip: Count donor atoms, not ligands: each en gives 2. The charge on the complex ion comes from the counter ion SO_4^{2-}.

Q.11 Write chemical equations for:

(a) Wurtz–Fittig reaction using bromobenzene and bromoethane.

(b) Friedel–Crafts alkylation of chlorobenzene with chloromethane.

Answer (2 marks)

(a) $C_6H_5Br + C_2H_5Br + 2Na \xrightarrow{\text{(dry ether)}} C_6H_5{-}C_2H_5 + 2NaBr$

(ethylbenzene)

(b) $C_6H_5Cl + CH_3Cl \xrightarrow{\text{(anhydrous } AlCl_3\text{)}}$ 1-chloro-2-methylbenzene + 1-chloro-4-methylbenzene (major) + HCl

(Cl is an ortho/para directing group; the para product is major.)

Marking: (a) Correct equation with Na/dry ether – 1 mark · (b) Correct o- and p-products with anhydrous $AlCl_3$ – 1 mark

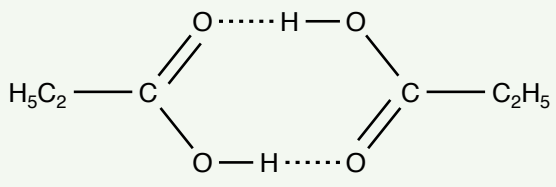
Examiner tip: In (b) show both ortho and para products (or the para product as major); a single meta product is wrong.

Q.12 Propanoic acid (molar mass 74 g mol^{-1}) boils at 414 K, whereas butan-1-ol (molar mass 74 g mol^{-1}) boils at 391 K. Explain.

Answer (2 marks)

Both compounds form intermolecular hydrogen bonds. But in carboxylic acids the –COOH group forms two hydrogen bonds between a pair of molecules, so propanoic acid exists as a cyclic dimer (two O–H·····O bonds, figure below), even in the vapour phase.

The hydrogen bonds in the acid are stronger (the O–H is more polar because of the adjacent C=O) and dimerisation effectively doubles the molecular size. More energy is needed to separate the molecules, so propanoic acid has a higher boiling point than the alcohol of the same molar mass.



····· = hydrogen bond (cyclic dimer of propanoic acid)

Marking: Intermolecular H-bonding in both; dimer formation in carboxylic acid – 1 mark · Stronger/more extensive H-bonding needs more energy, so higher b.p. – 1 mark

Examiner tip: Mention the dimer with two hydrogen bonds; 'carboxylic acid has hydrogen bonding' alone does not explain the difference, because the alcohol also has it.

Q.13 Write chemical equations for:
(a) N-Methylethanamine reacts with benzoyl chloride in the presence of pyridine.
(b) Propan-1-amine is treated with nitrous acid ($NaNO_2$ + dil. HCl).

Answer (2 marks)
(a) $C_2H_5–NH–CH_3 + C_6H_5COCl$ –(pyridine)→ $C_6H_5CO–N(CH_3)–C_2H_5 + HCl$
(N-ethyl-N-methylbenzamide; pyridine neutralises the HCl formed)
(b) $CH_3CH_2CH_2NH_2 + HNO_2 \rightarrow CH_3CH_2CH_2OH + N_2\uparrow + H_2O$
(the unstable aliphatic diazonium salt decomposes at once; N_2 gas is evolved and propan-1-ol is formed)

Marking: (a) Correct benzoylation product – 1 mark · (b) Alcohol + N_2 + H_2O, balanced – 1 mark

Examiner tip: Aliphatic primary amines do not give stable diazonium salts. Show N_2 evolution in (b).

Q.14 A kitchenware company in Nashik makes (a) handles for pressure cookers and (b) coating for non-stick frying pans. Name a suitable polymer for each and give one reason for each choice.

Answer (2 marks)
(a) Bakelite (phenol–formaldehyde resin). It is a thermosetting, cross-linked polymer: once set, it does not soften or melt on heating and it is a poor conductor of heat and electricity, so the handle stays firm and safe to hold.
(b) Teflon (polytetrafluoroethylene, $–(CF_2–CF_2)_n–$). The strong C–F bonds make it chemically inert and heat resistant, and food does not stick to its smooth surface.

Marking: (a) Bakelite with reason (thermosetting, does not soften on heating) – 1 mark · (b) Teflon with reason (C–F bond, inert, heat resistant, non-stick) – 1 mark

Examiner tip: A thermoplastic such as polythene would soften near a hot cooker; say 'thermosetting/cross-linked' for (a).

SECTION C Attempt any EIGHT of the following questions. (Q.15 to Q.26) **[24]**

Q.15 (a) In a mixed oxide, the oxide ions (O^{2-}) form a cubic close-packed (ccp) lattice. Monovalent cations A^+ occupy one-fourth of the tetrahedral voids and trivalent cations B^{3+} occupy one-half of the octahedral voids. Deduce the formula of the oxide and show that it is electrically neutral. [2]
(b) What is the coordination number of an ion that occupies (i) an octahedral void (ii) a tetrahedral void? [1]

Answer (3 marks)
(a) Let the number of O^{2-} ions = N
Number of tetrahedral voids = 2N; number of octahedral voids = N
$A^+ = (1/4) \times 2N = N/2$; $B^{3+} = (1/2) \times N = N/2$
A : B : O = N/2 : N/2 : N = 1 : 1 : 2
Formula: ABO_2
Charge check: (+1) + (+3) + 2(−2) = 1 + 3 − 4 = 0, so the compound is neutral.
(b) (i) 6 (ii) 4

Marking: (a) Number of voids 2N and N – ½ mark · (a) Ratio 1 : 1 : 2 – ½ mark · (a) Formula ABO_2 with charge check – 1 mark · (b) 6 and 4 – ½ mark each

Examiner tip: In a close-packed lattice of N spheres there are 2N tetrahedral and N octahedral voids; most mistakes come from swapping them.

Q.16 (a) 0.50 g of a protein isolated from soybean is dissolved in water to make 100 cm^3 of solution. The osmotic pressure of the solution at 300 K is 250 Pa. Calculate the molar mass of the protein. (R = 8.314 J K^{-1} mol^{-1}) [2]

(b) If this solution is diluted to 200 cm^3 at the same temperature, what will be its osmotic pressure? [1]

Answer (3 marks)

(a) $\pi = MRT = (W_2/M_2V)\,RT$, so $M_2 = W_2RT/(\pi V)$

$W_2 = 0.50$ g; $T = 300$ K; $\pi = 250$ Pa $= 250$ N m^{-2}; $V = 100$ $cm^3 = 1.0 \times 10^{-4}$ m^3

$M_2 = (0.50 \times 8.314 \times 300)/(250 \times 1.0 \times 10^{-4}) = 1247.1/0.025 = 4.99 \times 10^4$ g mol^{-1}

Ans: Molar mass $\approx 4.99 \times 10^4$ g mol^{-1} (about 50000 g mol^{-1})

(b) π is proportional to molarity. Doubling the volume halves the molarity, so $\pi = 250/2 = 125$ Pa.

Marking: (a) Formula $M_2 = W_2RT/\pi V$ – ½ mark · (a) Conversion of V to m^3 and substitution – ½ mark · (a) $M_2 \approx 4.99 \times 10^4$ g mol^{-1} – 1 mark · (b) 125 Pa with reason – 1 mark

Examiner tip: With R = 8.314 J K^{-1} mol^{-1}, π must be in Pa and V in m^3. Using cm^3 directly makes the answer 10^6 times too small.

Q.17 A 0.050 M aqueous solution of a weak monoacidic base BOH has a hydronium ion concentration of 1.0×10^{-11} mol dm^{-3} at 298 K. Calculate (a) its degree of dissociation, (b) its dissociation constant K_b and (c) pK_b. (log 2 = 0.3010)

Answer (3 marks)

$pH = -\log(1.0 \times 10^{-11}) = 11.0$; $pOH = 14 - 11.0 = 3.0$, so $[OH^-] = 1.0 \times 10^{-3}$ M

(a) $BOH \rightleftharpoons B^+ + OH^-$; $[OH^-] = \alpha c$

$\alpha = [OH^-]/c = (1.0 \times 10^{-3})/0.050 = 0.020$ (2 %)

(b) $K_b = \alpha^2 c$ (α is small) $= (0.020)^2 \times 0.050 = 4.0 \times 10^{-4} \times 0.050 = 2.0 \times 10^{-5}$

(Using $K_b = \alpha^2 c/(1 - \alpha)$ gives 2.04×10^{-5}; also accepted.)

(c) $pK_b = -\log(2.0 \times 10^{-5}) = 5 - \log 2 = 5 - 0.3010 = 4.699$

Ans: $\alpha = 0.020$; $K_b = 2.0 \times 10^{-5}$; $pK_b = 4.70$

Marking: $[OH^-] = 10^{-3}$ M (via pH/pOH or K_w) – ½ mark · (a) $\alpha = 0.020$ – ½ mark · (b) $K_b = \alpha^2 c = 2.0 \times 10^{-5}$ – 1 mark · (c) $pK_b = 4.70$ – 1 mark

Examiner tip: The data give $[H_3O^+]$, not $[OH^-]$: find $[OH^-] = K_w/[H_3O^+] = 10^{-3}$ M first. Using 10^{-11} as $[OH^-]$ is the commonest error.

Q.18 (a) Write the electronic configurations of Cr^{3+} (Z = 24) and Fe^{2+} (Z = 26) and calculate the spin-only magnetic moment of each. [2]

(b) What is observed when H_2S gas is passed through acidified potassium dichromate solution? Write the balanced equation. [1]

Answer (3 marks)

(a) Cr (Z = 24): [Ar] $3d^5\,4s^1$; Cr^{3+}: [Ar] $3d^3$ → 3 unpaired electrons

$\mu = \sqrt{(n(n+2))} = \sqrt{(3 \times 5)} = \sqrt{15} = 3.87$ BM

Fe (Z = 26): [Ar] $3d^6\,4s^2$; Fe^{2+}: [Ar] $3d^6$ → 4 unpaired electrons

$\mu = \sqrt{(4 \times 6)} = \sqrt{24} = 4.90$ BM

(b) H_2S is oxidised to a pale yellow precipitate of sulfur and the orange dichromate solution

turns green (Cr^{3+}):

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S\downarrow$

Marking: (a) Correct configurations of Cr^{3+} and Fe^{2+} – ½ mark each · (a) μ = 3.87 BM and 4.90 BM – ½ mark each · (b) Observation with balanced equation – 1 mark

Examiner tip: Remove the 4s electrons first when forming the ions; Fe^{2+} is $3d^6$, not $3d^4 4s^2$.

Q.19 (a) 0.50 mol of an ideal gas expands isothermally and reversibly at 300 K from a volume of 2.0 dm^3 to 20.0 dm^3. Calculate the work done. (R = 8.314 J K^{-1} mol^{-1}) [2]
(b) What are the values of ΔU and q for this process? [1]

Answer (3 marks)

(a) $W_{max} = -2.303\ nRT \log_{10}(V_2/V_1)$

$= -2.303 \times 0.50 \times 8.314 \times 300 \times \log (20.0/2.0)$

$= -2.303 \times 0.50 \times 8.314 \times 300 \times \log 10$

$= -2.303 \times 1247.1 \times 1 = -2872$ J ≈ −2.87 kJ

(Negative sign: the gas does work on the surroundings.)

(b) For an isothermal process of an ideal gas, internal energy depends only on temperature, so ΔU = 0.

By the first law, ΔU = q + W, so q = −W = +2872 J ≈ +2.87 kJ (heat is absorbed).

Marking: (a) Formula for reversible isothermal work – ½ mark · (a) Substitution – ½ mark · (a) W = −2.87 kJ – 1 mark · (b) ΔU = 0 and q = +2.87 kJ – ½ mark each

Examiner tip: Use 2.303 with $\log_{10}$ (or ln without 2.303). Keep the negative sign for expansion work.

Q.20 The active ingredient of a cough syrup decomposes by first order kinetics. At 25 °C, 25 % of it decomposes in 60 days. Calculate (a) the rate constant, (b) the time in which 10 % of the ingredient decomposes (its shelf life) and (c) the half-life. (log 4 = 0.6021, log 3 = 0.4771, log 9 = 0.9542)

Answer (3 marks)

(a) $k = (2.303/t) \log ([A]_0/[A]_t)$; after 25 % decomposition, $[A]_t$ = 75 % of $[A]_0$

$k = (2.303/60) \log (100/75) = (2.303/60) \log (4/3)$

$\log (4/3) = 0.6021 - 0.4771 = 0.1250$

$k = 0.03838 \times 0.1250 = 4.80 \times 10^{-3}$ day^{-1}

(b) For 10 % decomposition, $[A]_t$ = 90 % of $[A]_0$

$t = (2.303/k) \log (100/90) = (2.303/k) \log (10/9)$

$\log (10/9) = 1 - 0.9542 = 0.0458$

$t = (2.303/4.80 \times 10^{-3}) \times 0.0458 = 479.8 \times 0.0458 \approx 22.0$ days

(c) $t_{1/2} = 0.693/k = 0.693/(4.80 \times 10^{-3}) = 144.4$ days

Ans: (a) $k \approx 4.80 \times 10^{-3}$ day^{-1} (b) ≈ 22 days (c) ≈ 144 days

Marking: (a) $k = 4.80 \times 10^{-3}$ day^{-1} – 1 mark · (b) t ≈ 22 days – 1 mark · (c) $t_{1/2}$ ≈ 144 days – 1 mark

Examiner tip: '25 % decomposes' means 75 % remains; put $[A]_0/[A]_t$ = 100/75, not 100/25. Values 144–145 days for (c) are accepted.

Q.21 Write chemical equations for:
(a) Action of bromine water on phenol
(b) Kolbe's reaction
(c) Oxidation of propan-2-ol with acidified potassium dichromate

Answer (3 marks)

(a) $C_6H_5OH + 3Br_2(aq) \rightarrow$ 2,4,6-tribromophenol (white precipitate) + 3HBr

($C_6H_2Br_3OH$: Br at positions 2, 4 and 6; –OH activates the ring)

(b) $C_6H_5ONa + CO_2$ –(398 K, 6 atm)→ o-HO–C_6H_4–COONa (sodium salicylate)

o-HO–C_6H_4–COONa + HCl → o-HO–C_6H_4–COOH (salicylic acid) + NaCl

(c) CH_3–CH(OH)–CH_3 + [O] –($K_2Cr_2O_7$/dil. H_2SO_4)→ CH_3–CO–CH_3 + H_2O

(propanone; a secondary alcohol gives a ketone)

Marking: (a) Correct product 2,4,6-tribromophenol – 1 mark · (b) Sodium phenoxide + CO_2, conditions, salicylic acid – 1 mark · (c) Propanone – 1 mark

Examiner tip: In (a), bromine water gives the tribromo product; mono-bromophenols form only in a non-polar solvent such as CS_2.

Q.22 An organic compound A (C_4H_8O) gives a silver mirror with Tollens' reagent but does not give the iodoform test. On oxidation, A gives 2-methylpropanoic acid.

(a) Identify A, with reason. [1]

(b) Write the reaction of A with Tollens' reagent. [1]

(c) Write the reaction of A with HCN and name the product. [1]

Answer (3 marks)

(a) A gives a silver mirror, so it is an aldehyde. It gives an acid with the same carbon skeleton, 2-methylpropanoic acid $(CH_3)_2CH$–COOH, and it has no CH_3CO– group (no iodoform). Hence A is 2-methylpropanal, $(CH_3)_2CH$–CHO.

(b) $(CH_3)_2CH–CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow (CH_3)_2CH–COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O$

(c) $(CH_3)_2CH–CHO + HCN \rightarrow (CH_3)_2CH–CH(OH)–CN$

(2-methylpropanal cyanohydrin; IUPAC: 2-hydroxy-3-methylbutanenitrile)

Marking: (a) A = 2-methylpropanal with reason – 1 mark · (b) Tollens' reaction (silver mirror) – 1 mark · (c) Cyanohydrin with name – 1 mark

Examiner tip: Use all three clues: Tollens' (aldehyde), no iodoform (no CH_3CO–), and the acid's branched skeleton (2-methyl).

Q.23 Three isomeric amines P, Q and R have the molecular formula C_3H_9N. With benzenesulfonyl chloride (Hinsberg's reagent), P gives a product that dissolves in aqueous KOH, Q gives a product insoluble in aqueous KOH, and R does not react. Identify P, Q and R (one structure each) and write the reactions of P and Q with the reagent.

Answer (3 marks)

P is a primary amine: propan-1-amine, $CH_3CH_2CH_2NH_2$ (propan-2-amine is also correct)

Q is a secondary amine: N-methylethanamine, CH_3CH_2–NH–CH_3

R is a tertiary amine: N,N-dimethylmethanamine (trimethylamine), $(CH_3)_3N$

P: $C_6H_5SO_2Cl + H_2N–CH_2CH_2CH_3 \rightarrow C_6H_5SO_2–NH–CH_2CH_2CH_3 + HCl$

(N-propylbenzenesulfonamide; the H on N is acidic, so it dissolves in KOH)

Q: $C_6H_5SO_2Cl + HN(CH_3)C_2H_5 \rightarrow C_6H_5SO_2–N(CH_3)C_2H_5 + HCl$

(N-ethyl-N-methylbenzenesulfonamide; no H on N, so insoluble in KOH)

R has no H on nitrogen, so it does not react.

Marking: P, Q, R correctly identified – ½ mark each (1½) · Reaction of P with reason for solubility – ½ mark + ½ mark · Reaction of Q – ½ mark

Examiner tip: The key is the hydrogen left on nitrogen in the sulfonamide: it makes the 1° product acidic and soluble in alkali.

Q.24 (a) Write the reactions of glucose with (i) hydroxylamine and (ii) acetic anhydride. What does each reaction indicate about the structure of glucose? [2]
(b) What are anomers? [1]

Answer (3 marks)
(a) (i) $CHO–(CHOH)_4–CH_2OH + NH_2OH \rightarrow CH(=N–OH)–(CHOH)_4–CH_2OH + H_2O$
(glucose oxime) This shows that glucose contains a carbonyl (C=O) group.
(ii) $CHO–(CHOH)_4–CH_2OH + 5(CH_3CO)_2O \rightarrow CHO–(CH–OCOCH_3)_4–CH_2OCOCH_3 + 5CH_3COOH$
(glucose pentaacetate) This shows that glucose has five –OH groups, attached to five different carbon atoms.
(b) Anomers are cyclic stereoisomers of a sugar that differ only in the configuration at the anomeric carbon (C-1 in glucose), e.g. α-D-glucopyranose and β-D-glucopyranose.
Marking: (a)(i) Oxime equation and inference (C=O) – 1 mark · (a)(ii) Pentaacetate equation and inference (five –OH) – 1 mark · (b) Correct definition – 1 mark
Examiner tip: Always state the inference; an equation without 'what it shows' gets only half the mark.

Q.25 Propene can be made from 1-bromopropane: $CH_3CH_2CH_2Br + KOH\ (alc.) \rightarrow CH_3CH=CH_2 + KBr + H_2O$. 2-Bromopropane can be made from propene: $CH_3CH=CH_2 + HBr \rightarrow CH_3CHBrCH_3$.
(a) Calculate the % atom economy for the desired product in each reaction. (C = 12, H = 1, Br = 80, K = 39, O = 16) [2]
(b) Which reaction is greener according to the principle of atom economy? Why? [1]

Answer (3 marks)
% atom economy = (formula weight of desired product/sum of formula weights of all reactants) × 100
(a) Reaction 1 (desired product propene, C_3H_6 = 42 u)
Reactants: C_3H_7Br = 36 + 7 + 80 = 123 u; KOH = 39 + 16 + 1 = 56 u; total = 179 u
% atom economy = (42/179) × 100 = 23.5 %
Reaction 2 (desired product 2-bromopropane, C_3H_7Br = 123 u)
Reactants: C_3H_6 = 42 u; HBr = 81 u; total = 123 u
% atom economy = (123/123) × 100 = 100 %
(b) Reaction 2 (addition) is greener: all atoms of the reactants end up in the desired product, so no by-product waste is formed. Reaction 1 (elimination) wastes about 76 % of the reactant mass as KBr and H_2O.
Marking: (a) Formula – ½ mark · (a) 23.5 % for reaction 1 – 1 mark · (a) 100 % for reaction 2 – ½ mark · (b) Addition reaction greener with reason – 1 mark
Examiner tip: Include every reactant (also KOH) in the denominator. Answers 23.4–23.5 % are accepted.

Q.26 Give reasons:
(a) H_2O is a liquid at room temperature, while H_2S is a gas.
(b) Interhalogen compounds (XX′) are more reactive than the halogens (except fluorine).
(c) Fluorine forms only one oxoacid (HOF), whereas chlorine forms several oxoacids.

Answer (3 marks)
(a) Oxygen is small and highly electronegative, so H_2O molecules are associated by strong intermolecular hydrogen bonds. Sulfur is larger and less electronegative, so H_2S has no hydrogen bonding, only weak van der Waals forces. Hence H_2O is a liquid and H_2S a gas.
(b) In X–X′ the two atoms differ in electronegativity and size, so the X–X′ bond is weaker than the X–X bond (in X_2) or the X′–X′ bond (in X'_2). The weaker bond breaks more easily, so

interhalogens are more reactive.

(c) Fluorine is the most electronegative element (more electronegative than oxygen) and has no d orbitals in its valence shell, so it cannot show positive oxidation states. Chlorine is less electronegative than oxygen and has vacant 3d orbitals, so it shows +1, +3, +5 and +7 states in HOCl, $HClO_2$, $HClO_3$ and $HClO_4$. Hence fluorine forms only HOF.

Marking: (a) Hydrogen bonding in H_2O, absent in H_2S – 1 mark · (b) X–X′ bond weaker than X–X bond – 1 mark · (c) Highest electronegativity and no d orbitals, so no positive oxidation states – 1 mark

Examiner tip: In (c), give both points (highest electronegativity and absence of d orbitals) for the full mark.

SECTION D Attempt any THREE of the following questions. (Q.27 to Q.31) **[12]**

Q.27 (a) A hydrogen–oxygen fuel cell with hot aqueous KOH as electrolyte supplies power and drinking water on a spacecraft. Write the anode and cathode reactions and the net cell reaction. What mass of water is produced when the cell delivers 0.40 F of electricity? (H_2O = 18 g mol^{-1}) [2]

(b) A conductivity cell with cell constant 1.2 cm^{-1} is filled with 0.020 M formic acid (HCOOH) solution. Its resistance is 1500 Ω at 298 K. Calculate the conductivity, the molar conductivity and the degree of dissociation of formic acid. ($\lambda_0(H^+)$ = 349.6 Ω^{-1} cm^2 mol^{-1}; $\lambda_0(HCOO^-)$ = 54.4 Ω^{-1} cm^2 mol^{-1}) [2]

Answer (4 marks)

(a) Electrolyte: hot aqueous KOH; porous carbon electrodes with finely divided Pt.

Anode (−), oxidation: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Cathode (+), reduction: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Net cell reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Water produced: 4 mol of electrons (4 F) give 2 mol of H_2O, i.e. 1 F gives 0.5 mol H_2O.

0.40 F → 0.40 × 0.5 = 0.20 mol H_2O = 0.20 × 18 = 3.6 g

(b) κ = cell constant/R = 1.2/1500 = 8.0×10^{-4} Ω^{-1} cm^{-1}

$\Lambda = 1000\kappa/c = (1000 \times 8.0 \times 10^{-4})/0.020 = 40.0\ \Omega^{-1}\ cm^2\ mol^{-1}$

$\Lambda_0(HCOOH) = \lambda_0(H^+) + \lambda_0(HCOO^-) = 349.6 + 54.4 = 404.0\ \Omega^{-1}\ cm^2\ mol^{-1}$ (Kohlrausch's law)

$\alpha = \Lambda/\Lambda_0 = 40.0/404.0 = 0.099$ (9.9 %)

Marking: (a) Anode and cathode reactions – ½ mark each · (a) Net reaction – ½ mark; mass of water 3.6 g – ½ mark · (b) $\kappa = 8.0 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ – ½ mark · (b) $\Lambda = 40.0\ \Omega^{-1}\ cm^2\ mol^{-1}$ – ½ mark · (b) Λ_0 = 404.0 – ½ mark; α = 0.099 – ½ mark

Examiner tip: Use $\Lambda = 1000\kappa/c$ when c is in mol L^{-1} and κ in Ω^{-1} cm^{-1}. Dropping the 1000 makes α a thousand times too small.

Q.28 (a) Using crystal field theory, draw the d-orbital splitting diagrams for the octahedral complexes $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$. Predict the number of unpaired electrons and the spin-only magnetic moment of each, and state which one is a high spin complex. (Fe: Z = 26) [3]

(b) Write the IUPAC name of $[Fe(H_2O)_6]Cl_3$. [1]

Answer (4 marks)

(a) In both complexes Fe is +3: Fe (Z = 26) [Ar] $3d^6\ 4s^2$, so Fe^{3+} is [Ar] $3d^5$.

In an octahedral field the d orbitals split into a lower t_{2g} set (3 orbitals) and a higher e_g set (2 orbitals), separated by Δ_o.

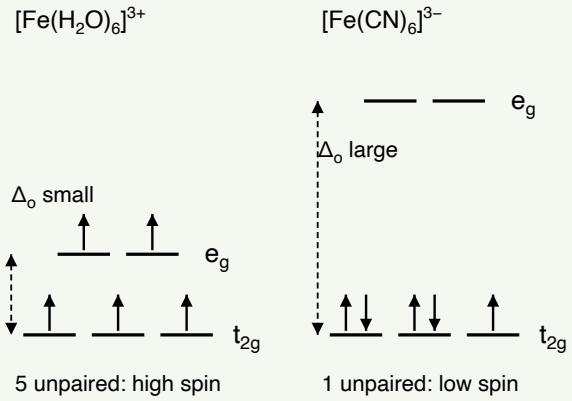
$[Fe(H_2O)_6]^{3+}$: H_2O is a weak field ligand, Δ_o < pairing energy (P). The five electrons occupy all five orbitals singly: $t_{2g}^3\ e_g^2$. Unpaired electrons = 5; $\mu = \sqrt{(5 \times 7)} = \sqrt{35} = 5.92$ BM. High spin

complex.

$[Fe(CN)_6]^{3-}$: CN^- is a strong field ligand, $\Delta_o > P$. The electrons pair up in t_{2g}: $t_{2g}^5\, e_g^0$. Unpaired electrons = 1; $\mu = \sqrt{(1 \times 3)} = \sqrt{3} = 1.73$ BM. Low spin complex.

So $[Fe(H_2O)_6]^{3+}$ is the high spin complex. (Splitting diagrams below.)

(b) Hexaaquairon(III) chloride



Marking: (a) $Fe^{3+} = 3d^5$ and splitting into t_{2g}/e_g – ½ mark · (a) Diagram and $t_{2g}^3 e_g^2$, 5 unpaired, 5.92 BM for the aqua complex – 1 mark · (a) Diagram and $t_{2g}^5 e_g^0$, 1 unpaired, 1.73 BM for the cyano complex – 1 mark · (a) High spin = $[Fe(H_2O)_6]^{3+}$ – ½ mark · (b) Correct name with 'hexaaqua' and (III) – 1 mark

Examiner tip: Remove the two 4s electrons and one 3d electron to get $Fe^{3+} = 3d^5$. Then compare Δ_o with the pairing energy P for each ligand; that decides whether the 4th and 5th electrons go to e_g or pair in t_{2g}.

Q.29 (a) 2-Bromo-2-methylbutane is hydrolysed by aqueous KOH by the S_N1 mechanism. Explain the mechanism, write the rate law, and explain why tertiary alkyl halides prefer the S_N1 path. [3]

(b) Write the IUPAC name of the major alkene formed when 2-bromo-2-methylbutane is heated with alcoholic KOH, and name the rule followed. [1]

Answer (4 marks)

(a) Overall: $(CH_3)_2C(Br)–CH_2CH_3 + OH^- \rightarrow (CH_3)_2C(OH)–CH_2CH_3 + Br^-$ (2-methylbutan-2-ol)

Step I (slow, rate determining): the C–Br bond undergoes heterolysis to give a planar tertiary carbocation:

$(CH_3)_2C(Br)–CH_2CH_3 \rightleftharpoons (CH_3)_2C^+–CH_2CH_3 + Br^-$

Step II (fast): the nucleophile OH^- attacks the planar (sp^2) carbocation from either side:

$(CH_3)_2C^+–CH_2CH_3 + OH^- \rightarrow (CH_3)_2C(OH)–CH_2CH_3$

Rate law: rate = $k[(CH_3)_2C(Br)CH_2CH_3]$ – only the substrate takes part in the slow step, so the reaction is unimolecular (first order).

Tertiary halides prefer S_N1 because (i) the tertiary carbocation is stabilised by the +I effect and hyperconjugation of the three alkyl groups, and (ii) the bulky alkyl groups hinder backside attack needed for S_N2, while the planar carbocation has no steric crowding.

(b) 2-Methylbut-2-ene, $(CH_3)_2C{=}CH–CH_3$ (major; 2-methylbut-1-ene is the minor product). Rule: Saytzeff rule – the more substituted alkene is the preferred product.

Marking: (a) Step I: slow heterolysis to tertiary carbocation – 1 mark · (a) Step II: fast attack by OH^-, product 2-methylbutan-2-ol – ½ mark · (a) Rate law (first order) – ½ mark · (a) Reasons: carbocation stability and steric hindrance to S_N2 – 1 mark · (b) 2-Methylbut-2-ene with Saytzeff rule – 1 mark

Examiner tip: Label the slow step clearly; the rate law must contain only the alkyl halide.

Q.30 (a) 2.84 g of sodium sulfate (Na_2SO_4, molar mass 142 g mol^{-1}) is dissolved in 500 g of water. The boiling point of water is raised by 0.0562 K. Calculate the van't Hoff factor and the degree of dissociation of Na_2SO_4. (K_b for water = 0.52 K kg mol^{-1}) [3]

(b) Why is the observed van't Hoff factor smaller than 3? [1]

Answer (4 marks)

(a) Molality $m = (W_2/M_2) \times (1000/W_1) = (2.84/142) \times (1000/500) = 0.02 \times 2 = 0.04$ mol kg^{-1}

$\Delta T_b = i\,K_b\,m$, so $i = \Delta T_b/(K_b\,m) = 0.0562/(0.52 \times 0.04) = 0.0562/0.0208 = 2.70$

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$; number of ions $n = 3$

$\alpha = (i - 1)/(n - 1) = (2.70 - 1)/(3 - 1) = 1.70/2 = 0.85$

Ans: $i = 2.70$; $\alpha = 0.85$ (85 % dissociated)

(b) Na_2SO_4 is not completely dissociated in solution at this concentration: interionic attractions hold some Na^+ and SO_4^{2-} ions together as ion pairs. So the number of particles is less than three per formula unit and i is less than 3.

Marking: (a) Molality = 0.04 mol kg^{-1} – ½ mark · (a) Formula $\Delta T_b = iK_bm$ – ½ mark · (a) i = 2.70 – 1 mark · (a) $\alpha = (i - 1)/(n - 1) = 0.85$ – 1 mark · (b) Incomplete dissociation / ion association – 1 mark

Examiner tip: n is the number of ions from one formula unit (3 for Na_2SO_4), not 2.

Q.31 (a) Write chemical equations for: (i) Rosenmund reduction of propanoyl chloride (ii) Heating sodium butanoate with soda lime. [2]

(b) How will you distinguish between aniline and benzylamine by a chemical test? Write the equations. [2]

Answer (4 marks)

(a) (i) $CH_3CH_2COCl + H_2 \xrightarrow{-(Pd/BaSO_4)} CH_3CH_2CHO + HCl$

(propanal; the poisoned catalyst stops reduction at the aldehyde stage)

(ii) $CH_3CH_2CH_2COONa + NaOH \xrightarrow{-(CaO,\ heat)} CH_3CH_2CH_3 + Na_2CO_3$

(propane; decarboxylation gives a hydrocarbon with one carbon atom less)

(b) Test: treat each with $NaNO_2$ + dil. HCl at 273–278 K, then add an alkaline solution of β-naphthol (or phenol).

Aniline (1° aromatic amine) forms a stable diazonium salt, which couples to give an orange-red azo dye:

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{-(273–278\ K)} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

$C_6H_5N_2^+Cl^-$ + β-naphthol $\xrightarrow{-(NaOH)}$ orange-red azo dye (1-phenylazo-2-naphthol)

Benzylamine (1° aliphatic-type amine; NH_2 on the side chain) gives an unstable diazonium salt that decomposes at once with brisk effervescence of N_2; no dye is formed:

$C_6H_5CH_2NH_2 + HNO_2 \rightarrow C_6H_5CH_2OH + N_2\uparrow + H_2O$

Marking: (a)(i) Rosenmund equation with $Pd/BaSO_4$ – 1 mark · (a)(ii) Decarboxylation to propane – 1 mark · (b) Correct test and observations for both – 1 mark · (b) Equations for both amines – 1 mark

Examiner tip: Benzylamine behaves like an aliphatic amine because $–NH_2$ is not attached to the ring; that is the key to the test.

All the best for your exam!