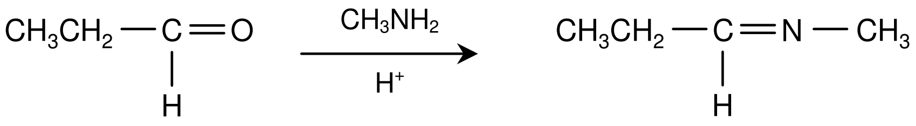
Answer **any four** questions

1 Aldehydes and ketones react with primary amines in slightly acidic solution to form imines which have the C=N functional group. For example, propanal reacts with methylamine to give *N*-methyl-1-propanimine.



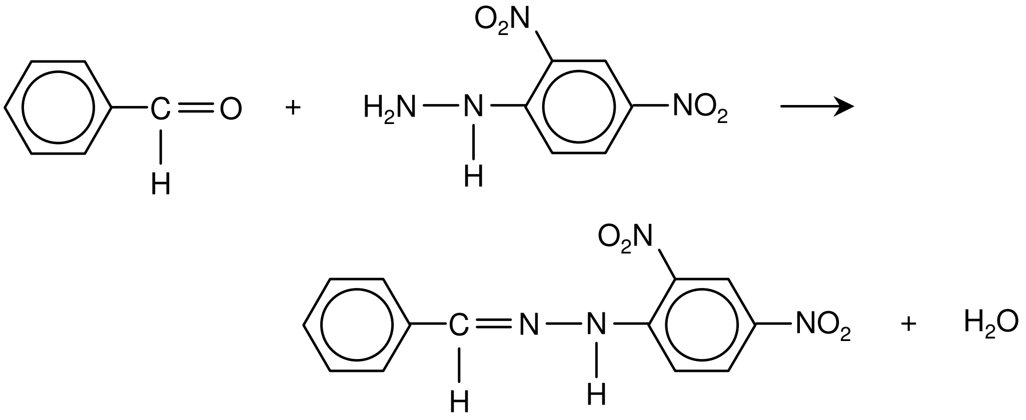
$$CH_3CH_2-\underset{\mathrm{H}}{\underset{|}{C}}=O \xrightarrow[H^+]{CH_3NH_2} CH_3CH_2-\underset{\mathrm{H}}{\underset{|}{C}}=N-CH_3$$

propanal

N-methyl-1-propanimine

(a) Aldehydes and ketones also react with 2,4-dinitrophenylhydrazine (2,4-DNPH) to give compounds that are closely related to imines.

(i) Write a balanced equation for the reaction between benzaldehyde and 2,4-DNPH.

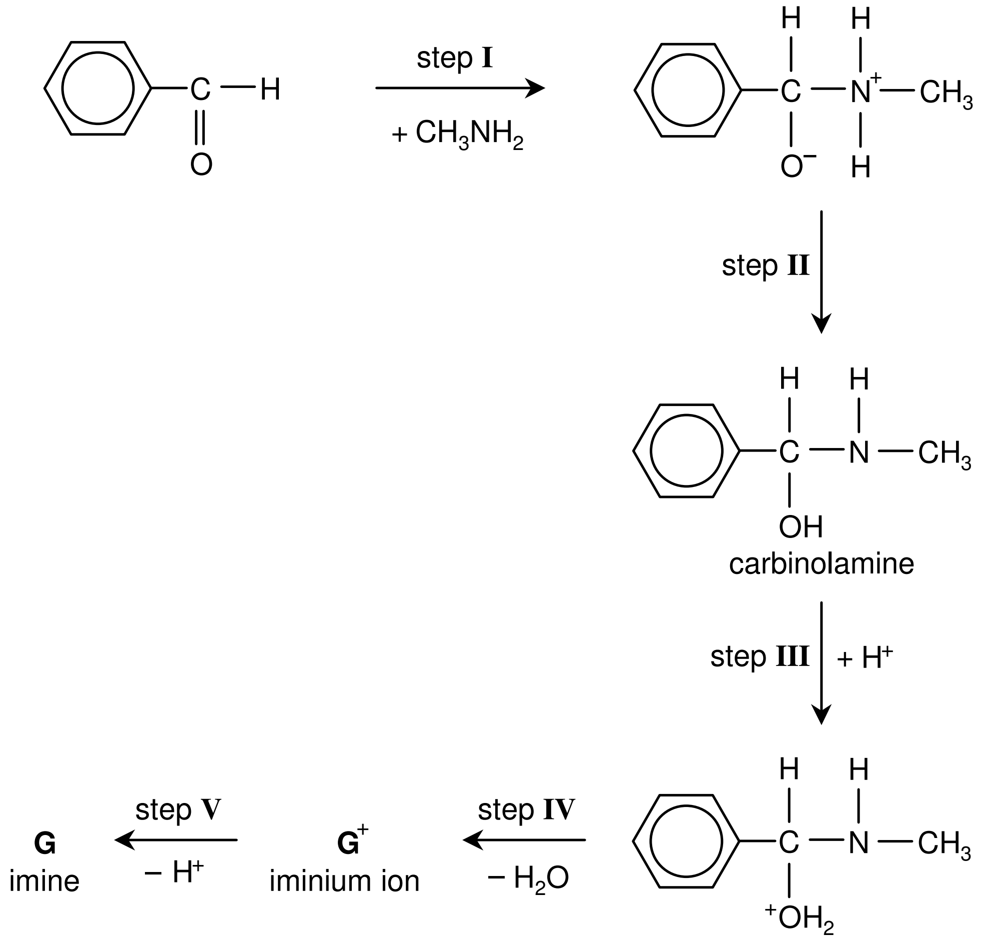


(ii) State what you would observe in the reaction with 2,4-DNPH. What is the type of reaction?

orange precipitate
condensation

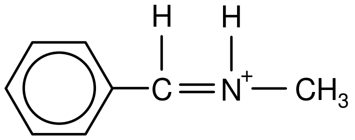
[4]

(b) The mechanism for the reaction between benzaldehyde and methylamine is shown below.

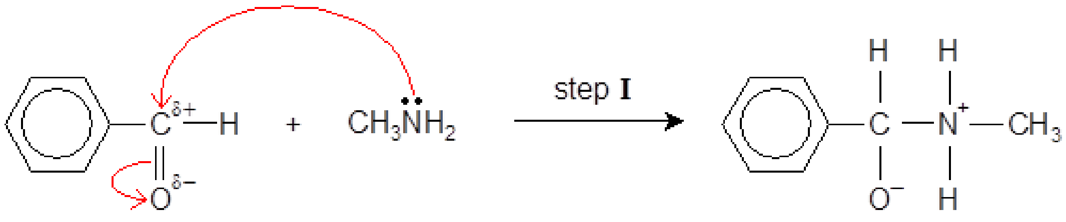


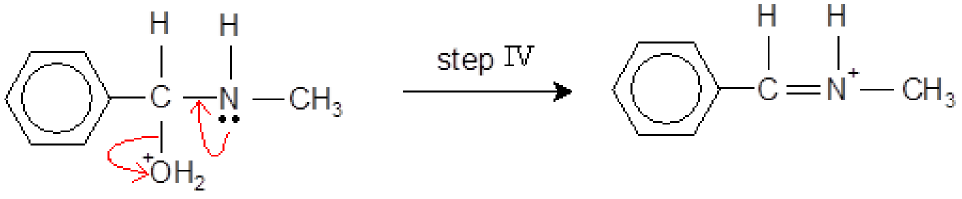
(i) What is the type of reaction in step **I**?
nucleophilic addition

(ii) The positive charge on the iminium ion, **G**$^+$, does **not** reside on a carbon atom. Suggest the structure of **G**$^+$.



(iii) Write equations for step **I** and step **IV** to show the movement of electrons, using curved arrow notation. Show the lone pairs of electrons, if any, that are involved in each step.



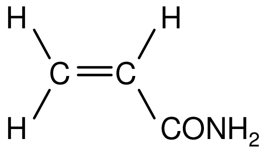


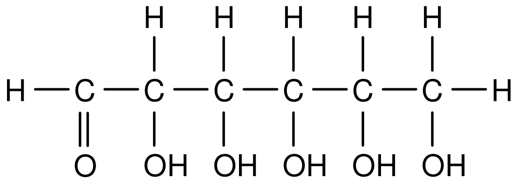
(iv) The maximum rate of formation of imines occurs at a pH of about 4.5. Explain why the rate is slow under very acidic conditions and under alkaline conditions.

acidic: amine protonated; no nucleophile (Step I)
alkaline: very low H^+ conc; no catalyst (Step III)

[6]

(c) Acrylamide is a carcinogen. It is formed when potato chips are heated to above 120 °C. Its formation has been linked to the presence of glucose ($C_6H_{12}O_6$) and an α-amino acid **L** found in relatively high amounts in potato.


acrylamide

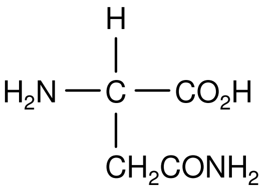

glucose

Glucose reacts with **L** to form an imine **M**. At high cooking temperatures, **M** decomposes to produce only three compounds in equimolar amounts: acrylamide, carbon dioxide and compound **N** ($C_6H_{13}NO_5$).

(i) Name the functional groups in acrylamide.

alkene , amide

(ii) Deduce the structure of **L**. Show clearly how you obtained your answer.

L :


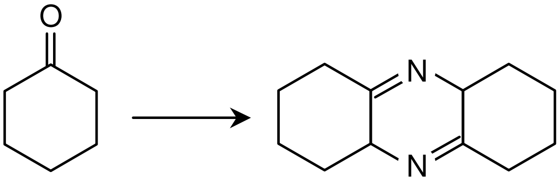
$$H_2N-\overset{\displaystyle H}{\underset{\displaystyle CH_2CONH_2}{C}}-CO_2H$$

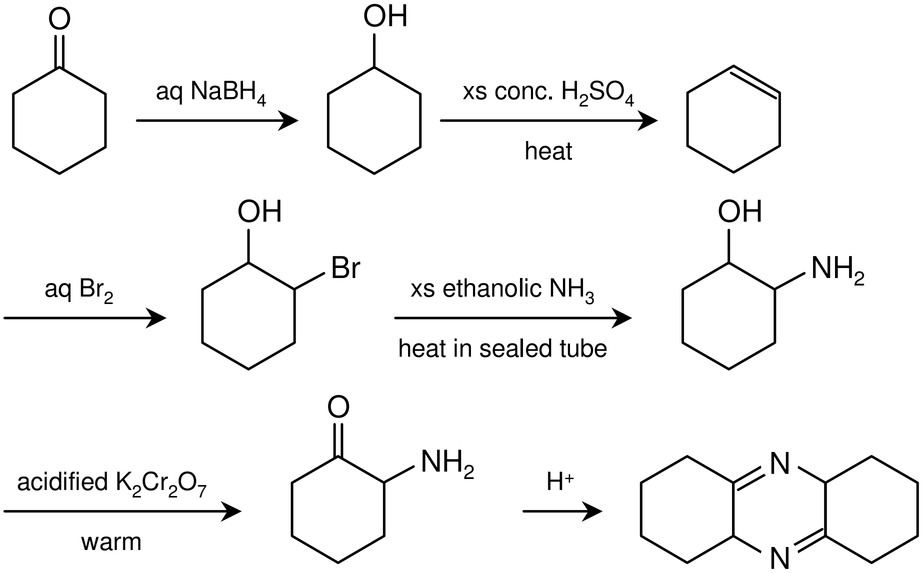
(asparagine).

Accept other possible alternatives.

[5]

(d) Suggest the reagents and conditions required to synthesise the following imine derivative. Identify all the intermediate compounds.





[5]

[Total: 20]

2 **(a)** A container holds a gaseous mixture of nitrogen and propane. The pressure in the container at 200 °C is 4.5 atm. At –40 °C, the propane completely condenses and the pressure drops to 1.5 atm. Calculate the mole fraction of propane in the original gaseous mixture. [3]

Let the amount of nitrogen and propane be n_1 and n_2 respectively. Since the gas constant, R, and volume of container, V, are constants, the gas equation becomes:

$$\frac{P}{T} = \frac{nR}{V} = kn \quad \text{where } k = \frac{R}{V}$$

$$\therefore \frac{4.5}{473} = k(n_1 + n_2) = 9.513 \times 10^{-3}$$

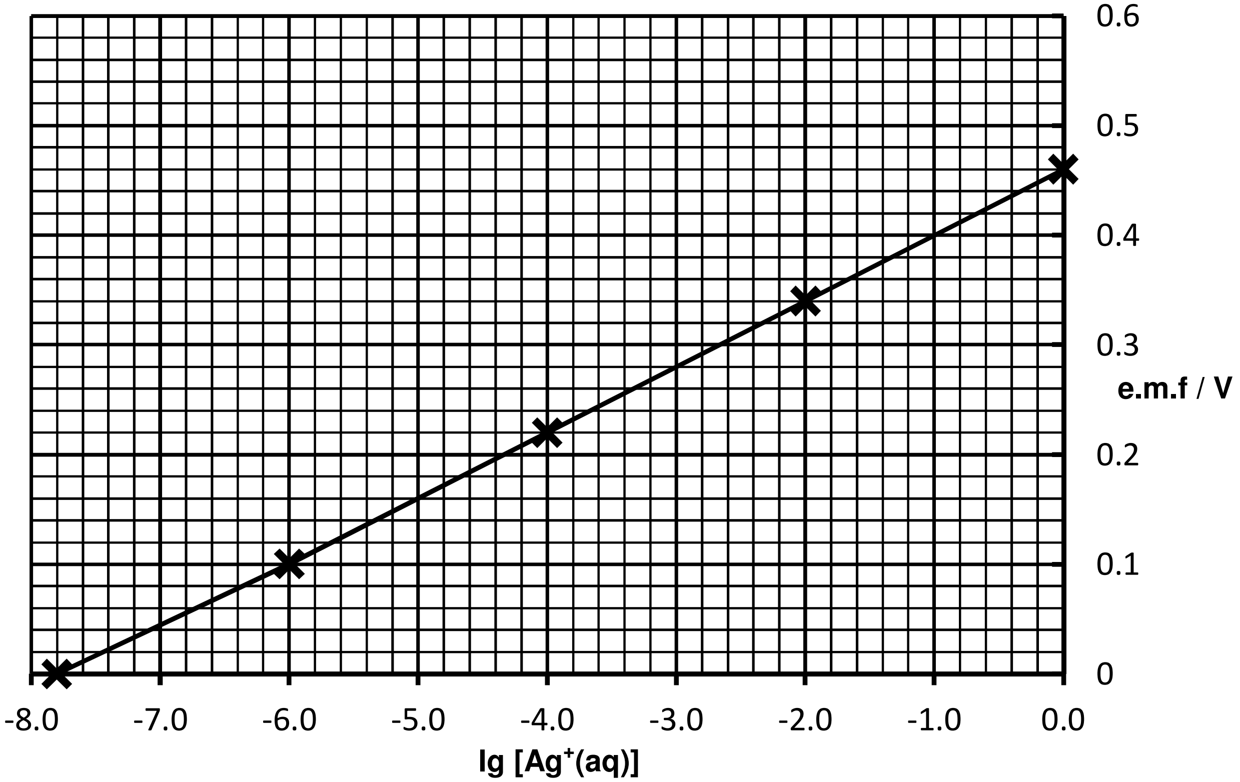
$$\text{and } \frac{1.5}{233} = kn_1 = 6.437 \times 10^{-3}$$

$$\therefore kn_2 = 9.513 \times 10^{-3} - 6.437 \times 10^{-3} = 3.076 \times 10^{-3}$$

$$\text{mole fraction of propane} = \frac{3.076 \times 10^{-3}}{9.513 \times 10^{-3}} = \underline{0.323}$$

(b) The graph below shows the variation in electromotive force (e.m.f.) of the following electrochemical cell with lg [Ag^+(aq)] at 298 K.

Cu(s) | Cu^{2+}(aq) || Ag^+(aq) | Ag(s)



(i) Using the information from the graph, calculate the standard electrode potential of the half-cell, Ag^+(aq) | Ag(s), at 298 K.

Let the standard electrode potential of $Ag^+(aq)$ | Ag(s) half-cell be x.
When $[Ag^+(aq)] = 1.00$ mol dm^{-3}, lg $[Ag^+(aq)] = 0$
$E^{\ominus}_{cell} = +0.46 = x - (+0.34)$
$x = +0.46 + (+0.34) = \underline{+0.80\ V}$

(ii) If the $Ag^+(aq)$ solution of the electrochemical cell is replaced by a saturated solution of silver bromate(V), $AgBrO_3$, in 0.1 mol dm^{-3} potassium bromate(V) and the e.m.f. of the cell measured at 298 K is +0.27 V, determine

(I) the concentration of $Ag^+(aq)$ ions in the saturated solution, and

From the graph, when e.m.f. of cell is +0.27 V, lg $[Ag^+(aq)] = -3.2$.
$[Ag^+(aq)] = \underline{6.309 \times 10^{-4}\ mol\ dm^{-3}}$

(II) the solubility product of silver bromate(V) at 298 K.

$K_{sp} = 6.309 \times 10^{-4} \times 0.1 = \underline{6.309 \times 10^{-5}\ mol^2\ dm^{-6}}$

[5]

(c) Solid silver nitrate was slowly dissolved in a solution **Q** containing ethanedioate, $C_2O_4^{2-}$, and chromate(VI), CrO_4^{2-}, ions of concentrations 2.50×10^{-2} mol dm^{-3} and 1.44×10^{-5} mol dm^{-3} respectively.

(i) When a permanent precipitate of silver ethanedioate first appeared, the concentration of silver ions in the solution was 2.10×10^{-5} mol dm^{-3}. Calculate the solubility product of silver ethanedioate.

$K_{sp}(Ag_2C_2O_4) = (2.10 \times 10^{-5})^2 \times 2.50 \times 10^{-2}$
$= \underline{1.10 \times 10^{-11}\ mol^3\ dm^{-9}}$

(ii) The dissolving of solid silver nitrate in **Q** was continued until a permanent red precipitate of silver chromate(VI) first appeared. Calculate the concentrations of silver ions and ethanedioate ions at that instant.
(K_{sp} of silver chromate(VI) is 1.2×10^{-12} mol^3 dm^{-9}.)

Given: $K_{sp}(Ag_2CrO_4)$ is 1.2×10^{-12} mol^3 dm^{-9}.
$1.2 \times 10^{-12} = [Ag^+]^2 \times 1.44 \times 10^{-5}$
$[Ag^+]^2 = 8.333 \times 10^{-8}$
$[Ag^+] = \underline{2.89 \times 10^{-4}\ mol\ dm^{-3}}$
$1.102 \times 10^{-11} = (2.886 \times 10^{-4})^2 \times [C_2O_4^{2-}]$
$[C_2O_4^{2-}] = \underline{1.32 \times 10^{-4}\ mol\ dm^{-3}}$

(iii) What is the amount of silver ethanedioate precipitated from 1.00 dm^3 of the solution?

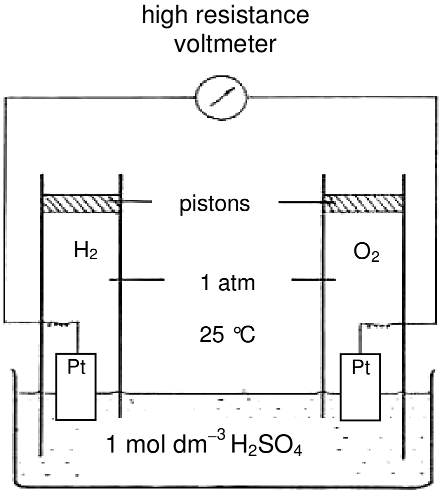
$n(C_2O_4^{2-})$ removed from solution = $2.50 \times 10^{-2} - 1.322 \times 10^{-4}$

= 0.02486 mol

∴ amount of silver ethanedioate ppted = <u>0.0249 mol.</u>

[7]

(d) An electrochemical cell containing an oxygen cathode and a hydrogen anode is shown below. The pistons above the gas chambers are frictionless.



(i) Write balanced equations for the half reactions and for the overall reaction in the cell.

Half reactions: **$H_2 \rightarrow 2H^+ + 2e^-$ (anode)**

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (cathode)

Overall reaction: **$2H_2 + O_2 \rightarrow 2H_2O$**

(ii) How does the concentration of sulfuric acid affect the equilibria of the half reactions?

$2H^+ + 2e^- \rightleftharpoons H_2$ 0.00V (anode)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23V (cathode)

Increase in concentration of sulfuric acid will increase $[H^+]$ and by Le Chatelier's Principle, cause the position of equilibrium of anode and cathode reactions to shift right.

(iii) If weights are added to the pistons of both chambers, how would the reading of the voltmeter change? Explain your answer.

If weights are added, the pressure will increase, resulting in position of equilibrium of anode reaction shifting left to remove excess pressure on hydrogen gas. The electrode potential will decrease to less than zero volt.
The position of equilibrium of the cathode reaction will shift right, resulting in a more positive electrode potential for the cathode. As a result, the reading on the voltmeter will be greater than 1.23 V.

[5]

[Total: 20]

3 **(a)** **(i)** Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4 and $K_2Cr_2O_7$.
Suggest a reason why these reagents do not attack an alkane such as CH_4.

Alkanes are non-polar or have no dipole or C–H bonds are strong or C and H have similar electronegativities.

(ii) It is found by experiment that, during free-radical substitution of alkane, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

type of hydrogen atom	reaction	relative rate
primary	$RCH_3 \rightarrow RCH_2Cl$	1
secondary	$R_2CH_2 \rightarrow R_2CHCl$	7
tertiary	$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number and type of hydrogen atoms within the molecule, predict the relative ratio of the two possible products **J** and **K** from the monochlorination of 2-methylpropane. Explain your answer.

J:K = 2.3 : 1 or 7:3 or 21:9
reason: straightforward relative rate suggests 21:1, but there are 9 primary to 1 tertiary, so divide this ratio by 9. 21/9 = 2.33

[3]

(b) Compounds **A** and **B** are amines with the same molecular formula. Both have a molecular mass of 73.0 and the following composition by mass: C, 65.8 % and H, 15.1 %.

Compound **A** has a pK_b of 3.23 and contains a tri-substituted N atom.

The pH of an aqueous solution of 0.0100 mol dm^{-3} of compound **B** is 11.5. When **B** undergoes free-radical substitution reaction, it only gives **one** mono-substituted organic product.

(i) Calculate the molecular formulae of compounds **A** and **B**.

C:H:N ratio: 65.8/12 : 15.1/1 : 19.1/14 = 4 : 11 : 1

Empirical Formula: $C_4H_{11}N$

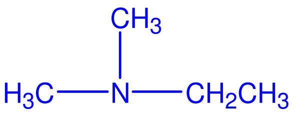
Let the molecular formula be $C_{4n}H_{11n}N_n$
$4n(12.0) + 11n(1.0) + n(14.0) = 73.0$
$n = 1$

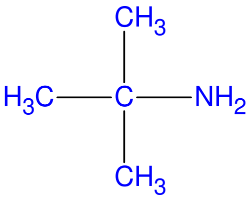
Hence molecular formula is $C_4H_{11}N$

(ii) Calculate the pK_b of compound **B**.

$10^{-(14-11.5)} = (0.0100 * K_b)^{1/2}$
$K_b = 1 \times 10^{-3}$ mol dm^{-3}
p$K_b = -\lg (1 \times 10^{-3}) = 3$

(iii) Suggest the structural formulae of compounds **A** and **B**.

A:

$H_3C{-}N(CH_3){-}CH_2CH_3$

B:

$(CH_3)_3C{-}NH_2$

(iv) State and explain the relative basicity of compounds **A** and **B**.

[7]

pK_b (**A**) = 3.23 pK_b (**B**) = 3

B (1° amine) is more basic than **A** (3° amine).

Although **A** has 3 electron-donating alkyl groups bonded to the N atom while **B** has only one electron-donating group, the **presence of 3 bulky substituents in A hinder the approach of H$^+$ to form dative bond with the lone pair of electrons on N.**

(c) **(i)** The hydrolysis of 2-bromo-2-methylpropane takes place as follows.

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$$

An experiment was conducted to determine the order of reaction with respect to 2-bromo-2-methylpropane. The following results were obtained.

time/s	19	28	50	69	154
[$(CH_3)_3COH$]/mol dm^{-3}	0.0030	0.0040	0.0060	0.0072	0.0095

It was found that the order of reaction with respect to 2-bromo-2-methylpropane is one and the half-life of the reaction is 34.5 s.

Using a non-graphical method, show that the concentration of 2-bromo-2-methylpropane at the start of the experiment is 0.0096 mol dm^{-3}.

The first $t_{1/2}$ corresponds to the time taken for half the final [$(CH_3)_3COH$] to be formed while the sum of two $t_{1/2}$ corresponds to the time taken for ¾ of the final [$(CH_3)_3COH$] to be formed.

The [$(CH_3)_3COH$] at time = 34.5 s is not given in the table but the [$(CH_3)_3COH$] at time = 2 x 34.5 = 69 s is given.

Hence, **¾ x final [$(CH_3)_3COH$] = 0.0072 mol dm^{-3}** ,
∴ final [$(CH_3)_3COH$] = 4/3 x 0.0072 = 0.0096 mol dm^{-3}

Since the mole ratio of $(CH_3)_3CBr : (CH_3)_3COH = 1:1$ and **assuming that the total volume of the reaction mixture remains constant**,
$[(CH_3)_3CBr]$ at the start of the experiment = final $[(CH_3)_3COH]$
= 0.0096 mol dm^{-3}

(ii) Hence, deduce how long the reaction has proceeded when concentration of $(CH_3)_3COH$ obtained is 0.0084 mol dm^{-3}.

$0.0084 = 7/8 \times 0.0096$

Hence, three half-lives have passed by.

Reaction has proceed for $3 \times 34.5 = 103.5$ s.

(iii) The following two mechanisms are both consistent with the reaction being overall first order.

mechanism **X** $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + H^+ + Br^-$

mechanism **Y** $(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + Br^-$ slow
$(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH + H^+$ fast

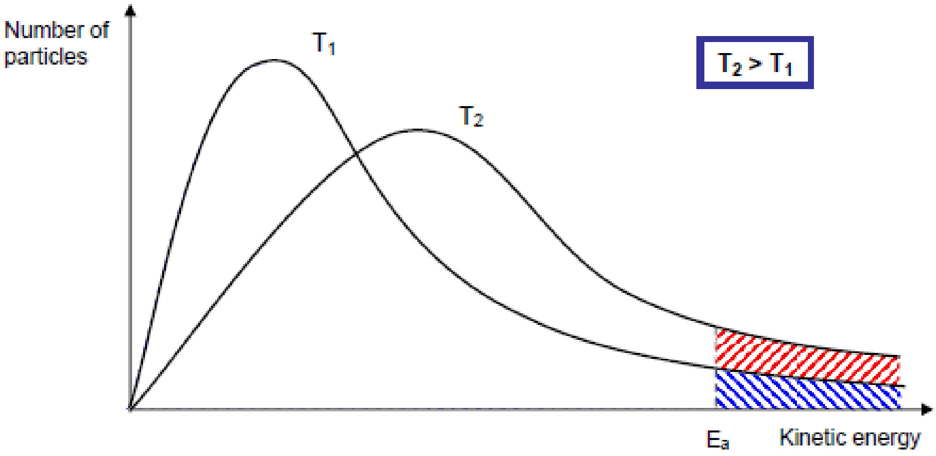
Explain why both mechanisms **X** and **Y** show overall first order kinetics.

H_2O is usually present in excess, hence its concentration is kept relatively constant. Since the given equation in mechanism 1 shows 1 molecule of $(CH_3)_3CBr$ participating in the reaction, the reaction is overall first order kinetics.

In mechanism 2, the slow step involves 1 molecule of $(CH_3)_3CBr$. Hence the rate equation is rate = $k[(CH_3)_3Br]$ which shows that the reaction is overall first order kinetics.

(iv) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane increases when the temperature is increased. Explain this observation with the aid of a suitable diagram.

- When the temperature increases,
  - ⇒ the average kinetic energy of particles increase
  - ⇒ more particles have energy ≥ E_a
  - ⇒ the frequency of effective collisions increase, hence rate increases



▨ Blue shaded region represents no. of particles with energy ≥ E_a at temperature

▨ + ▨ Blue and red shaded region represents no. of particles with energy ≥ E_a at temperature T_2

Figure 8.1: Diagram showing energy distribution of particles when temperature increases

(v) The rate of reaction for the hydrolysis of 2-bromo-2-methylpropane is R at T °C. What is the new rate if temperature is increased to (T+50) °C? Explain your answer.

Rate doubled when temperature increased by 10°C. Since temperature increased by 20°C, rate increased by 2^5 times. Hence the new rate is 32R.

[10]

[Total: 20]

4 This question is about thermal decomposition reactions of Group II compounds.

(a) A student investigates the thermal decomposition of some Group II nitrates. He separately heats equal amounts of the nitrates of magnesium, calcium and barium for one minute, passes the gases produced through aqueous sodium hydroxide and measures the volume of the remaining gas. The following table shows the results:

Element of nitrate	Mg	Ca	Ba
Volume of remaining gas / cm^3	90	19	9

(i) Explain the purpose of sodium hydroxide and identify the remaining gas.

NaOH: absorb NO_2. O_2 is remaining gas.

(ii) Draw an appropriate experimental set-up that allows the student to perform the experiment and measure the volume of the remaining gas.

Sealed boiling tube and Bunsen burner, connected to U-tube containing NaOH, connected to gas syringe.

(iii) Using suitable data from the *Data Booklet*, explain the results obtained by the student.

- Ionic radii Mg^{2+}(0.065 nm), Ca^{2+}(0.099 nm), Ba^{2+}(0.135 nm)
- Down the group, as ionic radii increases, charge density of the cation decreases, hence polarizes the nitrate anion to a lesser extent.
- Nitrate becomes more thermally stable and produces lesser gas after 1 min.

(iv) Hence, estimate the volume of remaining gas produced after 1 min if the student were to heat zinc nitrate.

- Ionic radii of Zn^{2+} is 0.074 nm, in between that of Mg^{2+} and Ca^{2+}.
- Hence, volume of gas produced is approximately 60 cm^3.

(v) The student heats a 10.0 g mixture of magnesium nitrate and calcium nitrate till no further changes. The volume of remaining gas produced was 780 cm^3 at room temperature. Calculate the mass of magnesium nitrate present.

Let mass of magnesium nitrate be x.

$$Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \tfrac{1}{2} O_2$$
$$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + \tfrac{1}{2} O_2$$

$n(Mg(NO_3)_2) = x / 148.3$

$n(O_2)$ produced by $Mg(NO_3)_2 = x / 296.6$

$V(O_2) = 24000x / 296.6$

$n(Ca(NO_3)_2) = (10.0 - x) / 164.1$

$n(O_2)$ produced by $Ca(NO_3)_2 = (10.0 - x) / 328.2$

$m(Mg(NO_3)_2) = 24000(10.0 - x) / 328.2$

Total volume $= [24000x / 296.6] + [24000(10.0 - x) / 328.2] = 780$

$328.2x + 296.6(10.0 - x) = 0.0325(296.6)(328.2)$

$x = 6.26$ g [12]

(b) The decomposition of calcium carbonate is as follows.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In order to determine the enthalpy change of decomposition, two pieces of calcium carbonate were selected, each with a mass of 1.25 g. The first piece was placed in 20 cm^3 of excess dilute hydrochloric acid and the temperature rose by 2 °C. The second piece was heated strongly for ten minutes to decompose it thoroughly. It was then allowed to cool to room temperature before it was added to 20 cm^3 of dilute hydrochloric acid. The temperature rose by 26 °C. The two experiments were estimated to be 90% efficient.

(i) By using the information above and drawing a suitable energy cycle, calculate the enthalpy change of decomposition of calcium carbonate, in kJ mol^{-1}, to 3 significant figures.

$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad \Delta H_1$

$\Delta H_1 = -[(20 \times 4.18 \times 2) / 0.9] / (1.25 / 100.1) = -14.9 \text{ kJ mol}^{-1}$

$CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad \Delta H_2$

$\Delta H_2 = -[(20 \times 4.18 \times 26) / 0.9] / (1.25 / 100.1) = -193.4 \text{ kJ mol}^{-1}$

$$\begin{tikzcd}
CaCO_3(s) \arrow[rr, "\Delta H"] \arrow[dr, "\Delta H_1 \; +2HCl"'] & & CaO(s) + CO_2(g) \arrow[dl, "\Delta H_2 \; +2HCl"] \\
& CaCl_2(aq) + H_2O(l) + CO_2(g) &
\end{tikzcd}$$

$\Delta H = 193.4 - 14.9 = 179 \text{ kJ mol}^{-1}$

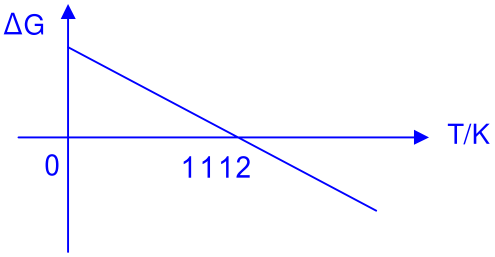
When calcium carbonate is heated in a sealed tube at its thermal decomposition temperature, the reaction eventually reaches an equilibrium.

(ii) Given that $\Delta S = +161 \text{ J mol}^{-1} \text{ K}^{-1}$ and your answer in part **(i)**, calculate the thermal decomposition temperature, in K.

$\Delta G = 0 = 179 - T(161/1000)$

$T = 1112 \text{ K}$

(iii) Hence sketch the graph of ΔG against T, labelling clearly the thermal decomposition temperature.



[8]

[Total: 20]

5 Iron is the sixth most abundant element in the Universe and the most common refractory element.

(a) Iron(III) oxide has a high melting point and is a good conductor of electricity when molten. Explain, in terms of its bonding and structure, why iron(III) oxide has these properties. [3]

Fe_2O_3 has giant ionic structure with strong ionic bonds between oppositely charged ions.
Large amount of energy required to overcome the strong ionic bonds hence it has a high melting point.
In molten state, there are free mobile ions to carry charges hence it can conduct electricity.

(b) Samples of iron(III) oxide and iron(III) chloride are added, with stirring, to separate beakers of pure water. Suggest the pH value of the resulting solution in each beaker after stirring, giving a reason for your choice. Write equations for any reactions occurring. [4]

pH 7 (Fe_2O_3). pH 3 ($FeCl_3$)
Fe_2O_3 is insoluble in water due to the very exothermic lattice energy.
$FeCl_3$ undergoes hydrolysis due to the high charge density of Fe^{3+}.
$FeCl_3 + 6H_2O \rightarrow Fe(H_2O)_6^{3+} + 3Cl^-$
$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$

(c) Give the ion-electron equations for the electrode reactions in the electrolysis of aqueous iron(III) chloride using inert electrodes. [2]

Cathode: $Fe^{3+} + e \rightarrow Fe^{2+}$
Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e$

(d) When water reacts with iron(III) ions, it acts as a *ligand* in the formation of the complex ion, $[Fe(H_2O)_6]^{3+}$ to give a coloured solution.

(i) Explain what is meant by the term *ligand*.

Ligand is a molecule or anion with at least one lone pair of electrons that it can use to form a coordinate bond to the central metal atom/ion in a complex ion.

(ii) Explain why solutions containing iron(III) ions are coloured but those containing zinc ions are colourless.

- In an octahedral iron(III) complex ion, the ligands cause a split in the energies of the 3d orbitals.
- The energy difference, $\Delta_o = h\nu$, corresponds to wavelengths in the visible spectrum.
- An electron is promoted from a d orbital of lower energy to one of higher energy by absorbing a photon with energy Δ_o.
- Unabsorbed wavelengths are transmitted.

- The colour of the complex is complementary to the colour absorbed.
- Zn^{2+} has completely filled d orbitals and no d-d transition can take place

[5]

(e) A solution contains a mixture of iron(III) and zinc ions. You are provided with NaOH(aq) and HNO_3(aq). You are to propose a series of test-tube experiments to separate the two cations so that each cation is present as its **aqueous** ions.

(i) Give a description of your proposed sequence of steps to separate the two cations, numbering each step.

1. To 2 cm depth of solution in a test tube, add NaOH(aq) dropwise till in excess.
2. Filter the mixture
3. Add excess HNO_3 to the filtrate. (Zn^{2+})
4. Add excess HNO_3 to the residue. (Fe^{3+})

(ii) With the aid of appropriate equations, explain the reactions involved.

Precipitation reaction:
$Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_2(s)$ (I)
$Zn^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Zn(OH)_2(s)$ (I)
Formation of soluble complex:
Excess NaOH(aq): $Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$ (II)

H^+ added will react with OH^- present and cause $[OH^-]$ to decrease in equilibrium (I) POE will shift left to replace the removed OH^- hence $Fe^{3+}(aq)$ and $Zn^{2+}(aq)$ are formed.

[6]

[Total: 20]

[End of Paper]