Please check the examination details below before entering your candidate information

Candidate surname: StemUp Model Solution

Other names:

Pearson Edexcel Level 3 GCE

Centre Number

Candidate Number

Time 2 hours 30 minutes

Paper reference **9CH0/03**

Chemistry

Advanced

PAPER 3: General and Practical Principles in Chemistry

Candidates must have: Scientific calculator
Data Booklet
Ruler

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
  – *there may be more space than you need.*

Information

- The total mark for this paper is 120.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- For the question marked with an **asterisk** (*), marks will be awarded for your ability to structure your answer logically showing the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.
- Good luck with your examination.

Turn over ▶

P67806A

©2021 Pearson Education Ltd.

1/1/1/1/1/1

P 6 7 8 0 6 A 0 1 3 6

Pearson

Answer ALL the questions.

Write your answers in the spaces provided.

1 This question is about chlorine.

(a) Chlorine has two isotopes with mass numbers 35 and 37.

(i) Complete the table to show the numbers of subatomic particles in a ^{35}Cl atom and a $^{37}Cl^-$ ion.

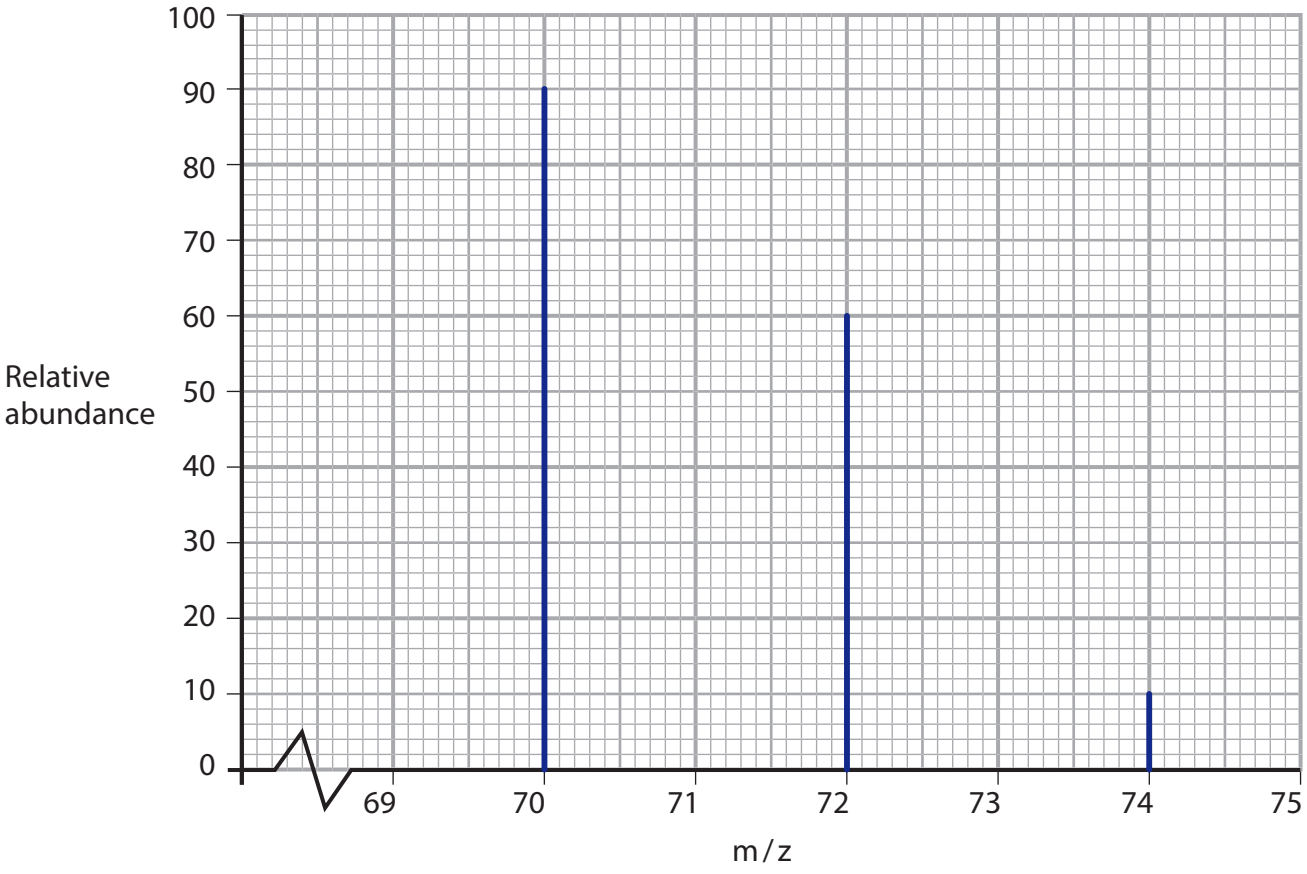
(2)

Particle	Protons	Neutrons	Electrons
^{35}Cl atom	17	18	17
$^{37}Cl^-$ ion	17	20	18

(ii) A sample of chlorine contained 75 % of ^{35}Cl and 25 % of ^{37}Cl.

Complete the mass spectrum to show the peaks you would expect for the molecular ion Cl_2^+ from this sample of chlorine gas.

(2)



DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(b) Write the formula of potassium chlorate(V).

(1)

$KClO_3$

(c) Write the equation for the first electron affinity of chlorine. Include state symbols.

(2)

(d) The standard electrode potential for the chlorine / chloride ion half-cell is

$Cl(g) + e^- \rightleftharpoons Cl^-(g)$

$\frac{1}{2}Cl_2(aq) + e^- \rightleftharpoons Cl^-(aq) \quad E^{\ominus}_{cell} = +1.36\ V$

(i) Identify an oxidising agent from the Data Booklet that will convert chloride ions into chlorine under standard conditions.

(1)

Acidified potassium manganate(VII), MnO_4^- / H^+

(ii) Calculate the value of $E^{\ominus}_{cell}$ for the reaction in (d)(i).

(1)

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \quad E^{\ominus} = +1.51\ V$

$E^{\ominus}_{cell} = +1.51 - (+1.36)$

$E^{\ominus}_{cell} = +0.15\ V$

(Total for Question 1 = 9 marks)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

2 Analysis shows that a compound has the molecular formula $C_4H_8O_2$.

A student suggests that the compound could be either **A** or **B**.

$CH_3CH_2CH_2COOH$ **A** or $HOCH_2CH{=}CHCH_2OH$ **B**

(a) Deduce a **chemical** test which would give a positive result for **A** but **not** for **B**. Include the reagent and observation.

(2)

Add sodium carbonate solution (or solid sodium hydrogencarbonate) to an aqueous solution of each compound.

A gives effervescence (fizzing): bubbles of a gas that turns limewater milky (CO_2) are given off.

B gives no effervescence.

(b) Deduce a **chemical** test which would give a positive result for **B** but **not** for **A**. Include the reagent and observation.

(2)

Add bromine water to each compound and shake.

B decolourises the bromine water: the orange solution turns colourless (B has a C=C double bond).

A has no effect: the bromine water stays orange.

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(c) Another student suggests that the compound could contain an aldehyde and an alcohol functional group, with structure **C**.

$HOCH_2CH_2CH_2CHO$

C

Complete the table to show how the infrared spectra of **A**, **B** and **C** would be expected to differ in the wavenumber range **1800–1600 cm^{-1}**.
Use information from the Data Booklet.

(3)

Absorbance	Wavenumber range / cm^{-1}
Absorbance expected in infrared spectrum of **A** but **not** in **B** or **C**	1700 to 1720
Absorbance expected in infrared spectrum of **B** but **not** in **A** or **C**	1645 to 1669
Absorbance expected in infrared spectrum of **C** but **not** in **A** or **B**	1725 to 1740

(Total for Question 2 = 7 marks)

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

3 This question is about aluminium chloride.

(a) Complete the electronic configuration of an aluminium atom.

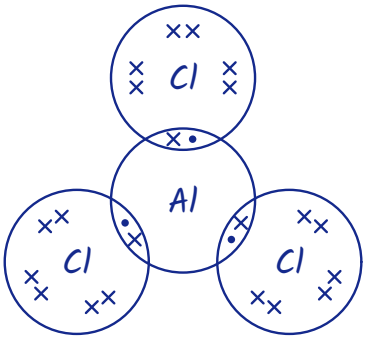
(1)

$1s^2$ $2s^2\ 2p^6\ 3s^2\ 3p^1$

(b) At high temperatures, aluminium chloride exists as $AlCl_3$ molecules.

(i) Draw a dot-and-cross diagram of an aluminium chloride molecule, $AlCl_3$. Show the outer shell electrons only.

(1)



· Al electron
× Cl electron

(ii) Predict the shape of an $AlCl_3$ molecule and the Cl–Al–Cl bond angle.

(2)

Shape of $AlCl_3$	trigonal planar
Cl–Al–Cl bond angle	120°

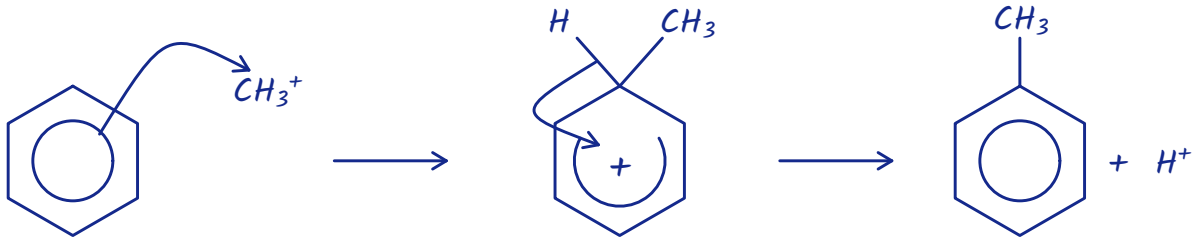
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(iii) Aluminium chloride is used as a catalyst in the alkylation of benzene.

Draw the mechanism for the reaction between benzene and chloromethane using aluminium chloride as the catalyst.
Include an equation for the formation of the electrophile, and any relevant curly arrows.

(4)

$CH_3Cl + AlCl_3 \rightarrow CH_3^+ + AlCl_4^-$



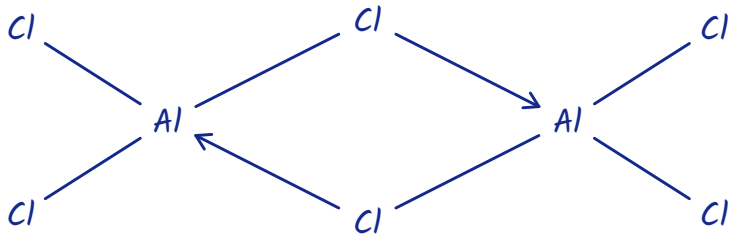
$H^+ + AlCl_4^- \rightarrow HCl + AlCl_3$ (catalyst regenerated)

(c) Aluminium chloride exists as a dimer, Al_2Cl_6, just above its boiling temperature.

(i) Draw a diagram to show how two $AlCl_3$ molecules are joined together in the dimer.

(1)

→ = dative (coordinate) bond: a lone pair on Cl is donated to the other Al atom



(ii) State the type of bond that joins the two $AlCl_3$ molecules together.

(1)

Dative (covalent) bonds, also called coordinate bonds.

(Total for Question 3 = 10 marks)

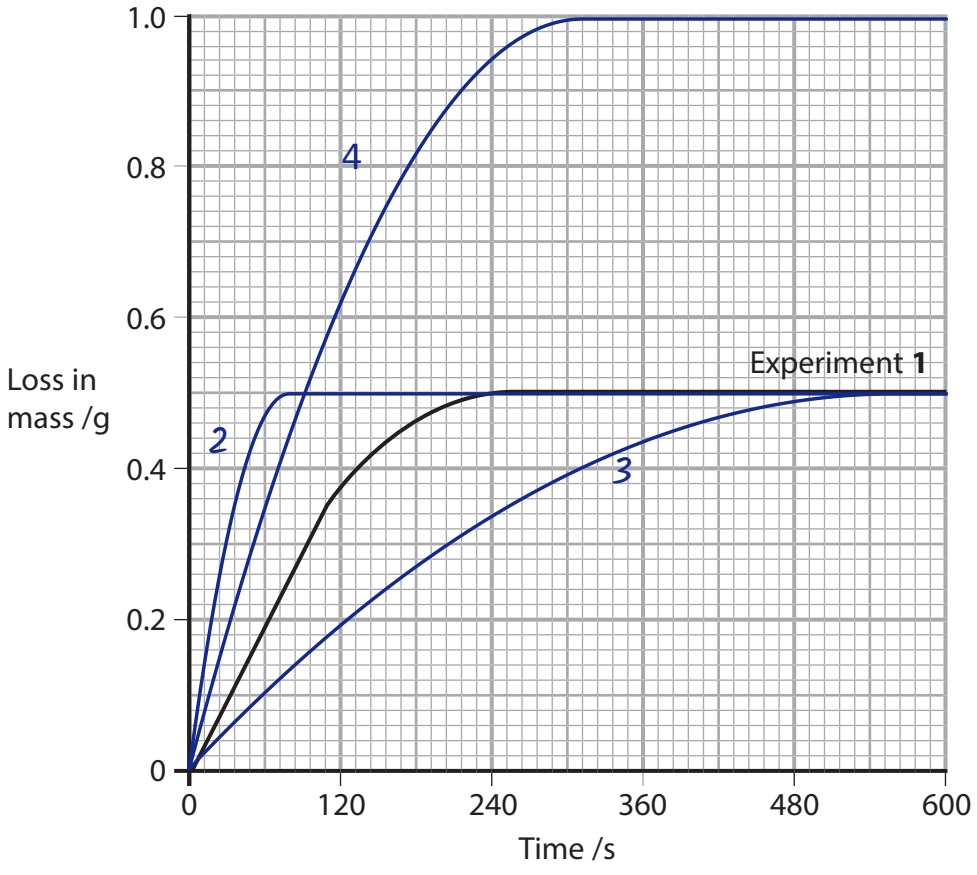
4 A series of experiments was carried out to investigate the factors which affect the rate of reaction between calcium carbonate and dilute hydrochloric acid.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

- 50.0 cm^3 of hydrochloric acid was added to 10 g of calcium carbonate (an excess) in a conical flask placed on an electronic balance.
- The loss in mass of the flask and its contents was recorded every 30 seconds for 10 minutes.
- The experiment was repeated using different sized pieces of calcium carbonate, a different concentration of hydrochloric acid or a different temperature.

Experiment	Size of calcium carbonate	Concentration of hydrochloric acid / mol dm^{-3}	Temperature /°C
1	small pieces	0.50	20
2	small pieces	0.50	60
3	one large piece	0.50	20
4	small pieces	1.00	20

The results of Experiment **1** are shown on the graph.



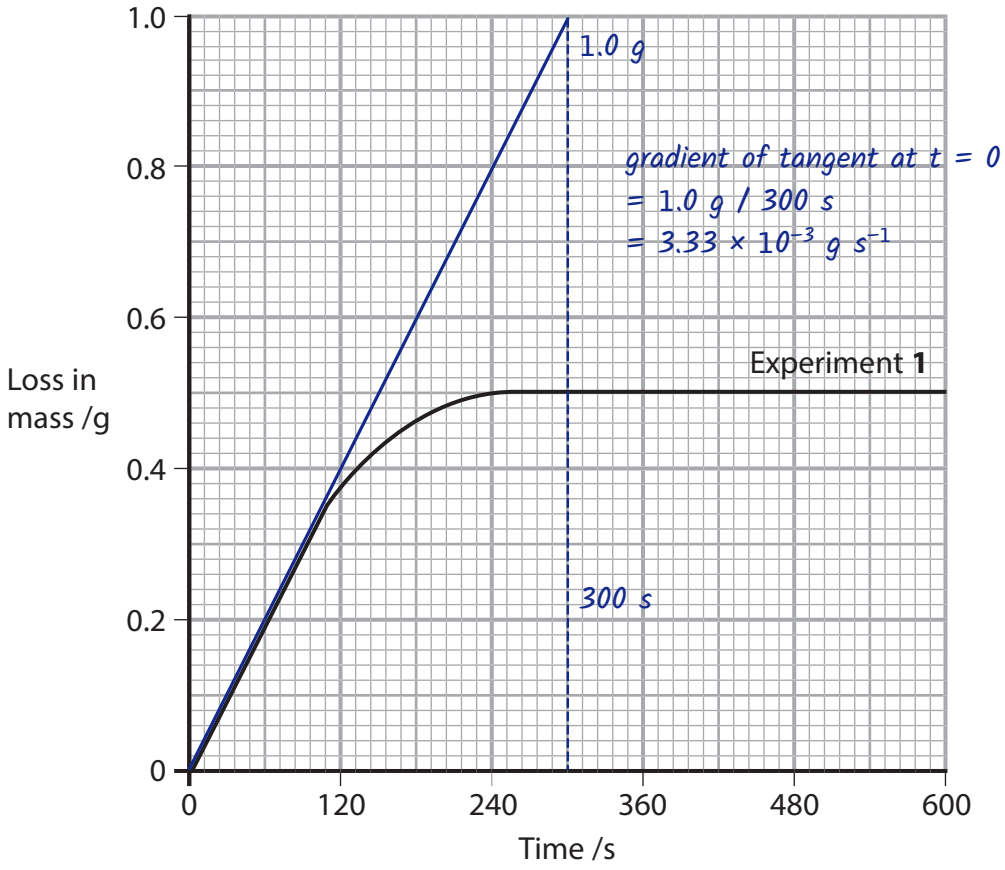
(a) Draw curves on the graph to show the results you would expect for Experiments **2**, **3** and **4**. Label the curves **2**, **3** and **4**.

(3)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(b) Determine the initial rate of reaction for Experiment **1**.
You must show your working on the graph.
Include units in your answer.

(3)



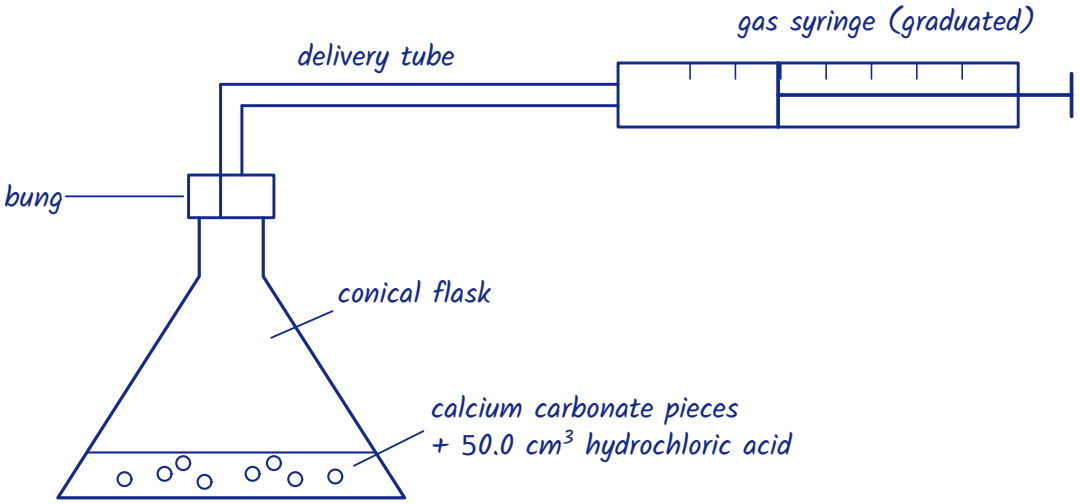
Initial rate of reaction 3.33 × 10⁻³ g s⁻¹

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(c) A student was required to devise an alternative method of carrying out this experiment that involved collecting the gas produced.

Outline the procedure that the student could use, including a diagram and the measurements needed.

(4)



Place the calcium carbonate in the conical flask and connect the delivery tube to the gas syringe (plunger fully in).

Add the 50.0 cm^3 of hydrochloric acid, immediately replace the bung and start the stopclock.

Record the volume of gas (CO_2) collected in the gas syringe at regular time intervals, e.g. every 30 s for 10 minutes.

Measurements: volume of gas collected (cm^3) and time (s).

(Total for Question 4 = 10 marks)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

BLANK PAGE

5 Tests are carried out on aqueous solutions of two salts, **X** and **Y**.

(a) **X** contains one cation and one anion.

The observations for each test are recorded in the table.

(i) Complete the table by writing the names or formulae of the species.

(2)

Test	Observation	Inference
Test 1 Add aqueous sodium hydroxide to an aqueous solution of **X**	A green precipitate forms The precipitate turns brown on the top after a few minutes	The cation in **X** is Fe^{2+} / iron(II)
Test 2 To an aqueous solution of **X**, add dilute hydrochloric acid followed by aqueous barium chloride	A white precipitate forms	The anion in **X** is SO_4^{2-} / sulfate

(ii) Write the ionic equation for the reaction between the cation in **X** and aqueous sodium hydroxide in **Test 1**. Include state symbols.

(2)

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

(iii) Give a reason why the green precipitate turns brown on the top after a few minutes.

(1)

The Fe^{2+} (iron(II) hydroxide) at the surface is oxidised by oxygen in the air to Fe^{3+}, forming brown iron(III) hydroxide.

(iv) Give a reason why dilute hydrochloric acid is needed in **Test 2**.

(1)

To react with and remove any carbonate (or sulfite) ions, which would otherwise also form a white precipitate with Ba^{2+} ions.

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(b) **Y** contains one cation and one anion.

The observations for each test are recorded in the table.

(i) Complete the table by writing the names or formulae of the species.

(2)

Test	Observation	Inference
Test 3 Add dilute aqueous ammonia to an aqueous solution of **Y** until it is present in excess	A pale blue precipitate forms The precipitate dissolves in excess ammonia to form a deep blue solution	The cation in **Y** is Cu^{2+} / copper(II)
Test 4 To an aqueous solution of **Y**, add dilute nitric acid followed by aqueous silver nitrate	A white precipitate forms	The anion in **Y** is Cl^- / chloride

(ii) Give the formula of the complex ion present in the deep blue solution at the end of **Test 3**.

(1)

$[Cu(NH_3)_4(H_2O)_2]^{2+}$

(iii) Give a reagent that could be added to the mixture at the end of **Test 4** to confirm the identity of the anion in **Y**.
Include the observation when this reagent is added.

(2)

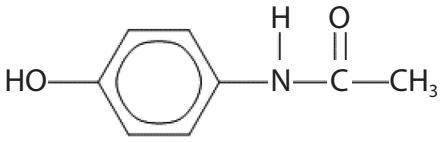
Add dilute aqueous ammonia to the mixture (and stir).

The white precipitate (of AgCl) dissolves, forming a colourless solution, confirming that the anion is chloride, Cl^-.

(Total for Question 5 = 11 marks)

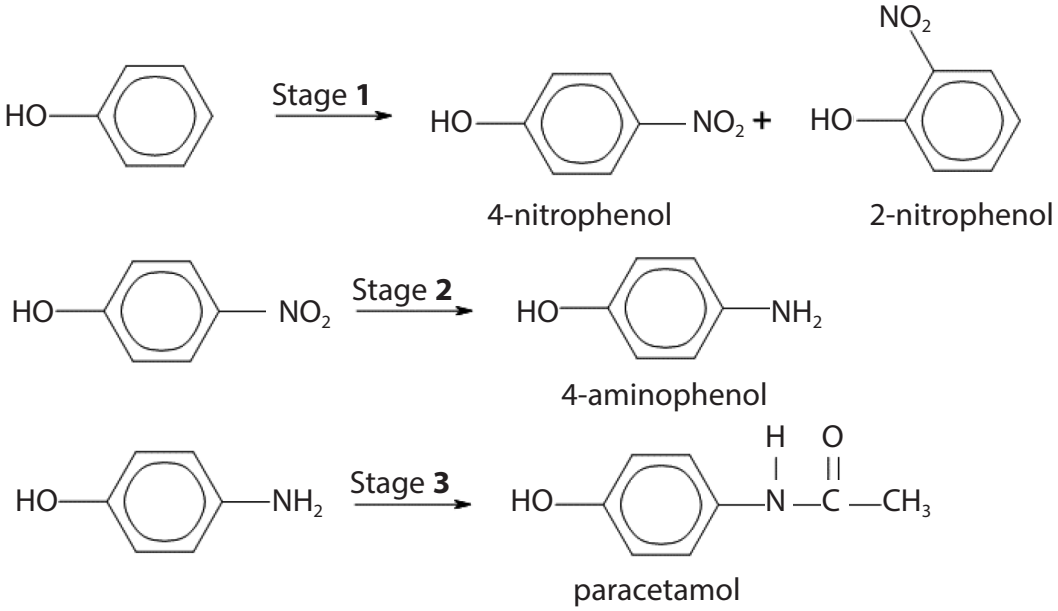
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

6 This question is about the preparation and analysis of paracetamol.



paracetamol

Paracetamol may be prepared from phenol in three stages.



(a) In Stage **1**, phenol is nitrated using dilute nitric acid.

The nitration of benzene requires concentrated nitric acid at 55°C with a catalyst of concentrated sulfuric acid.
Both these reactions are electrophilic substitution.

(i) Explain why phenol can be nitrated using milder conditions than benzene.

(2)

In phenol, a lone pair of electrons on the oxygen atom of the OH group overlaps with (is delocalised into) the π delocalised system of the benzene ring.

So the electron density of the ring is greater in phenol than in benzene, so the ring is more easily attacked by electrophiles (it can polarise the electrophile) and milder conditions can be used.

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(ii) A mixture of 2-nitrophenol and 4-nitrophenol is produced in Stage **1**.
They are separated by steam distillation.

The boiling temperature of 2-nitrophenol is 215°C and that of 4-nitrophenol is 279°C.

Explain, in terms of intermolecular forces, why 4-nitrophenol has a higher boiling temperature than 2-nitrophenol.
You may include a diagram in your answer.

(2)

Both nitrophenols form hydrogen bonds.

In 2-nitrophenol the OH and NO_2 groups are next to each other, so it forms intramolecular hydrogen bonds (within the molecule), so there are fewer intermolecular hydrogen bonds between molecules.

In 4-nitrophenol the groups are at opposite ends, so it forms intermolecular hydrogen bonds between molecules at both ends, so more energy is needed to separate them.

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

(b) State the **type** of reagent needed to convert 4-nitrophenol into 4-aminophenol in Stage **2**.

(1)

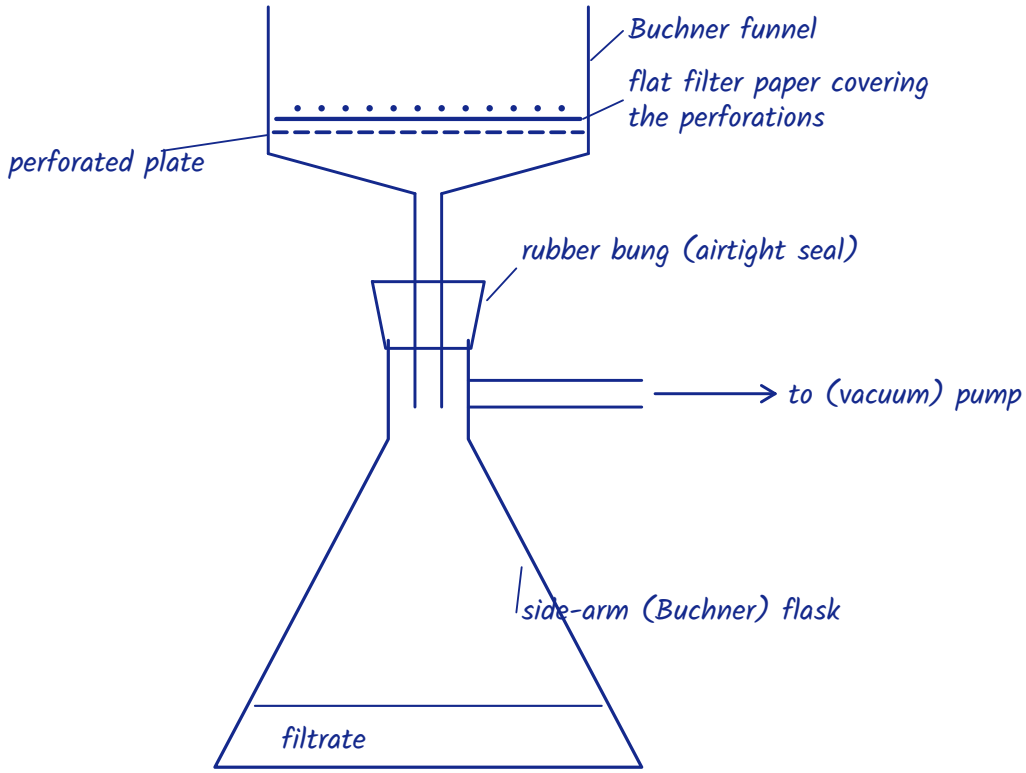
A reducing agent (reductant).

(c) The outline procedure for Stage **3** is:

- place 1.0 g of 4-aminophenol in a conical flask. Add 9 cm^3 of distilled water and stir the mixture
- add 1 cm^3 of ethanoic anhydride to the flask and shake the mixture until a precipitate of impure paracetamol forms
- remove the paracetamol by filtration under reduced pressure
- recrystallise the paracetamol using water as the solvent
- determine the melting temperature of the pure, dry paracetamol.

(i) Draw a labelled diagram of the apparatus used for filtration under reduced pressure.

(3)



DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(ii) Describe the recrystallisation process to obtain a pure, dry sample of paracetamol.

(5)

Add the impure paracetamol to a conical flask and dissolve it in the minimum volume of hot (near boiling) water.

If there are any insoluble impurities, filter the hot solution quickly through a fluted filter paper in a pre-warmed funnel.

Allow the filtrate to cool slowly to room temperature, then in an ice bath, so that crystals of paracetamol form; the soluble impurities stay dissolved in the solution.

Filter off the crystals under reduced pressure using a Buchner funnel.

Wash the crystals with a small amount of cold water (cold solvent) to remove the remaining solution.

Dry the crystals between filter papers, or in a desiccator, or in a warm oven below the melting temperature.

(iii) The melting temperature of pure paracetamol is 170°C.

Describe what happens to the melting temperature if the paracetamol is not pure.

(2)

The melting temperature is lower than 170 °C.

The paracetamol melts over a range of temperatures (the melting temperature is not sharp).

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

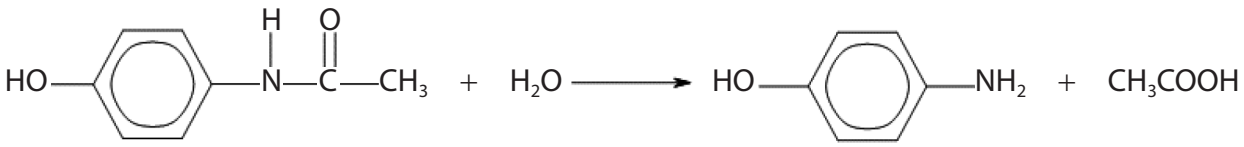
DO NOT WRITE IN THIS AREA

(d) The percentage by mass of paracetamol in three brands of paracetamol tablets are shown in the table.

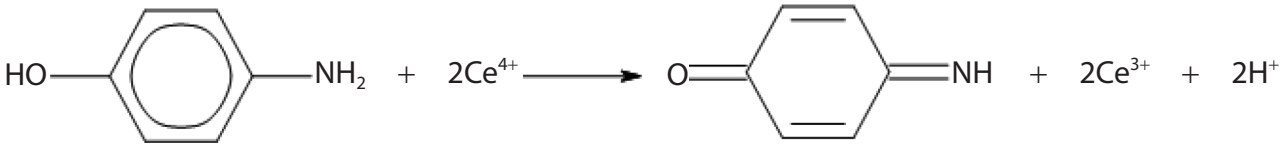
Brand of tablet	Percentage by mass of paracetamol
P	92.1
Q	93.6
R	99.7

The amount of paracetamol in a tablet can be determined using a titration with cerium(IV) ions.

The tablets are crushed and then hydrolysed in acid to form 4-aminophenol.



4-aminophenol is oxidised by cerium(IV) ions.



A tablet from one of the three brands of paracetamol was analysed following the outline procedure.

- one of the tablets was crushed and 0.500 g of the powder was added to dilute sulfuric acid
- the mixture was heated under reflux until the hydrolysis was complete
- the solution was made up to 100.0 cm^3 in a volumetric flask
- 25.0 cm^3 portions of the solution were titrated against 0.100 mol dm^{-3} Ce^{4+} using ferroin as indicator

Result

The mean titre was 16.50 cm^3.

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(i) Give the molecular formula of paracetamol.

(1)

$C_8H_9NO_2$

(ii) Determine, by calculation, which brand of tablet was analysed.

(5)

amount Ce^{4+} = 16.50 × 0.100 / 1000 = 1.65×10^{-3} mol

amount paracetamol (4-aminophenol) in 25.0 cm^3 = 1.65×10^{-3} / 2

= 8.25×10^{-4} mol

amount paracetamol in 100.0 cm^3 = 4 × 8.25×10^{-4} = 3.30×10^{-3} mol

M_r of $C_8H_9NO_2$ = (8 × 12) + (9 × 1) + 14 + (2 × 16) = 151

mass of paracetamol = 3.30×10^{-3} × 151 = 0.4983 g

percentage by mass = (0.4983 / 0.500) × 100 = 99.66 % (99.7 %)

So the tablet was from Brand R.

(Total for Question 6 = 21 marks)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

7 The enthalpy change for the decomposition of sodium hydrogencarbonate can be determined indirectly using Hess's Law.

$$2NaHCO_3(s) \xrightarrow{\Delta_r H} Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

A student carried out two experiments.

(a) **Experiment 1** involved the reaction between sodium hydrogencarbonate and hydrochloric acid.

The student used the following procedure:

- use a measuring cylinder to measure 50 cm^3 of 2.00 mol dm^{-3} hydrochloric acid and pour it into a polystyrene cup
- measure the initial temperature of the acid
- weigh the test tube containing sodium hydrogencarbonate
- tip the sodium hydrogencarbonate into the hydrochloric acid in the polystyrene cup, stir the mixture and record the lowest temperature reached
- weigh the empty test tube.

Results

Measurement	Value
Mass of test tube + $NaHCO_3$ / g	21.23
Mass of empty test tube / g	15.61
Mass of $NaHCO_3$ used / g	5.62
Initial temperature / °C	21.0
Final temperature / °C	14.4
Temperature fall / °C	6.6

(i) Complete the table.

(1)

(ii) Show, by calculation, that the hydrochloric acid is in excess.
You must show your working.

$$NaHCO_3(s) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

(2)

amount $NaHCO_3$ = 5.62 / 84.0 = 0.0669 mol (M_r = 23 + 1 + 12 + 48 = 84)

amount HCl = 50 × 2.00 / 1000 = 0.100 mol

The mole ratio $NaHCO_3$: HCl is 1 : 1, so 0.0669 mol $NaHCO_3$ needs only 0.0669 mol HCl; 0.100 > 0.0669, so the HCl is in excess (by 0.033 mol).

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(iii) Calculate the enthalpy change for the reaction between sodium hydrogencarbonate and hydrochloric acid, using the results of the experiment.
Include a sign and units in your answer.

[Assume: mass of reaction mixture = 50.0 g
specific heat capacity of the reaction mixture = 4.18 J g^{-1} $°C^{-1}$]

(3)

heat energy absorbed, Q = m c ΔT = 50.0 × 4.18 × 6.6

= 1379.4 J = 1.3794 kJ

ΔH = + Q / amount $NaHCO_3$ = + 1.3794 / 0.0669

= +20.619 kJ mol^{-1}

(positive because the temperature falls: endothermic)

ΔH = +20.6 kJ mol^{-1}

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(b) **Experiment 2** involved the reaction between sodium carbonate and hydrochloric acid.

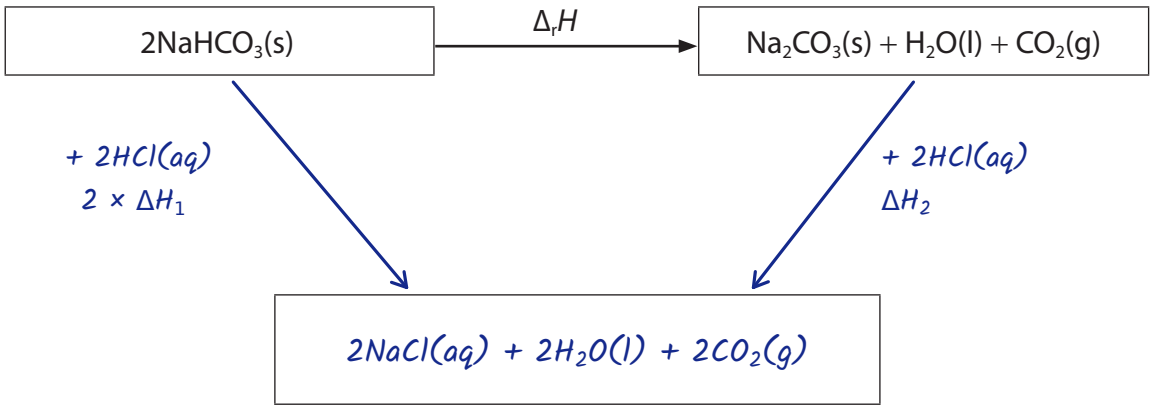
The student repeated the procedure for **Experiment 1** but used sodium carbonate instead of sodium hydrogencarbonate and measured the maximum temperature rise.

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

The student calculated the enthalpy change for this reaction as −29.4 kJ mol^{-1}.

(i) Complete the Hess cycle with appropriate formulae and labelled arrows.

(2)



(ii) Calculate the enthalpy change for the decomposition of sodium hydrogencarbonate.
Include a sign and units in your answer.

$$2NaHCO_3(s) \xrightarrow{\Delta_r H} Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

(3)

$\Delta H_1 = +20.6$ kJ mol^{-1} $\Delta H_2 = -29.4$ kJ mol^{-1}

$\Delta_r H = 2 \times \Delta H_1 - \Delta H_2$

$\Delta_r H = 2 \times (+20.619) - (-29.4)$

$= +41.238 + 29.4$

$\Delta_r H = +70.6$ kJ mol^{-1}

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(c) Another student carried out the same two experiments and obtained a value for the enthalpy change of decomposition of sodium hydrogencarbonate of +74 kJ mol^{-1}.

The data book value for this enthalpy change is +90 kJ mol^{-1}.

(i) Calculate the percentage error in this student's value.

(1)

percentage error = (90 − 74) / 90 × 100

= 17.8 %

(ii) Calculate the percentage uncertainties in measuring 50 cm^3 of hydrochloric acid using a burette and using a measuring cylinder.

(1)

Apparatus	Uncertainty	Percentage uncertainty
Measuring cylinder	±0.5 cm^3 for each volume measured	0.5/50 × 100 = 1 %
Burette	±0.05 cm^3 for each reading	2 × 0.05/50 × 100 = 0.2 %

(iii) Give a reason why using a burette rather than a measuring cylinder will not improve the accuracy of the experiment.

(1)

The difference in the percentage uncertainties (1 % and 0.2 %) is very small compared with the 17.8 % error in the value obtained, so other factors (such as heat loss) are much more significant.

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(iv) Describe changes to the method and how the data is used that would improve the accuracy of the determination of the temperature change in **Experiment 2**. Your description should involve the use of a clock and plotting a graph.

(5)

Put the 50 cm^3 of hydrochloric acid in the polystyrene cup (with a lid, in a beaker for insulation) and start the clock.

Measure the temperature of the acid every 30 s for 2½ minutes (to get a steady initial temperature).

At exactly 3 minutes, add the sodium carbonate and stir the mixture (do not take a reading at 3 minutes).

Continue to stir and measure the temperature of the mixture every 30 s from 3½ minutes for another 5 minutes.

Plot a graph of temperature (y-axis) against time (x-axis).

Draw a best fit straight line through the points before mixing, and a best fit straight line through the points after the maximum (the cooling section).

Extrapolate both lines to the time of mixing (3 minutes).

The vertical difference between the two lines at 3 minutes is the maximum temperature rise, which corrects for the heat lost to the surroundings during the reaction.

(Total for Question 7 = 19 marks)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

BLANK PAGE

8 This question is about some carbonyl compounds with the molecular formula $C_5H_{10}O$.

(a) Describe a chemical test, and its result, to distinguish between pentan-2-one, $CH_3CH_2CH_2COCH_3$, and pentan-3-one, $CH_3CH_2COCH_2CH_3$.

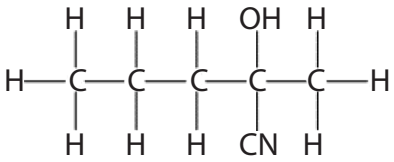
(2)

Warm each ketone with iodine in sodium hydroxide solution (alkaline iodine).

Only pentan-2-one gives a pale yellow precipitate (of triiodomethane, CHI_3, with an antiseptic smell), as it contains the CH_3CO group.

Pentan-3-one gives no precipitate.

(b) Pentan-2-one reacts with hydrogen cyanide in the presence of cyanide ions to form 2-hydroxy-2-methylpentanenitrile.

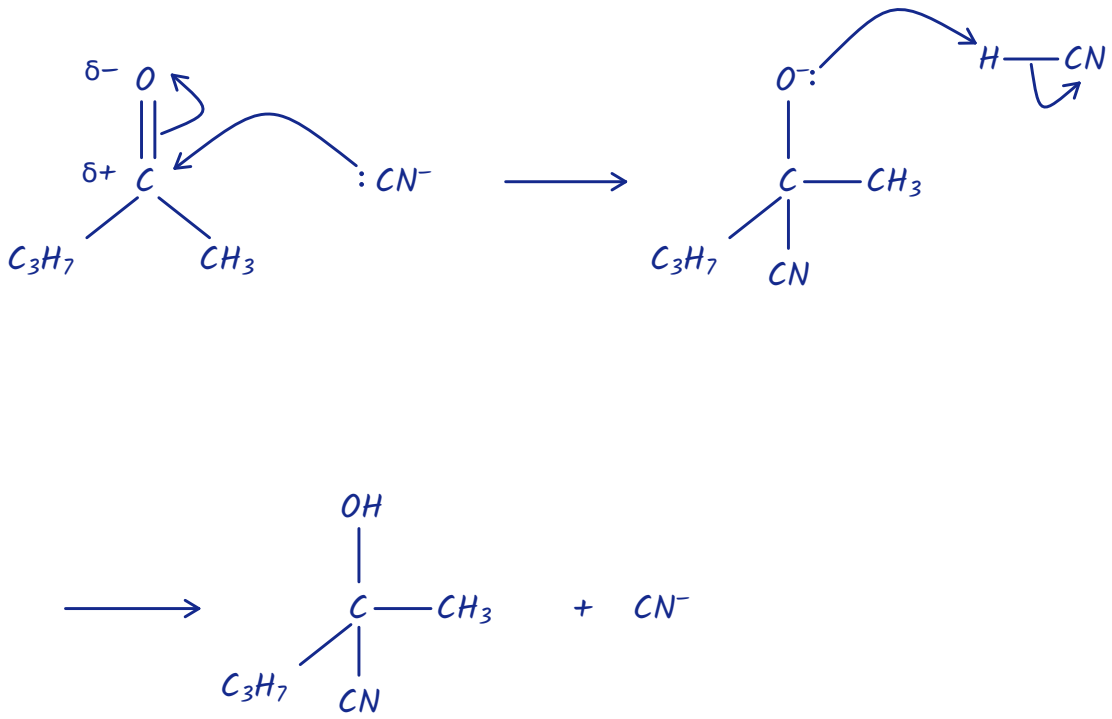


2-hydroxy-2-methylpentanenitrile

(i) Draw the mechanism for the reaction between pentan-2-one and hydrogen cyanide in the presence of cyanide ions.

Include curly arrows and any relevant lone pairs.

(4)



DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(ii) The product of this reaction, 2-hydroxy-2-methylpentanenitrile, has a chiral centre.
Explain why a racemic mixture of 2-hydroxy-2-methylpentanenitrile is formed in this reaction.

(2)

The bonds around the carbonyl carbon of pentan-2-one are trigonal planar (the C=O group and the two groups on it lie in one plane).

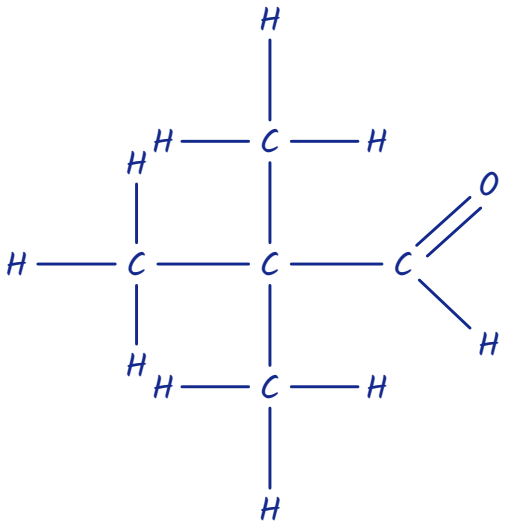
So the CN^- nucleophile can attack the carbonyl carbon equally from above and below the plane, forming equal amounts of the two enantiomers (a racemic mixture).

(c) An aldehyde with molecular formula $C_5H_{10}O$ has a ^{13}C NMR spectrum with three peaks.

The high resolution ^1H NMR spectrum of this aldehyde has two peaks and neither of them is split.

Deduce the **displayed** formula of this aldehyde.
Justify your answer by referring to both NMR spectra.

(4)



2,2-dimethylpropanal, $(CH_3)_3CCHO$

three C environments: 3 equivalent CH_3, the central C, and the CHO carbon

two H environments: 9 equivalent CH_3 H and the 1 CHO H

^{13}C: three peaks, so three carbon environments (the three equivalent CH_3 carbons, the central C and the CHO carbon).

^1H: two peaks, so two proton environments (9 CH_3 H and 1 CHO H).

Neither peak is split as there are no hydrogens on the adjacent carbon atom.

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

*(d) Describe the oxidation and reduction reactions of pentanal and pentan-3-one.

Include the reagents and the structures of the organic products formed in any reactions that take place.

(6)

Oxidation: pentanal can be oxidised by heating under reflux with acidified potassium dichromate(VI), $K_2Cr_2O_7$ with dilute H_2SO_4.

The orange solution turns green as the dichromate(VI) is reduced to Cr^{3+}, because the aldehyde group has a hydrogen atom on the carbonyl carbon which can be oxidised.

The organic product is pentanoic acid, $CH_3CH_2CH_2CH_2COOH$.

$CH_3CH_2CH_2CH_2CHO + [O] \rightarrow CH_3CH_2CH_2CH_2COOH$

Pentan-3-one, $CH_3CH_2COCH_2CH_3$, is a ketone, so it has no hydrogen atom on the carbonyl carbon; therefore it is not (easily) oxidised by acidified dichromate(VI) and the solution stays orange, so no reaction takes place.

Reduction: both carbonyl compounds are reduced by lithium tetrahydridoaluminate(III), $LiAlH_4$, in dry ether (ethoxyethane), followed by adding dilute acid.

Pentanal, an aldehyde, is reduced to a primary alcohol, pentan-1-ol, $CH_3CH_2CH_2CH_2CH_2OH$.

$CH_3CH_2CH_2CH_2CHO + 2[H] \rightarrow CH_3CH_2CH_2CH_2CH_2OH$

Pentan-3-one, a ketone, is reduced to a secondary alcohol, pentan-3-ol, $CH_3CH_2CH(OH)CH_2CH_3$.

$CH_3CH_2COCH_2CH_3 + 2[H] \rightarrow CH_3CH_2CH(OH)CH_2CH_3$

So both compounds are reduced by $LiAlH_4$, but only pentanal is oxidised.

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(Total for Question 8 = 18 marks)

9 Ammonia is manufactured by the Haber Process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_p = \frac{p(NH_3)^2}{p(N_2)p(H_2)^3}$$

(a) The pressure used in the Haber Process is 200 atm.

Explain the effect, if any, of increasing the pressure on the equilibrium yield of ammonia.

(2)

There are fewer moles (molecules) of gas on the right: 4 mol of gas on the left and 2 mol on the right.

So increasing the pressure shifts the position of equilibrium to the right (to reduce the pressure), so the equilibrium yield of ammonia increases.

(b) The equilibrium constants for K_p and K_c are related by the equation

$$K_p = \frac{K_c}{(RT)^{\Delta n}}$$

where Δn is the number of moles of reactants minus the number of moles of products.

Calculate the value of K_c at 500 K when the value of $K_p = 3.55 \times 10^{-2}$ atm^{-2}. Include the units for K_c.

[Use the value of $R = 0.0821$ dm^3 atm K^{-1} mol^{-1}]

(4)

$\Delta n = (1 + 3) - 2 = 2$

$K_c = K_p \times (RT)^{\Delta n} = 3.55 \times 10^{-2} \times (0.0821 \times 500)^2$

$= 3.55 \times 10^{-2} \times 41.05^2 = 3.55 \times 10^{-2} \times 1685.1$

$= 59.8$

$K_c = 59.8$ dm^6 mol^{-2}

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA

(c) A mixture of 1.0 mol of nitrogen and 3.0 mol of hydrogen is left to reach equilibrium at 700 K.

Calculate the total pressure, in atmospheres, needed to produce a yield of 0.30 mol of ammonia at 700 K.
Give your answer to an appropriate number of significant figures.

You must show your working.

[$K_p = 7.76 \times 10^{-5}$ atm^{-2} at 700 K]

(5)

	N_2	H_2	NH_3
initial / mol	1.0	3.0	0
equilibrium / mol	1.0 − 0.15 = 0.85	3.0 − 0.45 = 2.55	0.30

total moles at equilibrium = 0.85 + 2.55 + 0.30 = 3.70

partial pressures: $p(N_2) = 0.85P / 3.70$ $p(H_2) = 2.55P / 3.70$

$p(NH_3) = 0.30P / 3.70$

$K_p = (0.30P / 3.70)^2 / [(0.85P / 3.70) \times (2.55P / 3.70)^3]$

$7.76 \times 10^{-5} = 0.0065741\ P^2 / (0.075203\ P^4) = 0.087419 / P^2$

$P^2 = 0.087419 / 7.76 \times 10^{-5} = 1126.5$ atm^2

$P = 33.56$ atm

total pressure = 34 atm (2 s.f.)

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

(d) The value of the equilibrium constant, K_p, varies with temperature.
The equation relating the values of the equilibrium constant at two temperatures is

$$\ln\left[\frac{K_2}{K_1}\right] = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

The equilibrium constant, K_1, for the formation of ammonia is 6.76×10^5 atm^{-2} when the temperature $T_1 = 298$ K.
The enthalpy change $\Delta H = -92\,400$ J mol^{-1}.

Calculate the value of the equilibrium constant for this reaction at 310 K.

[Use the value of $R = 8.31$ J mol^{-1} K^{-1}]

(4)

$\ln (K_2 / 6.76 \times 10^5) = (-92\,400 / 8.31) \times (1/298 - 1/310)$

$= -11\,119.1 \times 1.299 \times 10^{-4}$

$= -1.4444$

$K_2 = 6.76 \times 10^5 \times e^{-1.4444}$

$K_2 = 1.59 \times 10^5$ atm^{-2}

(Total for Question 9 = 15 marks)

TOTAL FOR PAPER = 120 MARKS

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

BLANK PAGE

BLANK PAGE

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA
DO NOT WRITE IN THIS AREA

BLANK PAGE

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

* Lanthanide series

* Actinide series

P 6 7 8 0 6 A 0 3 6 3 6

DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA DO NOT WRITE IN THIS AREA