CAMBRIDGE
International Examinations

Cambridge International AS & A Level

Example Candidate Responses (Standards Booklet)

Cambridge International AS and A Level Chemistry

9701

Cambridge Advanced

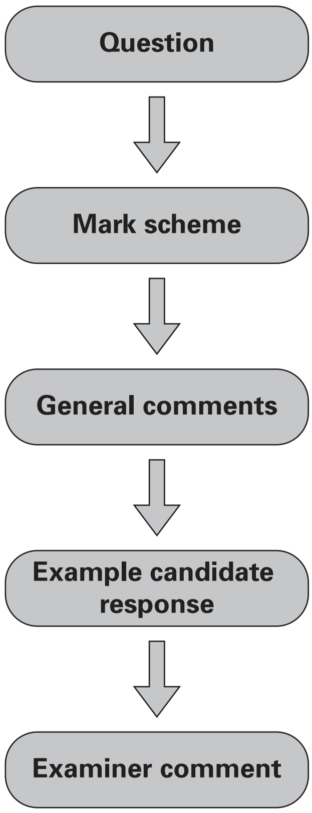
Contents

Introduction

The main aim of this booklet is to exemplify standards for those teaching Cambridge International AS and A Level Chemistry (9701), and to show how different levels of candidates' performance relate to the subject's curriculum and assessment objectives.

In this booklet a range of candidate responses has been chosen as far as possible to exemplify grades A, C and E. Each response is accompanied by a brief commentary explaining the strengths and weaknesses of the answers.

For ease of reference the following format for each paper of the subject has been adopted:



Each question is followed by an extract of the mark scheme used by examiners. This, in turn, is followed by examples of marked candidate responses, each with an examiner comment on performance. Comments are given to indicate where and why marks were awarded, and how additional marks could have been obtained. In this way, it is possible to understand what candidates have done to gain their marks and what they still have to do to improve their grades.

Past papers, Examiner Reports and other teacher support materials are available at http://teachers.cie.org.uk.

Assessment at a glance

Syllabus code 9701

- Candidates for Advanced Subsidiary (AS) certification will take Papers 1, 2 and either 31 or 32 at a single examination session.
- Candidates who, having received AS certification, wish to continue their studies to the full Advanced Level qualification may carry their AS marks forward and take just Papers 4 and 5 in the examination session in which they require certification.
- Candidates taking the complete Advanced Level qualification at the end of the course take all five papers in a single examination session.

Candidates may not enter for single papers either on the first occasion or for re-sit purposes. Candidates may only enter for the papers in the combinations indicated above.

Paper	Type of Paper	Duration	Marks	Weighting	
				AS Level	A Level
1	Multiple-choice	1 hour	40	31%	15%
2	AS structured questions	1 hour 15 min	60	46%	23%
31/32	Advanced Practical Skills	2 hours	40	23%	12%
4	A2 structured questions	2 hours	100		38%
5	Planning, Analysis and Evaluation	1 hour 15 min	30		12%

Paper 1

This paper will consist of 40 questions, thirty of the direct choice type and ten of the multiple completion type, all with four options. All questions will be based on the AS syllabus. Candidates will answer all questions. As candidates only select responses for this paper it is not included within this booklet.

Paper 2

This paper will consist of a variable number of structured questions of variable mark value.

All questions will be based on the AS syllabus. Candidates will answer all questions. Candidates will answer on the question paper.

Paper 31/Paper 32

Paper 31 and Paper 32 will be equivalent and each candidate will be required to take only one of them. This is to allow large Centres to split candidates into two groups: one group will take Paper 31, the other group will take Paper 32. Each of these papers will be timetabled on a different day.

Each paper will consist of two or three experiments drawn from different areas of chemistry.

The examiners will not be restricted by the subject content. Candidates will answer all questions. Candidates will answer on the question paper.

See the Practical Assessment section of the syllabus for full details.

Paper 4

This paper will consist of two sections.

Section A (70 marks) will consist of questions based on the A2 core syllabus but may include material first encountered in the AS syllabus.

Section B (30 marks) will consist of questions based on the section "Applications of Chemistry" but may include material first encountered in the core (AS and A2) syllabus.

Both sections will consist of a variable number of structured and free response style questions of variable mark value. Candidates will answer all questions. Candidates will answer on the question paper.

Paper 5

This paper will consist of a variable number of questions of variable mark value based on the practical skills of planning, analysis and evaluation. The examiners will not be restricted by the subject content.

Candidates will answer all questions. Candidates will answer on the question paper.

Teachers are reminded that the full syllabus is available at www.cie.org.uk

Paper 2 – Structured questions

Question 1

Answer **all** the questions in the space provided.

1 Compound **A** is an organic compound which contains carbon, hydrogen and oxygen.

When 0.240 g of the vapour of **A** is slowly passed over a large quantity of heated copper(II) oxide, CuO, the organic compound **A** is completely oxidised to carbon dioxide and water. Copper is the only other product of the reaction.

The products are collected and it is found that 0.352 g of CO_2 and 0.144 g of H_2O are formed.

(a) In this section, give your answers to three decimal places.

(i) Calculate the mass of carbon present in 0.352 g of CO_2.

Use this value to calculate the amount, in moles, of carbon atoms present in 0.240 g of **A**.

(ii) Calculate the mass of hydrogen present in 0.144 g of H_2O.

Use this value to calculate the amount, in moles, of hydrogen atoms present in 0.240 g of **A**.

(iii) Use your answers to calculate the mass of oxygen present in 0.240 g of **A**.

Use this value to calculate the amount, in moles, of oxygen atoms present in 0.240 g of **A**.

[6]

(b) Use your answers to **(a)** to calculate the empirical formula of **A**.

[1]

(c) When a 0.148 g sample of **A** was vapourised at 60 °C, the vapour occupied a volume of 67.7 cm^3 at a pressure of 101 kPa.

(i) Use the general gas equation $pV = nRT$ to calculate M_r of **A**.

M_r = ...

(ii) Hence calculate the molecular formula of **A**.

[3]

(d) Compound **A** is a liquid which does **not** react with 2,4-dinitrophenylhydrazine reagent or with aqueous bromine.

Suggest **two** structural formulae for **A**.

[2]

(e) Compound **A** contains only carbon, hydrogen and oxygen.

Explain how the information on the opposite page about the reaction of **A** with CuO confirms this statement.

....

.... [1]

[Total: 13]

Mark scheme

1 **(a)** (i) mass of C = $\frac{12 \times 0.352}{44}$ = 0.096g	(1)	
n(C) = $\frac{0.096}{12}$ = 0.008	(1)	
(ii) mass of H = $\frac{2 \times 0.144}{18}$ = 0.016g	(1)	
n(H) = $\frac{0.016}{1}$ = 0.016	(1)	
(iii) mass of oxygen = 0.240 – (0.096 + 0.016) = 0.128g	(1)	
n(O) = $\frac{0.128}{16}$ = 0.008	(1)	
allow ecf at any stage		[6]
(b) C : H : O = 0.008: 0.016 : 0.008 = 1:2:1		
allow C : H : O = $\frac{0.096}{12}$: $\frac{0.016}{1}$: $\frac{0.128}{16}$ = 1:2:1		
gives CH_2O	(1)	[1]
(c) (i) $M_r = \frac{mRT}{pV} = \frac{0.148 \times 8.31 \times 333}{1.01 \times 10^5 \times 67.7 \times 10^{-6}}$	(1)	
= 59.89		
allow 59.9 or 60	(1)	
(ii) $C_2H_4O_2$	(1)	[3]
(d) CH_3CO_2H	(1)	
HCO_2CH_3	(1)	[2]
(e) the only products of the reaction are the two oxides H_2O and CO_2 and copper	(1)	[1]
		[Total: 13]

General comment

The first part of the question tested candidates' understanding of calculations relating to the masses, and hence numbers of moles, of elements taking part in a simple reaction of the unknown compound **A**. Answers from this part were then used to calculate the empirical formula of **A**.

When they had substituted data in the equation $pV = nRT$ candidates were asked to use their earlier answers to deduce two structural formulae for compound **A**.

Those candidates who could carry out the early calculations correctly by using a clear and logical method were usually able to complete much of the rest of the question successfully. On the other hand, those candidates who did not understand how to answer part **(a)** usually struggled with the rest of the question.

Some candidates gave an empirical or molecular formula which was chemically impossible but usually did not attempt to identify the source of their error.

Example candidate response – grade A

1 Compound **A** is an organic compound which contains carbon, hydrogen and oxygen.

When 0.240 g of the vapour of **A** is slowly passed over a large quantity of heated copper(II) oxide, CuO, the organic compound **A** is completely oxidised to carbon dioxide and water. Copper is the only other product of the reaction.

The products are collected and it is found that 0.352 g of CO_2 and 0.144 g of H_2O are formed.

(a) In this section, give your answers to <u>three</u> decimal places.

(i) Calculate the mass of carbon present in 0.352 g of CO_2.

Mass CO_2 = $\frac{12}{44} \times 0.352 = 0.096\,g$ ✓

Use this value to calculate the amount, in moles, of carbon atoms present in 0.240 g of **A**.

n° of moles of Carbon atoms = $\frac{0.096}{12} = 8 \times 10^{-3}$ mol — dp x

= 8.000×10^{-3} mol

(ii) Calculate the mass of hydrogen present in 0.144 g of H_2O.

mass of H = $\frac{2}{18} \times 0.144 = 0.016\,g$

Use this value to calculate the amount, in moles, of hydrogen atoms present in 0.240 g of **A**.

n° of moles of H atoms = $\frac{0.016}{1} = 0.016$ mol ✓

(iii) Use your answers to calculate the mass of oxygen present in 0.240 g of **A**.

mass of O = 0.240 − (0.096 + 0.016)
= 0.128 g ✓

Use this value to calculate the amount, in moles, of oxygen atoms present in 0.240 g of **A**.

n° of moles of O = $\frac{0.128}{16} = 8.000 \times 10^{-3}$ mol ecf ✓

[6]

(b) Use your answers to **(a)** to calculate the empirical formula of **A**.

elements : C H O
Nº of moles : 0.008 0.016 0.008
(÷ smallest) : 1 2 1
simplest ratio : 1 : 2 : 1

∴ CH_2O (empirical formula)

[1]

(c) When a 0.148 g sample of **A** was vapourised at 60°C, the vapour occupied a volume of 67.7 cm^3 at a pressure of 101 kPa.

(i) Use the general gas equation $pV = nRT$ to calculate M_r of **A**.

$pV = nRT$

$pV = \frac{m}{M_r} RT$

$M_r = \frac{0.148 \times 8.31 \times 333}{101 \times 10^3 \times 67.7 \times 10^{-6}}$

∴ $M_r = 59.89587$

∴ $M_r = 60.0$

M_r = 60.0

(ii) Hence calculate the molecular formula of **A**.

∴ let $n \times (12 + 2(1) + 16) = 60$

$30n = 60$

$n = 2$

∴ $A \rightarrow C_2H_4O_2$

[3]

(d) Compound **A** is a liquid which does **not** react with 2,4-dinitrophenylhydrazine reagent or with aqueous bromine.

Suggest **two** structural formulae for **A**.

CH_3CO_2H	HCO_2CH_3

[2]

(e) Compound **A** contains only carbon, hydrogen and oxygen.

Explain how the information on the opposite page about the reaction of **A** with CuO confirms this statement.

Upon oxidation; only oxides of carbon (CO_2) and Hydrogen (H_2O) are produced; with copper being the only by-product.

[Total: 13]

Examiner comment – grade A

(a) This exemplary answer shows very clearly how the candidate tackled every step of the calculation.

(b) This is another very clearly set out and fully correct answer.

(c) Both parts have been correctly answered, once again with very clear setting out of the answer.

(d) The candidate drew two structures using the M_r calculated in part **(c)**. Each structure met the requirements of the question.

(e) This correct answer shows that the candidate fully understood the reaction concerned.

Example candidate response – grade C

1 Compound **A** is an organic compound which contains carbon, hydrogen and oxygen.

When 0.240 g of the vapour of **A** is slowly passed over a large quantity of heated copper(II) oxide, CuO, the organic compound **A** is completely oxidised to carbon dioxide and water. Copper is the only other product of the reaction.

The products are collected and it is found that 0.352 g of CO_2 and 0.144 g of H_2O are formed.

(a) In this section, give your answers to <u>three</u> decimal places.

(i) Calculate the mass of carbon present in 0.352 g of CO_2.

Mass of carbon $\frac{(12\times1)}{(12\times1)+(16\times2)} \times 0.352 = 0.096\text{ g}$

Use this value to calculate the amount, in moles, of carbon atoms present in 0.240 g of **A**.

No of mol of Carbon present in A $= \frac{0.096}{12}$

$= 0.008$ mol

(ii) Calculate the mass of hydrogen present in 0.144 g of H_2O.

$\frac{(1\times2)}{(1\times2)+(16\times1)} \times 0.144 = 0.016\text{ g}$

Use this value to calculate the amount, in moles, of hydrogen atoms present in 0.240 g of **A**.

No of mol of hydrogen present in A $= \frac{0.016}{1}$

$= 0.016$ mol.

(iii) Use your answers to calculate the mass of oxygen present in 0.240 g of **A**.

Mass of oxygen present $= 0.240 - [0.096 + 0.016]$

$= 0.240 - 0.112$

$= 0.128$ g.

Use this value to calculate the amount, in moles, of oxygen atoms present in 0.240 g of **A**.

No of mol $= \frac{0.128}{16}$

$= 0.008$ mol

[6]

(b) Use your answers to **(a)** to calculate the empirical formula of **A**.

	C	H	O
No of mol =	0.008	0.016	0.008
Divide by smallest =	1	= 2	= 1

Empirical formula = CH_2O

[1]

(c) When a 0.148 g sample of **A** was vapourised at 60 °C, the vapour occupied a volume of 67.7 cm^3 at a pressure of 101 kPa.

(i) Use the general gas equation $pV = nRT$ to calculate M_r of **A**.

$$Mr = \frac{mass\ RT}{pV} = \frac{0.148 \times 8.31 \times 360.7}{101 \times 0.0677}$$

$= 64.8$

$M_r =$ 64.88

(ii) Hence calculate the molecular formula of **A**.

$[CH_2O]_n = 64.88$

$12n + 2n + 16n = 64.88$

$30n = 64.88$

$n = 2.2$

≈ 2

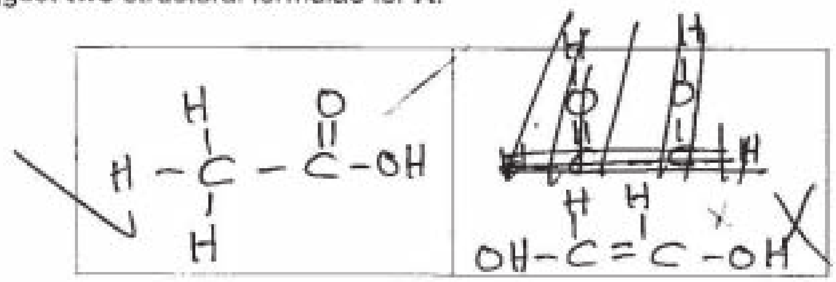
Molecular formula $= C_2H_4O_2$

ecf

[3]

(d) Compound **A** is a liquid which does **not** react with 2,4-dinitrophenylhydrazine reagent or with aqueous bromine.

Suggest **two** structural formulae for **A**.



[2]

(e) Compound **A** contains only carbon, hydrogen and oxygen.

Explain how the information on the opposite page about the reaction of **A** with CuO confirms this statement.

Because Copper is the only product of the reaction.
And complete oxidation took place with no impurities left after the reaction. [1]

[Total: 13]

Examiner comment – grade C

(a) This is another exemplary answer which is fully correct.

(b) This answer is also fully correct.

(c) **(i)** In this part, the answer shows that when using the equation *pV = nRT* the candidate did not know how to convert the values for pressure and volume from kPa and cm^3 into Nm^{-2} and m^3 respectively. In addition to this, the conversion of the temperature was wrongly carried out with 60 °C being shown as 360.7. It is not clear how this latter figure was calculated or what its units were.

(ii) As a result of the answer to part **(c)(i)**, the candidate experienced some difficulty in matching the empirical formula from part **(b)** to the value of the M_r. A reasonable approximation was made to produce a molecular formula for compound **A** which made it possible for the candidate to answer part **(d)**.

(d) One correct structure which corresponded to this molecular formula was drawn. However the second structure would not have behaved in the manner described in the question because it contained a carbon-carbon double bond and would have reacted with aqueous bromine.

(e) The candidate appeared to understand the reaction but did not state that CO_2 and H_2O were, with copper, the only products.

Example candidate response – grade E

Answer **all** the questions in the space provided.

1 Compound **A** is an organic compound which contains carbon, hydrogen and oxygen.

When 0.240 g of the vapour of **A** is slowly passed over a large quantity of heated copper(II) oxide, CuO, the organic compound **A** is completely oxidised to carbon dioxide and water. Copper is the only other product of the reaction.

The products are collected and it is found that 0.352 g of CO_2 and 0.144 g of H_2O are formed.

(a) In this section, give your answers to <u>three</u> decimal places.

(i) Calculate the mass of carbon present in 0.352 g of CO_2.

mass of carbon = 0.352 − 0.240
= 0.112 g X

n_{CO_2} = $\frac{0.352}{44}$
= 8×10^{-3}
= 0.008

Use this value to calculate the amount, in moles, of carbon atoms present in 0.240 g of **A**.

n carbon = $\frac{mass}{mr}$
= $\frac{0.112}{12}$
= 0.0093
= 0.009 moles. ✓ e/c

(ii) Calculate the mass of hydrogen present in 0.144 g of H_2O.

mass of hydrogen = ~~0.144~~ 0.240 − 0.144
= 0.096 g X

Use this value to calculate the amount, in moles, of hydrogen atoms present in 0.240 g of **A**.

n_H = $\frac{mass}{mr}$
= $\frac{0.096}{1.0}$
= 0.096 moles ✓ e/c

(iii) Use your answers to calculate the mass of oxygen present in 0.240 g of **A**.

Mass of oxygen = (0.352 + 0.112) − 0.240
= 0.496 − 0.240
= ~~0.259~~ 0.256 g X

Use this value to calculate the amount, in moles, of oxygen atoms present in 0.240 g of **A**.

n_O = $\frac{mass}{Mr}$
= $\frac{0.256}{16}$
= 0.016 moles ✓ e/c

[6]

(b) Use your answers to **(a)** to calculate the empirical formula of **A**.

	C	H	O
no moles	0.009	0.096	0.016
smallest ratio	$\frac{0.009}{0.009}$	$\frac{0.096}{0.009}$	$\frac{0.016}{0.009}$
	1	10.67 ≈ 11	1.78 ≈ 2

$CH_{11}O_2$

too far from whole nos –

[1]

(c) When a 0.148 g sample of **A** was vapourised at 60°C, the vapour occupied a volume of 67.7 cm^3 at a pressure of 101 kPa.

(i) Use the general gas equation $pV = nRT$ to calculate M_r of **A**.

$T = 60 + 273 = 333\,k$

$V = 67.6 \times 10^{-6} = 6.77 \times 10^{-5}$

$P = 101{,}000$ Pa

$(101{,}000)(6.77 \times 10^{-5}) = n(8.31)(333)$

$6.8377 = n(2767.23)$

$n = \frac{6.8377}{2767.23} = 2.471 \times 10^{-3}$

$n = \frac{mass}{mr}$

$mr = \frac{0.148}{2.471 \times 10^{-3}}$

$= 58.896$

$M_r = $ 59.896

(ii) Hence calculate the molecular formula of **A**.

$(\text{emp. formula}\ (Mr))_n = $ molecular formular.

$(12 + 1 + 16)\,n = 59.896$

$29\,n = 59.896$

$n = \frac{59.896}{29}$

$n = 2.065 \approx 2$

∴ Mol formula

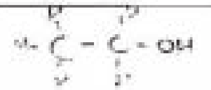
$(CH_{12}O_2)_2$

$C_2H_{24}O_4$

[3]

(d) Compound **A** is a liquid which does **not** react with 2,4-dinitrophenylhydrazine reagent or with aqueous bromine.

Suggest **two** structural formulae for **A**.

 CH_3CH_2OH	~~$CH_3CH(OH)$~~ $CH_3(OH)CH_3$.

[2]

(e) Compound **A** contains only carbon, hydrogen and oxygen.

Explain how the information on the opposite page about the reaction of **A** with CuO confirms this statement.

There was no substitution reaction, whereby copper ~~was~~ replaced an ~~atom~~ atom in organic compound. Moreover, A used oxygen atom to get itself oxidised. [1]

[Total: 13]

Examiner comment – grade E

(a) This answer shows that the candidate was unable to calculate the mass of each of the elements present in 0.240 g of compound **A**.

However, the candidate was able to convert each of the calculated masses into the corresponding number of moles of the element concerned by using a correct method, and received credit for doing so.

Each of these answers was given to three decimal places as the question required, with the answer to part **(i)** showing the calculated answer of 0.0093 being finally given as 0.009.

(b) The candidate correctly used the numbers of moles calculated in part **(a)** but the calculated ratio of C : H : O = 1 : 10.67 : 1.78 was then given as 1 : 11 : 2 which was too large an approximation to receive credit.

The resulting empirical formula, $CH_{11}O_2$ is impossible in chemical terms and this should have suggested to the candidate that a serious error had been made which needed to be investigated.

(c) **(i)** This was correctly answered with the candidate successfully converting the figures for pressure, volume and temperature into appropriate values for use in the equation $pV = nRT$.

(ii) When calculating the molecular formula of compound **A** the candidate did not use the empirical formula previously calculated. However, the result of this incorrect process was then used with the calculated empirical formula to give the incorrect molecular formula $C_2H_{24}O_4$.

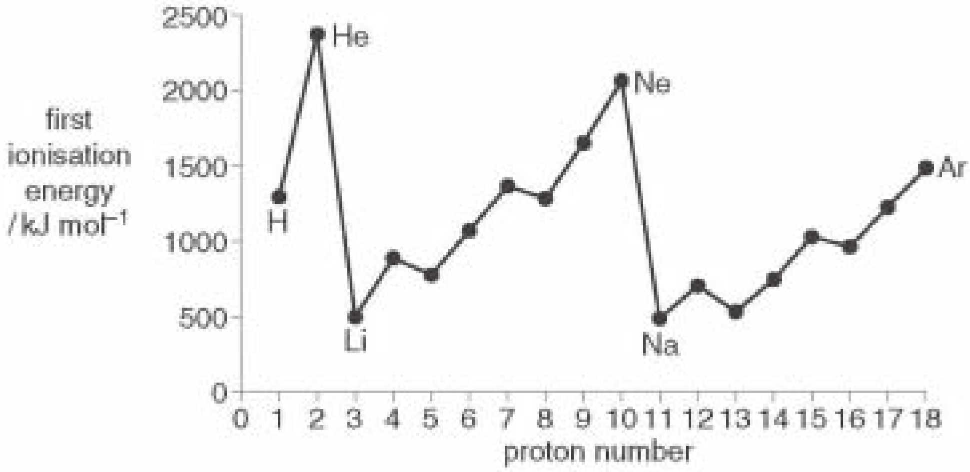
(d) The answers to this part should have used the M_r calculated in part **(c)(i)**. The resultant compound, C_2H_6O, was never justified in the calculation and thus received no credit.

(e) This answer suggests that the candidate did not understand that the formation of CO_2 and H_2O, with copper as the only other product, confirms that compound **A** contains carbon, hydrogen and oxygen.

Question 2

2 The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



(a) Give the equation, including state symbols, for the first ionisation energy of sulfur.

.... [2]

(b) Explain why there is a **general** increase in first ionisation energies across the Period from sodium to argon.

....

....

....

.... [3]

(c) **(i)** Explain why the first ionisation energy of magnesium is greater than that of aluminium.

....

....

....

(ii) Explain why the first ionisation energy of phosphorus is greater than that of sulfur.

....

....

.... [4]

The table below refers to the elements of the third Period sodium to sulfur and is incomplete.

element	Na	Mg	Al	Si	P	S
conductivity			high			
melting point			high			

(d) **(i)** Complete the 'conductivity' row by using **only** the words 'high', 'moderate' or 'low'.

(ii) Complete the 'melting point' row by using **only** the words 'high' or 'low'. [5]

When Mendeleev published his first Periodic Table, he left gaps for elements that had yet to be discovered. He also predicted some of the physical and chemical properties of these undiscovered elements.

For one element, **E**, he correctly predicted the following properties.

melting point of the element	high
melting point of the oxide	high
boiling point of the chloride	low

The element **E** was in the fourth Period and was one of the elements from gallium, proton number 31, to bromine, proton number 35.

(e) By considering the properties of the third Period elements aluminium to chlorine, suggest the identity of the fourth Period element **E**.

.... [1]

[Total: 15]

Mark scheme

2 **(a)** $S(g) \rightarrow S^{+}(g) + e^{-}$

correct equation (1)

correct state symbols (1) [2]

(b) **from Na to Ar,**

electrons are added to the same shell/have same shielding (1)

electrons are subject to increasing nuclear charge/proton number (1)

electrons are closer to the nucleus **or** atom gets smaller (1) [3]

(c) **(i)** **Mg and A*l***

in Mg outermost electron is in 3s **and**

in A*l* outermost electron is in 3p (1)

3p electron is at higher energy **or**

is further away from the nucleus **or**

is more shielded from the nucleus (1)

(ii) **S and P**

for S one 3p orbital has paired electrons **and**

for P 3p sub-shell is singly filled (1)

paired electrons repel (1) [4]

(d) **(i) and (ii)**

element	Na	Mg	A*l*	Si	P	S
conductivity	high	high	—	moderate	low	low
melting point	low	high	—	high	low	low
	(1)	(1)		(1)	(1)	(1)

one mark for each correct column [5]

(e) germanium/Ge (1) [1]

[Total: 15]

General comment

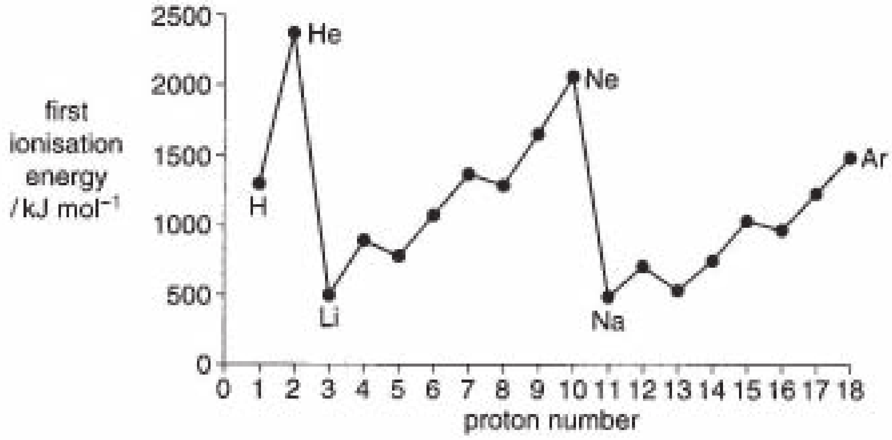
The first parts of this question asked candidates to show their understanding of first ionisation energy and of the factors that affect it. This is an important part of the study of periodicity which the more able candidates had mastered.

Candidates were also asked to show their knowledge of the properties of some of the elements. The less strong candidates were usually able to score marks in these parts.

Example candidate response – grade A

2 The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



(a) Give the equation, including state symbols, for the first ionisation energy of sulfur.

$S_{(g)} \longrightarrow S^{+}_{(g)} + e^{-}$ [2]

(b) Explain why there is a **general** increase in first ionisation energies across the Period from sodium to argon.

As we move from sodium to argon, nuclear charge increases successively while shielding effect remains constant. Thus, effective nuclear charge increases and the nucleus exerts a greater attractive force on the electrons such that atomic radius decreases and first ionisation energy increases. [3]

(c) **(i)** Explain why the first ionisation energy of magnesium is greater than that of aluminium.

Mg : $1s^2 2s^2 2p^6 3s^2$

Al : $1s^2 2s^2 2p^6 3s^2 3p^1$

As shown, the outermost electron of Aluminium is in the 3p orbital which is further away from the nucleus. The 3s sublevel also shields the positive charge of the nucleus in Aluminium such that energy required to remove outermost electron is less.

(ii) Explain why the first ionisation energy of phosphorus is greater than that of sulfur.

P : $1s^2 2s^2 2p^6 3s^2 3p^3$

S : $1s^2 2s^2 2p^6 3s^2 3p^4$

As shown, phosphorus has singly occupied 3p orbitals such that interelectronic repulsion is minimised. In sulfur, the paired electron in the outermost 3p sublevel increases interelectronic repulsion such that energy of the system is raised and ionisation energy is lower. [4]

The table below refers to the elements of the third Period sodium to sulfur and is incomplete.

element	Na	Mg	Al	Si	P	S
conductivity	high	high	high	low	low	low
melting point	low	high	high	high	low	low

(d) **(i)** Complete the 'conductivity' row by using **only** the words 'high', 'moderate' or 'low'.

(ii) Complete the 'melting point' row by using **only** the words 'high' or 'low'. [5]

When Mendeleev published his first Periodic Table, he left gaps for elements that had yet to be discovered. He also predicted some of the physical and chemical properties of these undiscovered elements.

For one element, **E**, he correctly predicted the following properties.

melting point of the element	high
melting point of the oxide	high
boiling point of the chloride	low

The element **E** was in the fourth Period and was one of the elements from gallium, proton number 31, to bromine, proton number 35.

(e) By considering the properties of the third Period elements aluminium to chlorine, suggest the identity of the fourth Period element **E**.

Selenium X [1]

[Total: 15]

Examiner comment – grade A

(a) The equation was completely correct.

(b) The candidate gave three different contributory factors in an exemplary answer.

(c) In this answer the electronic configuration of each of the four elements concerned was stated. This enabled clear explanations to be given in both parts.

(i) The candidate gave a very good explanation in terms of the greater distance from the nucleus of the 3p electron in aluminium.

(ii) By giving the electronic configurations, the reference to the repulsion between a pair of electrons in sulfur is easy to follow.

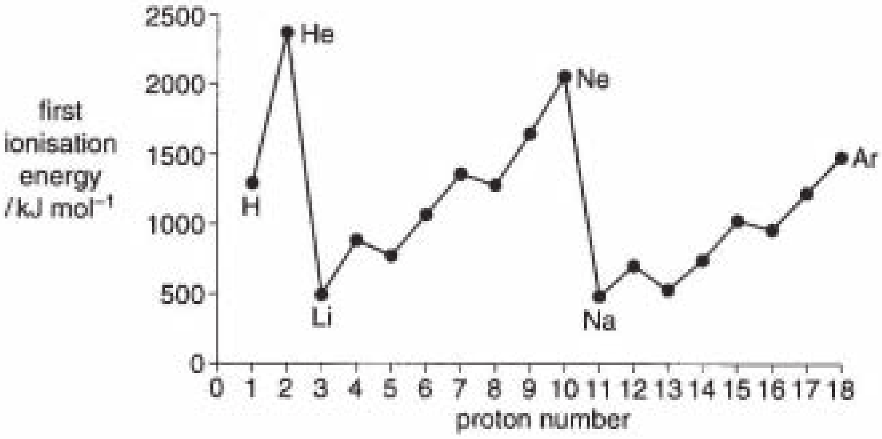
(d) The candidate demonstrated a sound knowledge of the properties of the elements but did not know the conductivity of silicon.

(e) The deduction that element **E** would be selenium was incorrect.

Example candidate response – grade C

2 The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



(a) Give the equation, including state symbols, for the first ionisation energy of sulfur.

~~[illegible]~~ S – é → S$^{(+)}$ [2]

(b) Explain why there is a **general** increase in first ionisation energies across the Period from sodium to argon.

from sodium to argon, there is a general increase in the first ~~th~~ ionisation energy which is a result of the decrease the atomic radius, increase in nuclear attraction and a constant ~~shel~~ shielding effect. [3]

(c) (i) Explain why the first ionisation energy of magnesium is greater than that of aluminium.

Mg $1s^2 2s^2 2p^6 3s^2$, Al $1s^2 2s^2 2p^6 3s^2 3p^1$

The electron to be removed from the magnesium is from the 3s-orbital which is near to the nucleus than the 3p-orbital from which the electron need to be removed for * aluminium. Hence more energy is required for magnesium.

(ii) Explain why the first ionisation energy of phosphorus is greater than that of sulfur.

The ionisation energy of sulfur is less because its' electron repel while phosphorus contains singly filled p-orbitals. Hence phosphorus is more stable and therefore needs more energy. [4]

The table below refers to the elements of the third Period sodium to sulfur and is incomplete.

element	Na	Mg	Al	Si	P	S
conductivity	high	high	high	~~low~~ moderate	low	low
melting point	low	low	high	high ~~medium~~	low	low.

(d) **(i)** Complete the 'conductivity' row by using **only** the words 'high', 'moderate' or 'low'.

(ii) Complete the 'melting point' row by using **only** the words 'high' or 'low'. [5]

When Mendeleev published his first Periodic Table, he left gaps for elements that had yet to be discovered. He also predicted some of the physical and chemical properties of these undiscovered elements.

For one element, **E**, he correctly predicted the following properties.

melting point of the element	high
melting point of the oxide	high
boiling point of the chloride	low

The element **E** was in the fourth Period and was one of the elements from gallium, proton number 31, to bromine, proton number 35.

(e) By considering the properties of the third Period elements aluminium to chlorine, suggest the identity of the fourth Period element **E**.

germanium ...... [1]

[Total: 15]

Examiner comment – grade C

(a) The equation was wrong with an anion being formed and no state symbols given.

(b) Two correct explanations for the increase in first ionisation energy from Na to Ar were given but the most obvious one – the increase in proton number – was omitted.

(c) **(i)** The candidate gave the electronic configurations for both elements and then explained very clearly why a 3p electron is more easy to remove than a 3s electron.

(ii) In this part however, there were no electronic configurations. The answer included imprecise phrases in terms of singly filled p orbitals and electrons repelling. This was too general to be given credit.

(d) The candidate demonstrated a sound knowledge of the properties of the elements but did not know that magnesium has a high melting point.

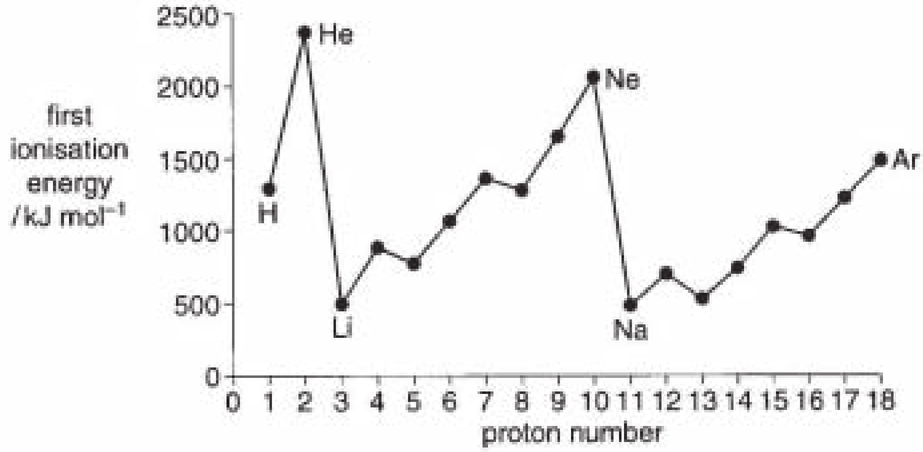
(e) The candidate correctly deduced that element **E** must be germanium.

Example candidate response – grade E

2 The Periodic Table we currently use is derived directly from that proposed in 1869 by Mendeleev who had noticed patterns in the physical and chemical properties of the elements he had studied.

For Examiner's Use

The diagram below shows the first ionisation energies of the first 18 elements of the Periodic Table.



(a) Give the equation, including state symbols, for the first ionisation energy of sulfur.

$S \longrightarrow S^{+} + e^{-}$ [2]

(b) Explain why there is a **general** increase in first ionisation energies across the Period from sodium to argon.

Across the period, there is a general increase in first ionisation energy ~~because the~~ from sodium to argon because there is an increase in their neucleon and proton number ~~in~~ ; in other words, shells increase. [3]

(c) **(i)** Explain why the first ionisation energy of magnesium is greater than that of aluminium.

First ionisation energy of magnesium is greater that that of aluminium because it electronic configuration is larger

(ii) Explain why the first ionisation energy of phosphorus is greater than that of sulfur.

Phosphorus' ~~too~~ first ionisation energy too is greater than that of sulfur due to an increase in ~~shells~~ number of shells. [4]

The table below refers to the elements of the third Period sodium to sulfur and is incomplete.

element	Na	Mg	Al	Si	P	S
conductivity	high	high	high	high	low	low
melting point	Low	high	high	high	moderate	low

(d) (i) Complete the 'conductivity' row by using **only** the words 'high', 'moderate' or 'low'.

(ii) Complete the 'melting point' row by using **only** the words 'high' or 'low'. [5]

When Mendeleev published his first Periodic Table, he left gaps for elements that had yet to be discovered. He also predicted some of the physical and chemical properties of these undiscovered elements.

For one element, **E**, he correctly predicted the following properties.

melting point of the element	high
melting point of the oxide	high
boiling point of the chloride	low

The element **E** was in the fourth Period and was one of the elements from gallium, proton number 31, to bromine, proton number 35.

(e) By considering the properties of the third Period elements aluminium to chlorine, suggest the identity of the fourth Period element **E**.

Germanium [1]

[Total: 15]

Examiner comment – grade E

(a) The equation was correct but did not include the required state symbols.

(b) The candidate rewrote the question before describing the increase in proton number from Na to Ar. No other contributory factors were given in this three mark question.

(c) No electronic configurations were given in either part. The first section of each answer consisted of rewriting the question for which no credit is given. The explanations that followed were vague and received no credit.

(d) Reasonable knowledge of the properties of the elements was shown with three of them being correctly described. However, the candidate did not read the question carefully and put 'moderate' in the 'melting point' row rather than the 'conductivity' row as the question expected.

(e) The candidate correctly deduced that element **E** must be germanium.

Question 3

3 For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

....

....

.... [2]

In order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1

30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C.
When 0.0200 mol of potassium carbonate, K_2CO_3, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) **(i)** Construct a balanced equation for this reaction.

....

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.
Use relevant data from the *Data Booklet* and assume that all solutions have the same specific heat capacity as water.

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of K_2CO_3.
Give your answer in kJ mol^{-1} and include a sign in your answer.

(iv) Explain why the hydrochloric acid must be in an excess.

....

.... [4]

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, $KHCO_3$.
All other conditions were the same.
In the second experiment, the temperature fell from 21.0 °C to 17.3 °C.

(c) **(i)** Construct a balanced equation for this reaction.

....

(ii) Calculate the quantity of heat absorbed in **experiment 2**.

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of $KHCO_3$.
Give your answer in kJ mol^{-1} and include a sign in your answer.

[3]

(d) When $KHCO_3$ is heated, it decomposes into K_2CO_3, CO_2 and H_2O.

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

Use Hess' Law and your answers to **(b)(iii)** and **(c)(iii)** to calculate the enthalpy change for this reaction.
Give your answer in kJ mol^{-1} and include a sign in your answer.

[2]

[Total: 11]

Mark scheme

3 (a)		the overall enthalpy change/energy change/ΔH for a reaction	(1)	
		is independent of the route taken **or** is independent of the number of steps involved provided the initial and final conditions are the same	(1)	[2]
(b)	(i)	$K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2$	(1)	
	(ii)	heat produced $= m \times c \times \delta T = 30.0 \times 4.18 \times 5.2$ $= 652.08$ J per 0.0200 mol of K_2CO_3	(1)	
	(iii)	0.020 mol K_2CO_3 = 652.08 J 1 mol $K_2CO_3 = \dfrac{652.08 \times 1}{0.0200} = 32604$ J enthalpy change = –32.60 kJmol^{-1}	(1)	
	(iv)	to prevent the formation of $KHCO_3$ **or** to ensure complete neutralisation	(1)	[4]
(c)	(i)	$KHCO_3 + HCl \rightarrow KCl + H_2O + CO_2$	(1)	
	(ii)	heat absorbed $= m \times c \times \delta T = 30.0 \times 4.18 \times 3.7$ $= 463.98$ J per 0.0200 mol of $KHCO_3$	(1)	
	(iii)	0.020 mol $KHCO_3$ = 463.98 J 1 mol $KHCO_3 = \dfrac{463.98 \times 1}{0.0200} = 23199$ J enthalpy change = +23.20 kJmol^{-1}	(1)	[3]
(d)		$\Delta H = 2 \times (+23.20) - (-32.60) = +79.00$ kJ mol^{-1}	(2)	[2]
				[Total: 11]

General comment

Answering thermochemical questions correctly requires candidates to use a rigorous approach in which great care is taken with units and with signs. It is the ability to do this that distinguishes the best answers from the rest.

Those candidates who were unable to carry out the calculations correctly were usually able to gain credit in most of the other parts of the question.

Example candidate response – grade A

3 For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

It states that the enthalpy change of a reaction ΔH_r is constant irrespective of the pathway / route taken provided that the initial and final conditions are the same. So ΔH_r is independent of the route taken but depends on the initial and ..... [2]

In order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1

30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C.
When 0.0200 mol of potassium carbonate, K_2CO_3, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) (i) Construct a balanced equation for this reaction.

$2HCl + K_2CO_3 \longrightarrow 2KCl + CO_2 + H_2O$

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.
Use relevant data from the *Data Booklet* and assume that all solutions have the same specific heat capacity as water.

$Q = mc\Delta T$
$= 30.0 \times 4.18 \times (26.2 - 21.0)$
$= 652.08\ J = 652\ J$ (3 s.f.)

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of K_2CO_3.
Give your answer in kJ mol^{-1} and include a sign in your answer.

$\Delta H = -\dfrac{652.08}{0.0200} = -32604\ J\,mol^{-1}$
$= -32.6\ kJ\,mol^{-1}$

(iv) Explain why the hydrochloric acid must be in an excess.

So as to ensure that all the K_2CO_3 has reacted

..... [4]

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, $KHCO_3$.
All other conditions were the same.
In the second experiment, the temperature fell from 21.0 °C to 17.3 °C.

(c) **(i)** Construct a balanced equation for this reaction.

$HCl + KHCO_3 \longrightarrow KCl + H_2O + CO_2$

(ii) Calculate the quantity of heat absorbed in **experiment 2**.

$Q = mc\Delta T$
$= 30.0 \times 4.18 \times (21.0 - 17.3)$
$= 463.98\ J = 464\ J$

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of $KHCO_3$.
Give your answer in kJ mol^{-1} and include a sign in your answer.

$\Delta H = + \dfrac{463.98}{0.0200}$
$= +23199\ J\,mol^{-1} = +23.2\ kJ\,mol^{-1}$

[3]

(d) When $KHCO_3$ is heated, it decomposes into K_2CO_3, CO_2 and H_2O.

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

Use Hess' Law and your answers to **(b)(iii)** and **(c)(iii)** to calculate the enthalpy change for this reaction.
Give your answer in kJ mol^{-1} and include a sign in your answer.

$2HCl + 2KHCO_3 \xrightarrow{\Delta H_r} K_2CO_3 + CO_2 + H_2O + 2HCl$

$+23.199 \times 2 = \Delta H_1$

$\Delta H_2 = -32.604\ kJ\,mol^{-1}$

$2KCl + 2H_2O + 2CO_2$

[2]

$\Delta H_r + \Delta H_2 = \Delta H_1$

$\Delta H_r = \Delta H_1 - \Delta H_2$
$= +23.199 \times 2 - (-32.604)$
$= +79.002\ kJ\,mol^{-1}$
$= +79.0\ kJ\,mol^{-1}$

[Total: 11]

11

Examiner comment – grade A

(a) The definition was fully correct.

(b) All four parts were correctly answered, the calculation being done in an exemplary manner.

(i) This part was answered correctly.

(ii) The candidate used the expression enthalpy change = $mc\Delta T$ correctly and gave the answer in the correct unit, J, which comes from the units for the specific heat capacity of water, given in the Data Booklet.

(iii) The calculation used the answer to part **(ii)** correctly and the final answer, which contained the correct sign, was given in kJ mol^{-1} as required.

(iv) The candidate received full marks for this answer.

(c) All three parts were answered to the same standard as those in part **(b)**.

(d) This calculation was very clearly carried out, with Hess' Law being applied correctly. The final answer contained the correct sign and units, as required.

Example candidate response – grade C

3 For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

Hess' Law states that the overall enthalpy change is constant and not dependant on the routes taken provided the initial and final states are the same. ✓✓ [2]

In order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1

30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C.
When 0.0200 mol of potassium carbonate, K_2CO_3, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) **(i)** Construct a balanced equation for this reaction. ✓

$K_2CO_3 + 2HCl \longrightarrow 2KCl + CO_2 + H_2O$

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.
Use relevant data from the *Data Booklet* and assume that all solutions have the same specific heat capacity as water.

$\Delta H = mc\Delta\theta$

$= 30 \times 4.18 \times (\cancel{[illegible]}\ 26.2 + 21.0)$ ✓

$= \cancel{[illegible]}\ 652.08\ J$

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of K_2CO_3.
Give your answer in kJ mol^{-1} and include a sign in your answer.

0.0200 mol produces ~~[illegible]~~ 652.08 J

1 mol $\longrightarrow$ $\dfrac{652.08}{0.0200}$ + 32.6 ~~[illegible]~~ kJ mol⁻¹ (3 s.f.)

(iv) Explain why the hydrochloric acid must be in an excess.

So as to be able to be able to calculate enthalpy change with respect to number of moles of K_2CO_3. [4]

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, $KHCO_3$.
All other conditions were the same.
In the second experiment, the temperature fell from 21.0 °C to 17.3 °C.

(c) **(i)** Construct a balanced equation for this reaction.

~~0.0200~~ $KHCO_3 + HCl \longrightarrow KCl + CO_2 + H_2O$ ✓

(ii) Calculate the quantity of heat absorbed in **experiment 2**.

$\Delta H = 30 \times 4.18 \times (21.0 - 17.3)$ ✓

$= 463.98\ J$

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of $KHCO_3$.
Give your answer in kJ mol^{-1} and include a sign in your answer.

$0.0200\ mol\ KHCO_3 \longrightarrow 463.98\ J$

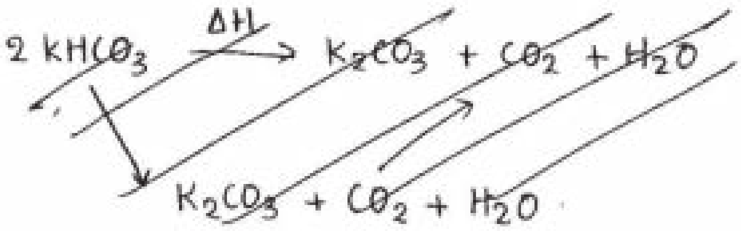
$1\ mol\ KHCO_3 \longrightarrow \frac{463.98}{0.0200}$ ✓

$= -23.2\ kJ\ mol^{-1}$ (3 s.f.) [3]

(d) When $KHCO_3$ is heated, it decomposes into K_2CO_3, CO_2 and H_2O.

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

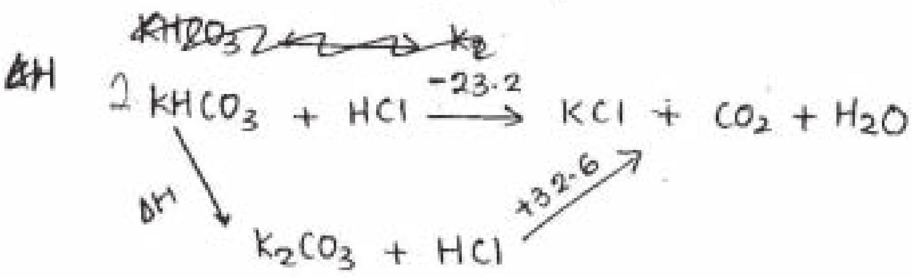
Use Hess' Law and your answers to **(b)(iii)** and **(c)(iii)** to calculate the enthalpy change for this reaction.
Give your answer in kJ mol^{-1} and include a sign in your answer.



[2]

~~2KHCO3 → K2CO3 + CO2 + H2O~~

[Total: 11]



$-23.2 = \Delta H + 32.6$ 1 error

$\Delta H = -55.8\ kJ\ mol^{-1}$

Examiner comment – grade C

(a) The definition was correct.

(b) In this part, and also in part **(c)**, the answer was affected by errors in the calculations.

(i) This was correctly answered.

(ii) The candidate used the expression enthalpy change $= mc\Delta T$ correctly and gave the answer in the correct units.

(iii) This answer was numerically correct but the sign for this exothermic reaction was + which was incorrect. However, the candidate did give the final answer in kJ mol^{-1}, as required.

(iv) The answer here suggests that the candidate did not understand that all of the K_2CO_3 must be reacted in order to be able to calculate the enthalpy change per mole of K_2CO_3.

(c) The answers to this part were very similar to those in part **(b)**. In part **(iii)**, the answer was numerically correct, with the correct units but had been given the wrong sign.

(d) In the final calculation the candidate did not correctly use the equation

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

which was given in the question. As a result, the term -23.2 was not multiplied by 2.

Apart from this mistake, the application of Hess' Law was correctly carried out for the candidate's answers to parts **(b)(iii)** and **(c)(iii)** and some credit was given.

Example candidate response – grade E

3 For some chemical reactions, such as the thermal decomposition of potassium hydrogencarbonate, $KHCO_3$, the enthalpy change of reaction cannot be measured directly.

In such cases, the use of Hess' Law enables the enthalpy change of reaction to be calculated from the enthalpy changes of other reactions.

(a) State Hess' Law.

Hess's law states ~~that~~ enthalpy change of reaction is independant on the reaction route provided initial and final conditions are the same [2]

In order to determine the enthalpy change for the thermal decomposition of potassium hydrogencarbonate, two separate experiments were carried out.

experiment 1 $KCO_3 + 2HCl \rightarrow 2KCl + CO_2 + H_2O$

30.0 cm^3 of 2.00 mol dm^{-3} hydrochloric acid (an excess) was placed in a conical flask and the temperature recorded as 21.0 °C.
When 0.0200 mol of potassium carbonate, K_2CO_3, was added to the acid and the mixture stirred with a thermometer, the maximum temperature recorded was 26.2 °C.

(b) (i) Construct a balanced equation for this reaction.

~~$K_2CO_3 + 2HCl \rightarrow KHCO_3 + 2KCl + CO_2$~~ $H_2O +$

(ii) Calculate the quantity of heat produced in **experiment 1**, stating your units.
Use relevant data from the *Data Booklet* and assume that all solutions have the same specific heat capacity as water.

N° of mol of HCl $= 2.00 \times 0.03 = 0.06$ mol

Increase in temp $= 5.2°$

Heat produced $= 0.06 \times 4.18 \times 5.2 = 1.304$ KJ X

(iii) Use your answer to (ii) to calculate the enthalpy change per mole of K_2CO_3.
Give your answer in kJ mol^{-1} and include a sign in your answer.

0.06 mol produces 1.304 KJ energy

1 mol produces $\frac{1.304}{0.06} \times 1$ KJ energy ECF

$= -21.736$ KJ/mol

(iv) Explain why the hydrochloric acid must be in an excess.

HCl must be in excess to ensume complete ~~decomposition~~ reaction has occured [4]

experiment 2

The experiment was repeated with 0.0200 mol of potassium hydrogencarbonate, $KHCO_3$.
All other conditions were the same.
In the second experiment, the temperature fell from 21.0 °C to 17.3 °C.

(c) **(i)** Construct a balanced equation for this reaction.

$2KHCO_3 + 2HCl \rightarrow 2KCl + 2H_2O + 2CO_2$

X

(ii) Calculate the quantity of heat absorbed in **experiment 2**.

Heat absorbed = 0.0200 × 4.18 × 3.7

X = 0.030932 kJ.

(iii) Use your answer to **(ii)** to calculate the enthalpy change per mole of $KHCO_3$.
Give your answer in kJ mol^{-1} and include a sign in your answer.

0.0200 mol → 0.030932 kJ

1 mol → $\frac{0.030932}{0.200}$

= +15.466 kJ/mol. X

[3]

(d) When $KHCO_3$ is heated, it decomposes into K_2CO_3, CO_2 and H_2O.

$$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$$

Use Hess' Law and your answers to **(b)(iii)** and **(c)(iii)** to calculate the enthalpy change for this reaction.
Give your answer in kJ mol^{-1} and include a sign in your answer.

(−21.736) − (+)15.466)

= −37.202 kJ

X

$2KHCO_3 \rightarrow K_2CO_3 + CO_2 + H_2O$

[2]

−21.736

C

15.466

[Total: 11]

Examiner comment – grade E

(a) The definition was correct.

(b) **(i)** There was a simple error in the first formula in the equation which was otherwise correct.

(ii) The candidate did not use the expression enthalpy change = $mc\Delta T$ correctly, the 30.0 cm^3 of 2.00 mol dm^{-3} HCl being converted into the number of moles present rather than their mass in g. The units were given as kJ rather than J.

(iii) In this part, the candidate mistook the number of moles of K_2CO_3 given in the question (0.0200) for the number of moles of HCl calculated in part **(ii)**.

(iv) This was correctly answered.

(c) **(i)** This was correctly answered.

(ii) As in part **(b)(ii)**, the mass used in the expression enthalpy change = $mc\Delta T$ was incorrect, being the number of moles of $KHCO_3$. Once again, the answer was in kJ rather than J.

(iii) The candidate attempted to carry out the correct process using the answer from part **(c)(ii)** but divided it by 0.200 rather than 0.0200.

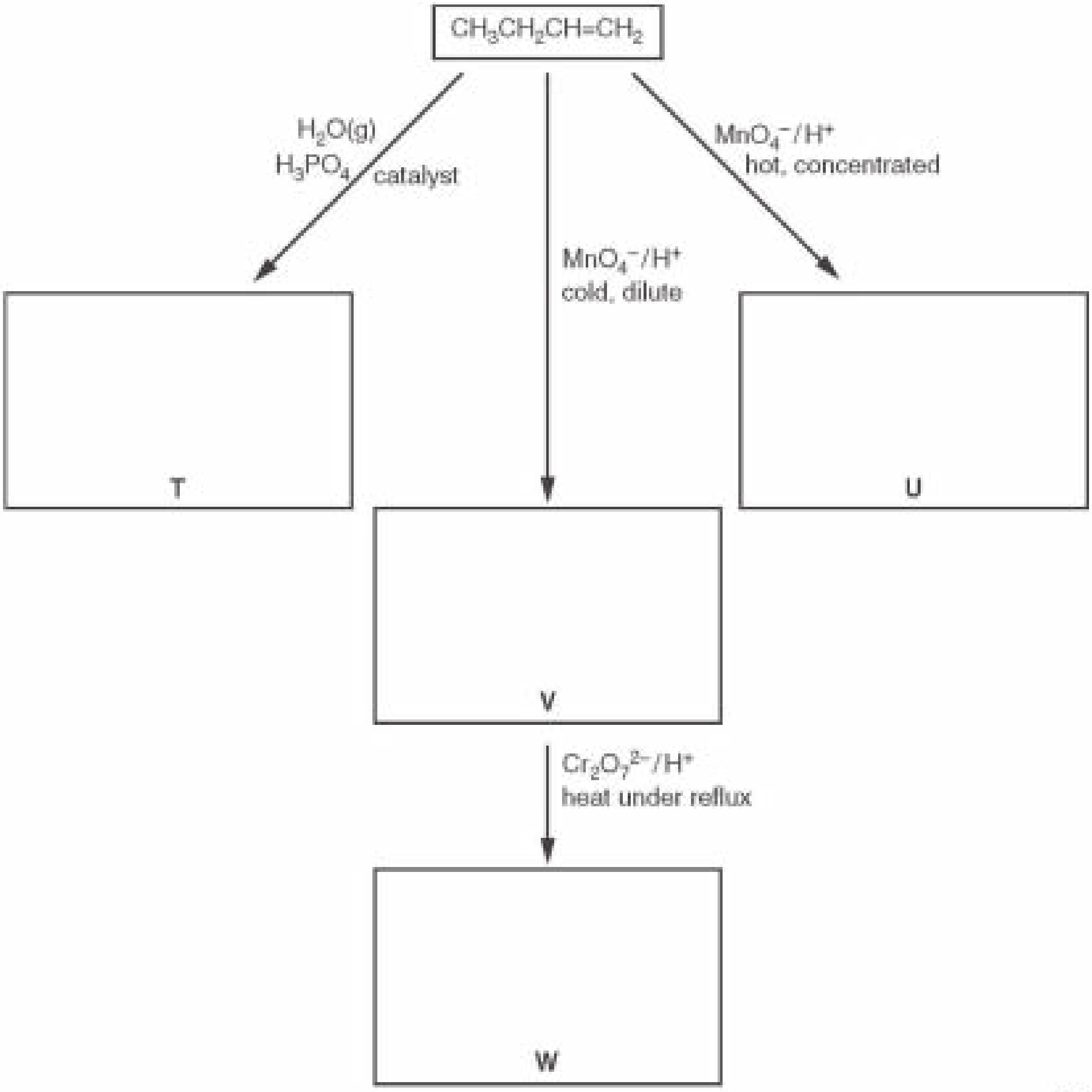
(d) The candidate did not correctly apply Hess' Law. Despite the inclusion of the equation towards the end of the answer, the candidate did not multiply the answer 15.466 by 2 and subtracted the two calculated values incorrectly.

Question 4

4 But-1-ene, $CH_3CH_2CH{=}CH_2$, is an important compound in the petrochemical industry.

(a) Some reactions of but-1-ene are given below.

In **each** empty box, draw the structural formula of the organic compound formed.



[5]

(b) Compound **T** reacts with compound **U**.

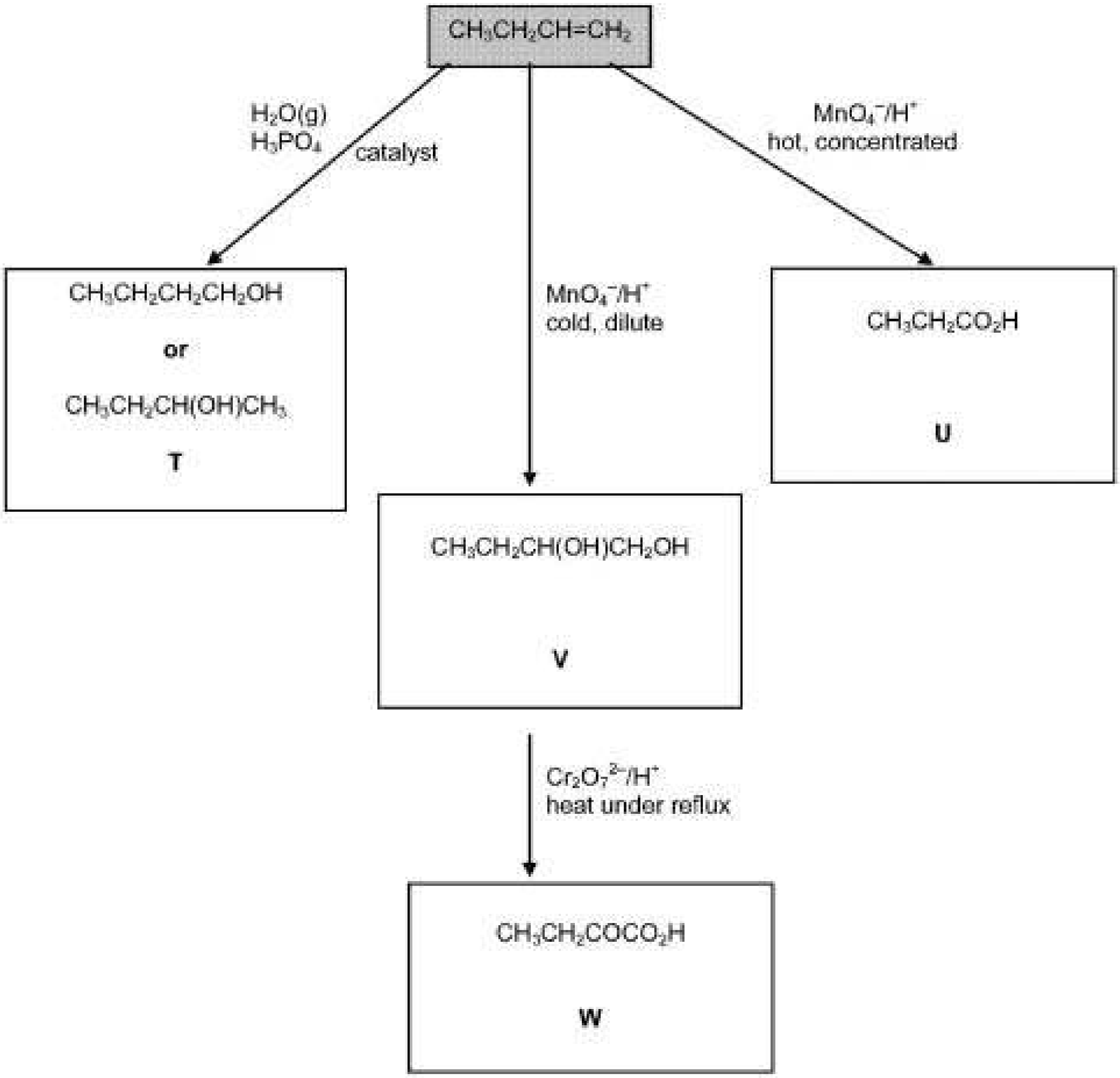
Draw the **displayed** formula of the organic product of this reaction.

[2]

[Total: 7]

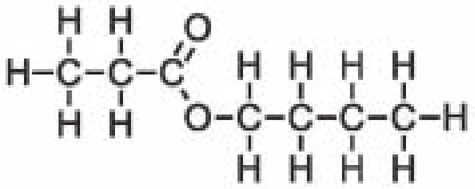
Mark scheme

4 (a)

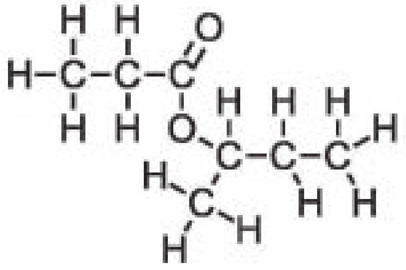


correct **T**	(1)	
correct **U**	(1)	
correct **V**	(1)	
correct > CO group in **W**	(1)	
correct $-CO_2H$ group in **W**	(1)	[5]

(b) T + U



or



correct structures (1)
correctly displayed ester group (1) [2]

[Total: 7]

General comment

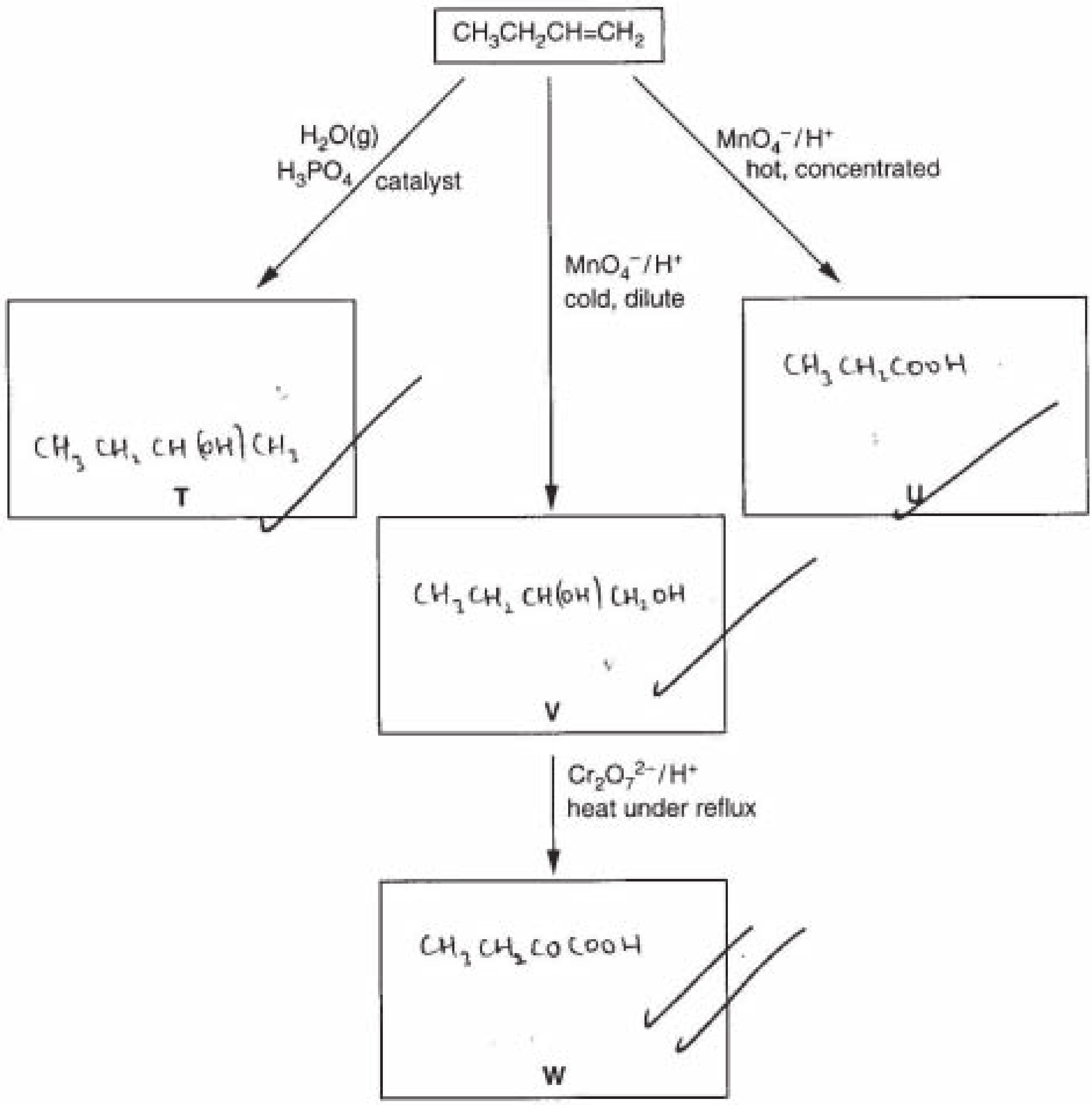
Knowledge of the important reactions of a number of organic compounds was tested in this question. Those candidates who had learned the relevant chemistry were usually able to apply their knowledge here and gain credit for it.

Example candidate response – grade A

4 But-1-ene, $CH_3CH_2CH{=}CH_2$, is an important compound in the petrochemical industry.

(a) Some reactions of but-1-ene are given below.

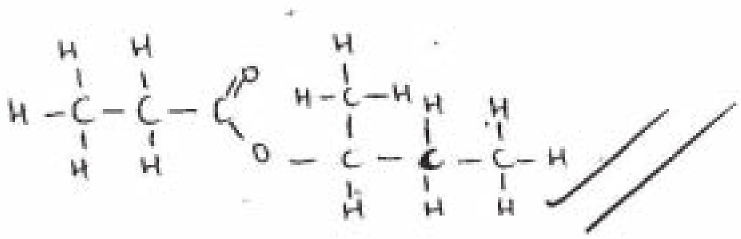
In **each** empty box, draw the structural formula of the organic compound formed.



[5]

(b) Compound **T** reacts with compound **U**.

Draw the **displayed** formula of the organic product of this reaction.



[2]

[Total: 7]

Examiner comment – grade A

(a) This was an exemplary answer, each structure being drawn very clearly.

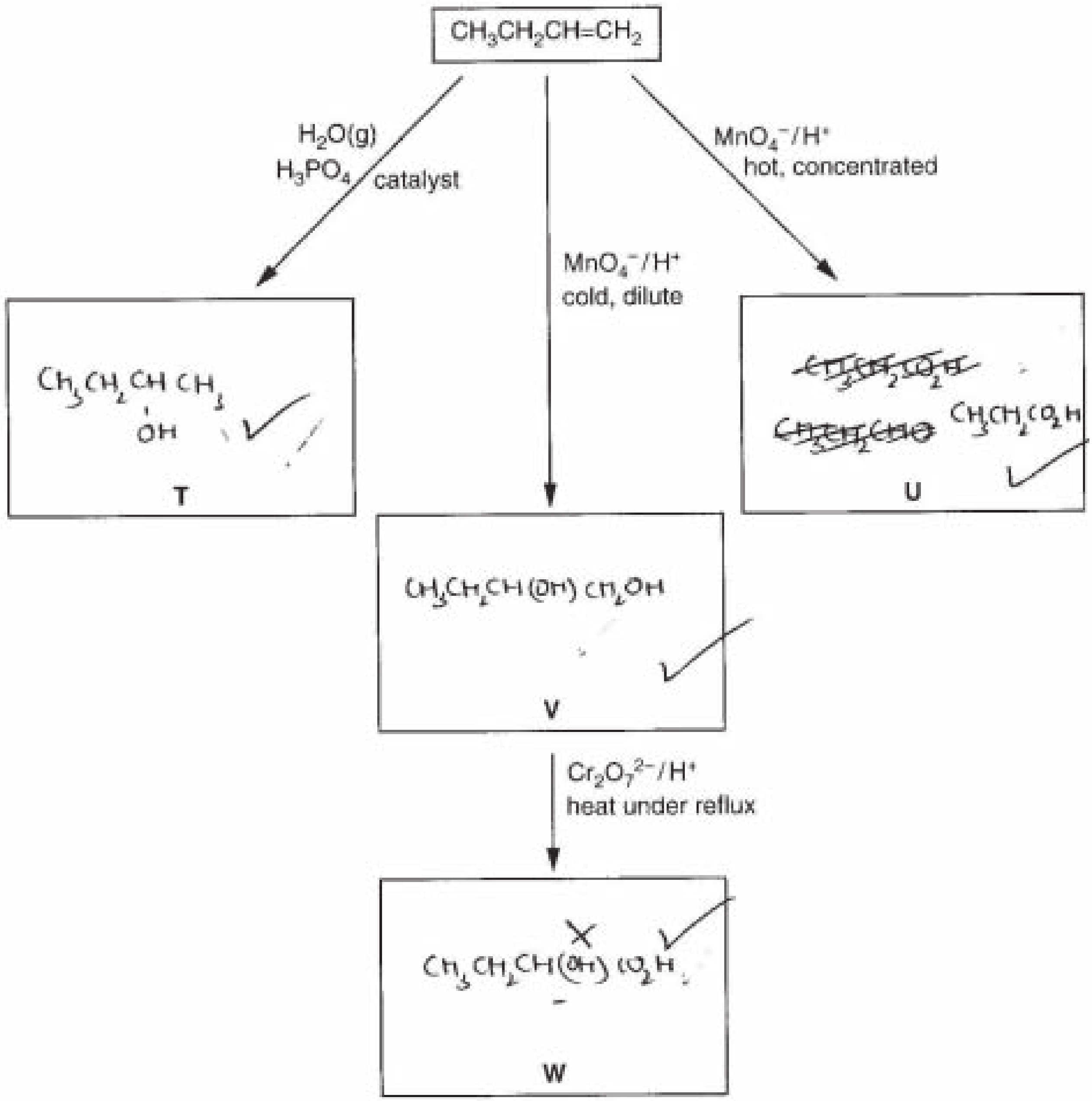
(b) This fully correct answer matches the candidate's compounds **T** and **U**.

Example candidate response – grade C

4 But-1-ene, $CH_3CH_2CH{=}CH_2$, is an important compound in the petrochemical industry.

(a) Some reactions of but-1-ene are given below.

In **each** empty box, draw the structural formula of the organic compound formed.



[5]

(b) Compound **T** reacts with compound **U**.

Draw the **displayed** formula of the organic product of this reaction.

$CH_3CH_2CH(OH)CH_3 + CH_3CH_2CO_2H$

$\downarrow$

$CH_3CH_2\overset{O}{\overset{\|}{C}}-O-CH_2CH_2CH_2CH_3 + H_2O$ [2]

incorrect based on T

[Total: 7]

Examiner comment – grade C

(a) This answer was largely correct with compound **W** showing one error.

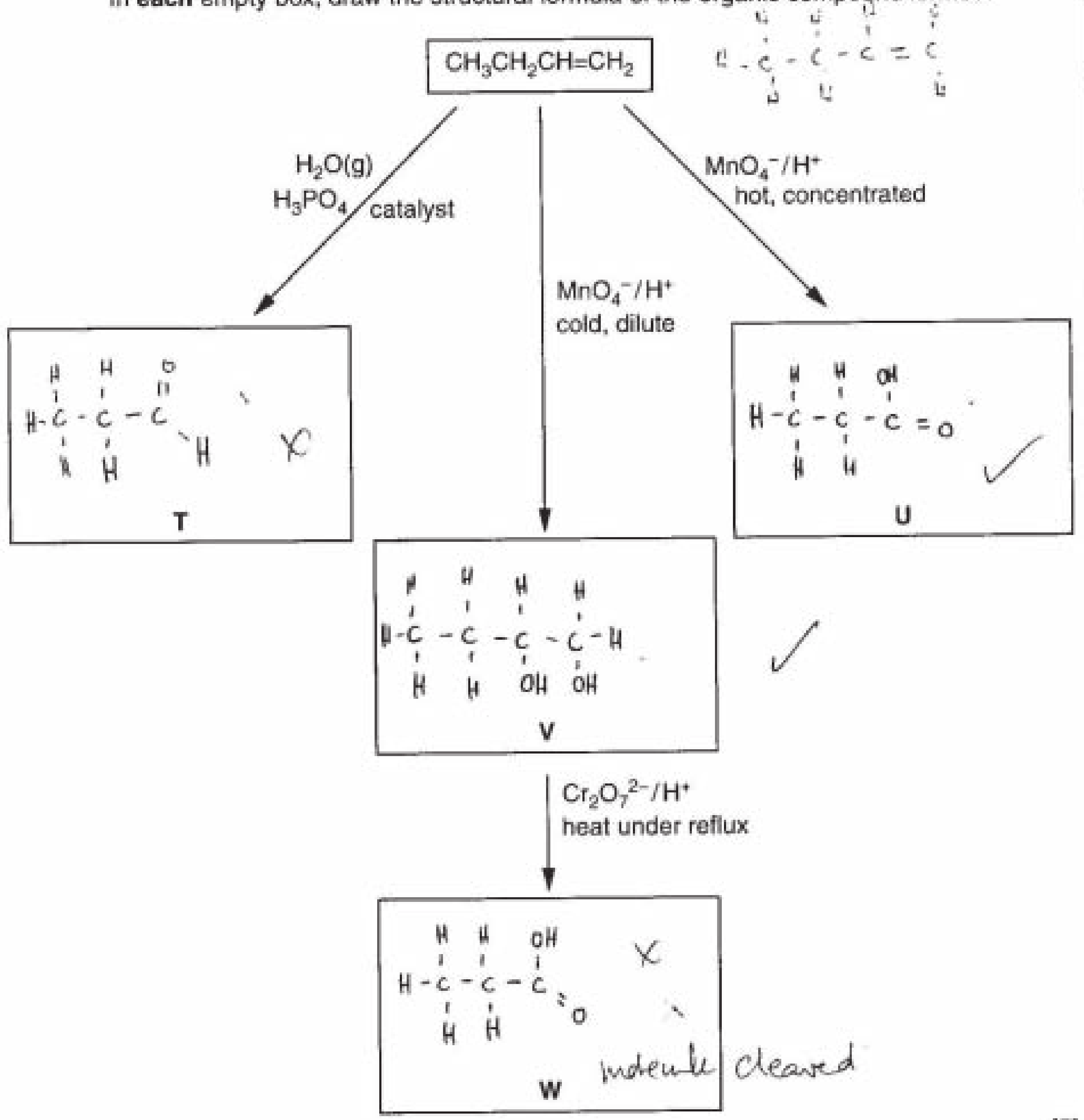
(b) The ester group was fully displayed but the compound could not have been produced from the candidate's compounds **T** and **U**.

Example candidate response – grade E

4 But-1-ene, $CH_3CH_2CH{=}CH_2$, is an important compound in the petrochemical industry.

(a) Some reactions of but-1-ene are given below.

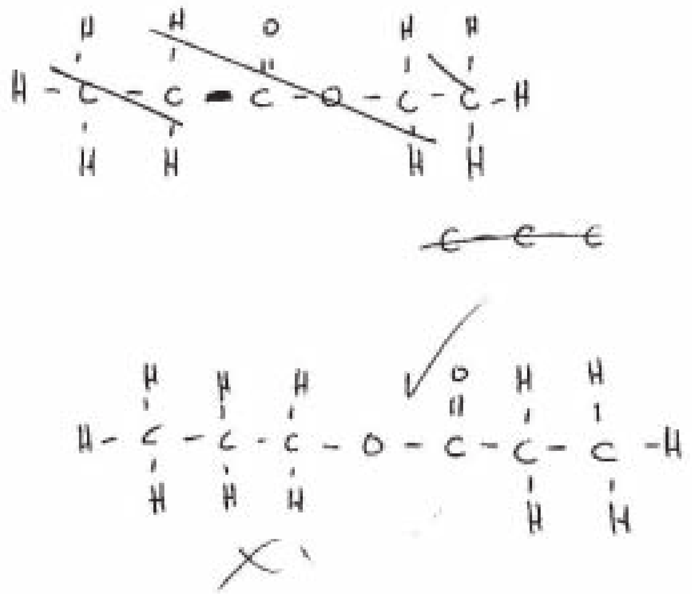
In **each** empty box, draw the structural formula of the organic compound formed.



[5]

(b) Compound **T** reacts with compound **U**.

Draw the **displayed** formula of the organic product of this reaction.



[2]

[Total: 7]

Examiner comment – grade E

(a) In this answer the candidate showed limited knowledge of the reactions concerned.

(b) The ester group was fully displayed but the compound could not have been produced from the candidate's compounds **T** and **U**.

Question 5

5 Astronomers using modern telescopes of various types have found many molecules in the dust clouds in space. Many of these molecules are those of organic compounds and astronomers constantly look for evidence that amino acids such as aminoethanoic acid, $H_2NCH_2CO_2H$, are present.

One molecule that has been found in the dust clouds is hydroxyethanal, $HOCH_2CHO$.

(a) Hydroxyethanal contains two functional groups.

(i) Name, **as fully as you can**, each of the functional groups present in hydroxyethanal.

1 ....

2 ....

(ii) For **each** functional group, identify a reagent that will react with this group and **not** react with the other functional group present.
In each case, describe what would be observed when this reaction is carried out.

functional group 1 reagent ....

observation..

functional group 2 reagent ....

observation.. [7]

(b) Give the **skeletal** formulae of the organic compounds formed when hydroxyethanal is reacted separately with the following.

(i) $NaBH_4$

(ii) $Cr_2O_7^{2-}/H^+$ under reflux conditions

[2]

In a school or college laboratory, it is possible to convert a sample of hydroxyethanal into aminoethanoic acid in a three-step process.

$$HOCH_2CHO \xrightarrow{\text{step 1}} \mathbf{X} \xrightarrow{\text{step 2}} \mathbf{Y} \xrightarrow{\text{step 3}} H_2NCH_2CO_2H$$

By considering the possible reactions of the functional groups present in hydroxyethanal, you are to deduce a possible route for this conversion.

(c) (i) In the boxes below, draw the structural formulae of your suggested intermediates **X** and **Y**.

X	**Y**

(ii) State the reagents for **each** of the three steps you have chosen.

step 1 ....

step 2 ....

step 3 .... [5]

[Total: 14]

Mark scheme

5 (a) (i) 1 primary (1)
alcohol **not** hydroxyl (1)

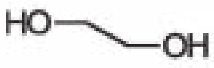
2 aldehyde **not** carbonyl (1)

(ii)

test 1			
reagent	Na	$PCl_3/PCl_5/PBr_3$	RCO_2H/H^+
observation	gas/H_2/effervescence/ fizzing	HCl/HBr steamy fumes	fruity smell
test 2			
reagent	Tollens' reagent	Fehling's reagent	2,4-dinitro-phenylhydrazine
observation	Ag mirror/silver/ black ppt	brick-red ppt red ppt	orange/red/yellow ppt/solid

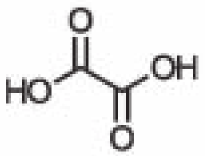
only award the observation mark if reagent is correct (4) [7]

(b) (i)



(1)

(ii)



(1) [2]

5 (c)

route	starting compound	first reagent	intermediate X	second reagent	intermediate Y	third reagent	final compound
A/1	$HOCH_2CHO$	PCl_3 PCl_5 $SOCl_2$ etc.	$ClCH_2CHO$	$K_2Cr_2O_7/H^+$ $KMnO_4/H^+$ $KMnO_4/OH^-$ Tollens' or Fehling's reagents	$ClCH_2CO_2H$	NH_3	$H_2NCH_2CO_2H$
A/2	$HOCH_2CHO$	HBr P/Br_2 etc.	$BrCH_2CHO$	$K_2Cr_2O_7/H^+$ $KMnO_4/H^+$ $KMnO_4/OH^-$ Tollens' or Fehling's reagents	$BrCH_2CO_2H$	NH_3	$H_2NCH_2CO_2H$
B/1	$HOCH_2CHO$	PCl_3 PCl_5 $SOCl_2$ etc.	$ClCH_2CHO$	NH_3	H_2NCH_2CHO	$K_2Cr_2O_7/H^+$ $KMnO_4/H^+$ $KMnO_4/OH^-$ Tollens' or Fehling's reagents	$H_2NCH_2CO_2H$
B/2	$HOCH_2CHO$	HBr P/Br_2 etc.	$BrCH_2CHO$	NH_3	H_2NCH_2CHO	$K_2Cr_2O_7/H^+$ $KMnO_4/H^+$ $KMnO_4/OH^-$ Tollens' or Fehling's reagents	$H_2NCH_2CO_2H$
C	$HOCH_2CHO$	Tollens' or Fehling's reagents	$HOCH_2CO_2H$	KBr/conc. H_2SO_4	$BrCH_2CO_2H$	NH_3	$H_2NCH_2CO_2H$
mark		(1)	(1)	(1)	(1)	(1)	

[5]

[Total: 14]

General comment

The ability to use knowledge of some organic compounds and reactions was tested in this question. Those candidates who were able to apply the relevant chemistry usually scored well in this question. However, many candidates struggled to draw the two skeletal formulae.

Example candidate response – grade A

5 Astronomers using modern telescopes of various types have found many molecules in the dust clouds in space. Many of these molecules are those of organic compounds and astronomers constantly look for evidence that amino acids such as aminoethanoic acid, $H_2NCH_2CO_2H$, are present.

One molecule that has been found in the dust clouds is hydroxyethanal, $HOCH_2CHO$.

(a) Hydroxyethanal contains two functional groups.

(i) Name, **as fully as you can**, each of the functional groups present in hydroxyethanal.

1 Primary alcohol

2 aldehyde

(ii) For **each** functional group, identify a reagent that will react with this group and **not** react with the other functional group present.
In each case, describe what would be observed when this reaction is carried out.

functional group 1 reagent sodium

observation effervescence occurs

functional group 2 reagent 2,4 dinitrophenylhydrazine

observation an orange precipitate is formed

[7]

(b) Give the **skeletal** formulae of the organic compounds formed when hydroxyethanal is reacted separately with the following.

(i) $NaBH_4$

(ii) $Cr_2O_7^{2-}/H^+$ under reflux conditions

[2]

In a school or college laboratory, it is possible to convert a sample of hydroxyethanal into aminoethanoic acid in a three-step process.

$$HOCH_2CHO \xrightarrow{\text{step 1}} X \xrightarrow{\text{step 2}} Y \xrightarrow{\text{step 3}} H_2NCH_2CO_2H$$

By considering the possible reactions of the functional groups present in hydroxyethanal, you are to deduce a possible route for this conversion.

(c) **(i)** In the boxes below, draw the structural formulae of your suggested intermediates **X** and **Y**.

$ClCH_2CHO$ ✓	H_2NCH_2CHO ✓
X	**Y**

(ii) State the reagents for **each** of the three steps you have chosen.

step 1 PCl_5 ✓

step 2 concentrated ammonia ✓

step 3 acidified potassium dichromate (VI) ✓ **[5]**

[Total: 14]

Examiner comment – grade A

(a) This was an exemplary answer.

(b) **(i)** This skeletal formula was correct.

(ii) In this skeletal formula the compound incorrectly contained three carbon atoms. The carboxyl groups were also incorrectly portrayed.

(c) This was another exemplary answer with both intermediates being suitable. In addition, the reagents were described in sufficient detail to be given full credit.

Example candidate response – grade C

5 Astronomers using modern telescopes of various types have found many molecules in the dust clouds in space. Many of these molecules are those of organic compounds and astronomers constantly look for evidence that amino acids such as aminoethanoic acid, $H_2NCH_2CO_2H$, are present.

One molecule that has been found in the dust clouds is hydroxyethanal, $HOCH_2CHO$.

(a) Hydroxyethanal contains two functional groups.

(i) Name, **as fully as you can**, each of the functional groups present in hydroxyethanal.

1 Primary Alcohol

2 aldehyde

(ii) For **each** functional group, identify a reagent that will react with this group and **not** react with the other functional group present.
In each case, describe what would be observed when this reaction is carried out.

functional group 1 reagent Potassium dichromate

observation colour changes from orange to green

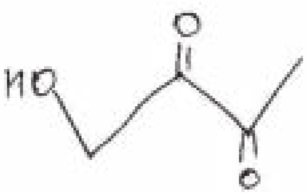
functional group 2 reagent Tollen's Reagent

observation Silver mirror, black ppt [7]

(b) Give the **skeletal** formulae of the organic compounds formed when hydroxyethanal is reacted separately with the following.

(i) $NaBH_4$

(ii) $Cr_2O_7^{2-}/H^+$ under reflux conditions



[2]

In a school or college laboratory, it is possible to convert a sample of hydroxyethanal into aminoethanoic acid in a three-step process.

$$HOCH_2CHO \xrightarrow{\text{step 1}} X \xrightarrow{\text{step 2}} Y \xrightarrow{\text{step 3}} H_2NCH_2CO_2H$$

By considering the possible reactions of the functional groups present in hydroxyethanal, you are to deduce a possible route for this conversion.

(c) (i) In the boxes below, draw the structural formulae of your suggested intermediates **X** and **Y**.

$ClCH_2CHO$

X

$ClCH_2CO_2H$

Y

(ii) State the reagents for **each** of the three steps you have chosen.

step 1 ~~aq NH_3~~ $COCl_2$ PCl_5 / heat

step 2 $Cr_2O_7^{2-}$ / H^+ heat under reflux

step 3 aq NH_3 [5]

[Total: 14]

Examiner comment – grade C

(a) **(i)** Both functional groups were correctly and fully identified.

(ii) The reagent suggested for identifying the primary alcohol would react with both functional groups present in hydroxyethanal. The reagent and observation for the aldehyde group were correct.

(b) Neither skeletal formula was correct. The first one incorrectly contained three carbon atoms and the second one four, rather than the correct number, two.

(c) The suggested route would be possible and the reagents were identified with sufficient detail to be given full credit.

Example candidate response – grade E

5 Astronomers using modern telescopes of various types have found many molecules in the dust clouds in space. Many of these molecules are those of organic compounds and astronomers constantly look for evidence that amino acids such as aminoethanoic acid, $H_2NCH_2CO_2H$, are present.

One molecule that has been found in the dust clouds is hydroxyethanal, $HOCH_2CHO$.

(a) Hydroxyethanal contains two functional groups.

(i) Name, **as fully as you can**, each of the functional groups present in hydroxyethanal.

1 ....Alcohol..........

2 ....Aldehyde..........

(ii) For **each** functional group, identify a reagent that will react with this group and **not** react with the other functional group present.
In each case, describe what would be observed when this reaction is carried out.

functional group 1 reagent ....aqueous bromine..........

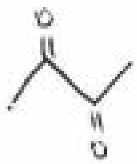
observation..........white ppt..........

functional group 2 reagent ....2,4 DNPH..........

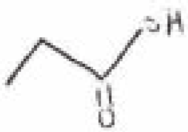
observation..........orange precipitate.......... [7]

(b) Give the **skeletal** formulae of the organic compounds formed when hydroxyethanal is reacted separately with the following.

(i) $NaBH_4$



(ii) $Cr_2O_7^{2-}/H^+$ under reflux conditions



[2]

In a school or college laboratory, it is possible to convert a sample of hydroxyethanal into aminoethanoic acid in a three-step process.

$$HOCH_2CHO \xrightarrow{\text{step 1}} \mathbf{X} \xrightarrow{\text{step 2}} \mathbf{Y} \xrightarrow{\text{step 3}} H_2NCH_2CO_2H$$

By considering the possible reactions of the functional groups present in hydroxyethanal, you are to deduce a possible route for this conversion.

(c) (i) In the boxes below, draw the structural formulae of your suggested intermediates **X** and **Y**.

X	**Y**
$H_2NCHCHO$ ~~H_2NCH_2CHO~~	H_2NCH_2CHO

(ii) State the reagents for **each** of the three steps you have chosen.

step 1 NH_3 (aq) in ethanol

step 2 $LiAlH_4$

step 3 $KMnO_4$ Δ [5]

[Total: 14]

Examiner comment –grade E

(a) **(i)** While the two functional groups were correct, the candidate did not state that the alcohol is primary.

(ii) The reagent suggested for identifying the alcohol would not react with either of the functional groups present in hydroxyethanal. The reagent and observation for the aldehyde group were correct.

(b) Neither skeletal formula was correct. The first one contained four carbon atoms and the second one three, rather than the correct number, two.

(c) **(i)** The candidate's compound **X** had an incorrect structural formula and was not given credit. Compound **Y** was given credit because it can be oxidised to aminoethanoic acid.

(ii) The reagents for steps 1 and 2 were incorrect. For the oxidation in step 3 the $KMnO_4$ must be acidified. The candidate did not state this and the answer was not given any credit.

Paper 3 – Advanced practical skills

Question 1(a)

1 You are to determine the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide and also the concentration of the aqueous sodium hydroxide. These can be found by measuring the temperature change when solutions of the acid and alkali are mixed.

For Examiner's Use

FA 1 is aqueous sodium hydroxide, NaOH.
FA 2 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

(a) Method

- Fill a burette with **FA 1**. **[Care: FA 1 is corrosive]**
- Support the plastic cup in a 250 cm^3 beaker.
- Use a measuring cylinder to transfer 25 cm^3 of **FA 2** into a 100 cm^3 beaker.
- Use a measuring cylinder to add 35 cm^3 of distilled water to the acid in the beaker.
- Measure and record, in the table below, the initial temperature of the mixture in the beaker.
- Run 5.0 cm^3 of **FA 1** from the burette into the plastic cup.
- Add the mixture of acid and water from the 100 cm^3 beaker to the **FA 1** in the plastic cup.
- Stir carefully and measure the highest temperature obtained.
- Record this temperature in the table.
- Rinse the plastic cup with water.
- Repeat the experiment using 25 cm^3 of **FA 2**, 30 cm^3 of distilled water and 10.0 cm^3 of **FA 1** as shown for experiment **2** in the table.
- Carry out experiments **3** to **7** in the same way.
- Complete the table for each experiment.

Results

experiment number	1	2	3	4	5	6	7
volume of **FA 2** / cm^3	25	25	25	25	25	25	25
volume of water / cm^3	35	30	25	20	15	10	5
volume of **FA 1** / cm^3	5.0	10.0	15.0	20.0	25.0	30.0	35.0
initial temperature of acid mixture / °C							
highest temperature / °C							
temperature change / °C							

[7]

I	
II	
III	
IV	
V	
VI	
VII	

Mark scheme

Question	Sections	Indicative material	Mark	
1 (a)	PDO Recording	**I** Thermometer readings for all experiments recorded to 0.0 or 0.5°C. (At least one recorded to 0.5°C.)	1	
	ACE Interpretation	**II** Calculation of all temperature changes correct.	1	
	MMO Quality	Award **III** for a temperature rise followed by constant temperature (within 0.5°C).	1	
		Award **IV** and **V** for a **maximum** rise within 0.5°C of supervisor.	1	
		Award **IV** for a **maximum** rise within 1.0°C of supervisor.	1	
		Award **VI** and **VII** for the experiment **3** temperature rise within 0.5°C of supervisor.	1	
		Award **VI** for the experiment **3** temperature rise within 1.0°C of supervisor.	1	[7]

General comment

In the examples for this paper, separate candidates may have been used for each question part therefore answers may not necessarily follow on from previous example candidate responses for that grade.

Almost all candidates completed the seven experiments and were able to calculate the rise in temperature correctly. However, some weaker candidates read the thermometer incorrectly (2.00 °C instead of 20.0 °C) and a large number did not record the thermometer readings to the expected level of precision. Good candidates achieved the expected constant temperature rise in the latter experiments. Weaker candidates, who are likely to have carried out a thermometric titration which produces a drop in temperature after the end point is reached, did not achieve this. Generally the accuracy marks tended to be Centre dependent although there were good results from individual candidates where others from the Centre had performed poorly. However, the majority of candidates gained at least three out of the five accuracy marks available.

Example candidate response – grade A

1 You are to determine the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide and also the concentration of the aqueous sodium hydroxide. These can be found by measuring the temperature change when solutions of the acid and alkali are mixed.

For Examiner's Use

FA 1 is aqueous sodium hydroxide, NaOH.
FA 2 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

(a) Method

- Fill a burette with **FA 1**. **[Care: FA 1 is corrosive]**
- Support the plastic cup in a 250 cm^3 beaker.
- Use a measuring cylinder to transfer 25 cm^3 of **FA 2** into a 100 cm^3 beaker.
- Use a measuring cylinder to add 35 cm^3 of distilled water to the acid in the beaker.
- Measure and record, in the table below, the initial temperature of the mixture in the beaker.
- Run 5.0 cm^3 of **FA 1** from the burette into the plastic cup.
- Add the mixture of acid and water from the 100 cm^3 beaker to the **FA 1** in the plastic cup.
- Stir carefully and measure the highest temperature obtained.
- Record this temperature in the table.
- Rinse the plastic cup with water.
- Repeat the experiment using 25 cm^3 of **FA 2**, 30 cm^3 of distilled water and 10.0 cm^3 of **FA 1** as shown for experiment **2** in the table.
- Carry out experiments **3** to **7** in the same way.
- Complete the table for each experiment.

Results

experiment number	1	2	3	4	5	6	7
volume of **FA 2** / cm^3	25	25	25	25	25	25	25
volume of water / cm^3	35	30	25	20	15	10	5
volume of **FA 1** / cm^3	5.0	10.0	15.0	20.0	25.0	30.0	35.0
initial temperature of acid mixture / °C	28.0	28.0	28.0	28.0	28.0	28.0	28.0
highest temperature / °C	30.5	33.5	36.0	39.0	39.0	39.0	39.0
temperature change / °C	2.5	5.5	8.0	11.0	11.0	11.0	11.0

$\delta =$ 0.0 6.0

11.0
8.0

[7]

I	✓
II	✓
III	✓
IV	✓
V	✓
VI	✓
VII	✓

7

Examiner comment – grade A

This answer was typical in that full marks were gained for the accuracy with which the experiment was carried out. Thermometer readings are expected to be taken to the nearest 0.5 °C, without interpolation, and for at least one of the readings to be at 0.5 °C.

Example candidate response – grade C

For Examiner's Use

NaOH [NaOH]

1 You are to determine the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide and also the concentration of the aqueous sodium hydroxide. These can be found by measuring the temperature change when solutions of the acid and alkali are mixed.

FA 1 is aqueous sodium hydroxide, NaOH.
FA 2 is 2.00 mol dm^{-3} hydrochloric acid, HCl.

(a) Method

- Fill a burette with **FA 1**. **[Care: FA 1 is corrosive]**
- Support the plastic cup in a 250 cm^3 beaker.
- Use a measuring cylinder to transfer 25 cm^3 of **FA 2** into a 100 cm^3 beaker.
- Use a measuring cylinder to add 35 cm^3 of distilled water to the acid in the beaker.
- Measure and record, in the table below, the initial temperature of the mixture in the beaker.
- Run 5.0 cm^3 of **FA 1** from the burette into the plastic cup.
- Add the mixture of acid and water from the 100 cm^3 beaker to the **FA 1** in the plastic cup.
- Stir carefully and measure the highest temperature obtained.
- Record this temperature in the table.
- Rinse the plastic cup with water.
- Repeat the experiment using 25 cm^3 of **FA 2**, 30 cm^3 of distilled water and 10.0 cm^3 of **FA 1** as shown for experiment **2** in the table.
- Carry out experiments **3** to **7** in the same way.
- Complete the table for each experiment.

Results

experiment number	1	2	3	4	5	6	7
volume of **FA 2** / cm^3	25	25	25	25	25	25	25
volume of water / cm^3	35	30	25	20	15	10	5
volume of **FA 1** / cm^3	5.0	10.0	15.0	20.0	25.0	30.0	35.0
initial temperature of acid mixture / °C	26.5	26.5	26.5	26.5	26.5	26.5	26.5
highest temperature / °C	29.5	32.0	34.5	37.5	37.5	37.5	42.5
temperature change / °C	3.0	5.5	8.0	11.0	11.0	11.0	16.0

[7]

I	✓
II	✓
III	✗
IV	✓
V	✓
VI	✓
VII	✓

8.0 11.0

Examiner comment – grade C

Much of this answer was very good and many candidates gaining a grade C were equally competent in this section. A mark was lost owing to the much higher temperature rise in experiment 7. The candidate would have benefited from repeating it.

Example candidate response – grade E

1 You are to determine the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide and also the concentration of the aqueous sodium hydroxide. These can be found by measuring the temperature change when solutions of the acid and alkali are mixed.

For Examiner's Use

FA 1 is aqueous sodium hydroxide, NaOH.
FA 2 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

(a) Method

- Fill a burette with **FA 1**. **[Care: FA 1 is corrosive]**
- Support the plastic cup in a 250 cm^3 beaker.
- Use a measuring cylinder to transfer 25 cm^3 of **FA 2** into a 100 cm^3 beaker.
- Use a measuring cylinder to add 35 cm^3 of distilled water to the acid in the beaker.
- Measure and record, in the table below, the initial temperature of the mixture in the beaker.
- Run 5.0 cm^3 of **FA 1** from the burette into the plastic cup.
- Add the mixture of acid and water from the 100 cm^3 beaker to the **FA 1** in the plastic cup.
- Stir carefully and measure the highest temperature obtained.
- Record this temperature in the table.
- Rinse the plastic cup with water.
- Repeat the experiment using 25 cm^3 of **FA 2**, 30 cm^3 of distilled water and 10.0 cm^3 of **FA 1** as shown for experiment **2** in the table.
- Carry out experiments **3** to **7** in the same way.
- Complete the table for each experiment.

Results

experiment number	1	2	3	4	5	6	7
volume of **FA 2** / cm^3	25	25	25	25	25	25	25
volume of water / cm^3	35	30	25	20	15	10	5
volume of **FA 1** / cm^3	5.0	10.0	15.0	20.0	25.0	30.0	35.0
initial temperature of acid mixture / °C	19	19	19	19	19	19	19
highest temperature / °C	23	25	27	29	28	28	28
temperature change / °C	4	6	8	10	9	9	9

[7]

7 11

δ= 1.0 1.0

I	X
II	✓
III	✓
IV	✓
V	X
VI	✓
VII	X

4/7

Examiner comment – grade E

In this answer the candidate needed to show more precision in the thermometer readings and the experimental results differed from those of the Supervisor. Although there was no change in temperature rise in the final three experiments they were 1.0 °C lower than the maximum, which should not have occurred as the same number of moles of water would have been formed.

Question 1(b)

(b) On the grid below plot the temperature **change** (*y*-axis) against the volume of **FA 1** (*x*-axis). Using these points, draw two straight lines that intersect.

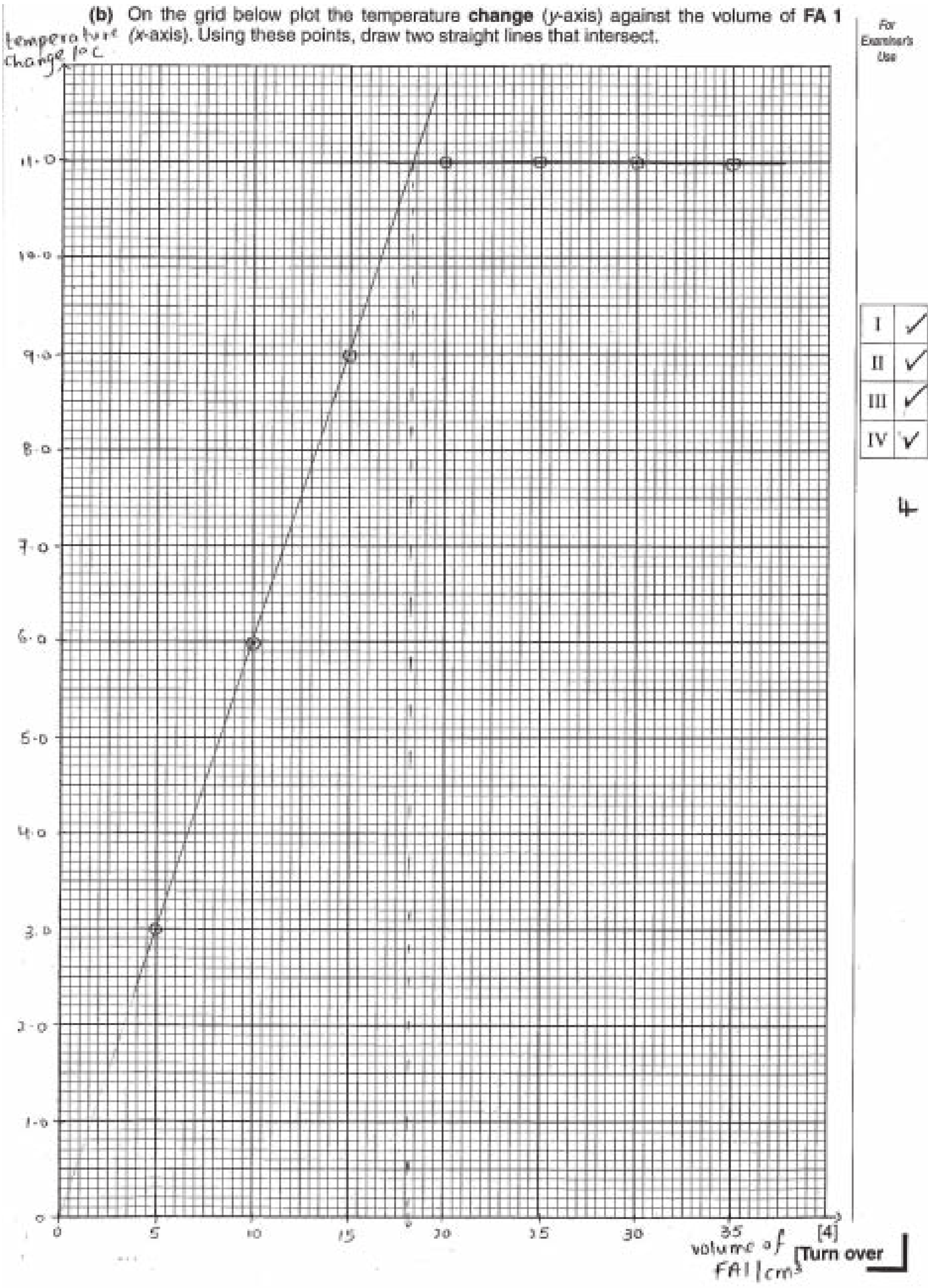
Mark scheme

(b)	PDO Layout	I	Axes correct and labelled: temperature change/ T change/ΔT and volume/vol/V (of) sodium hydroxide/NaOH/**FA 1** **and** correct units /°C or (°C) or 'in °C'; /cm^3 or (cm^3) (allow NaOH in cm^3)	1	
		II	Scales chosen so that graph occupies at least half the available length for *x*- and *y*-axes.	1	
		III	Plotting – all points accurate to within half a small square and in the correct square.	1	
		IV	Draws two straight lines of best fit which intersect.	1	[4]

General comment

A large majority of candidates chose scales so that at least half the available squares were used, and plotted all points correctly. However, some chose difficult scales so that plotting and then reading the intercept was difficult for both candidate and examiner. A few did not label the axes or did not record units in any of the forms specified in the syllabus. The mark most commonly withheld was for the two best fit intersecting straight lines: a number of candidates left more points to one side of the line than the other. The use of (0,0) may have assisted some candidates to improve the line for the increase in temperature rise. If candidates realise that one of their results is anomalous they should circle or otherwise indicate this decision on the graph so that the point is not considered by examiners when awarding marks for best fit lines.

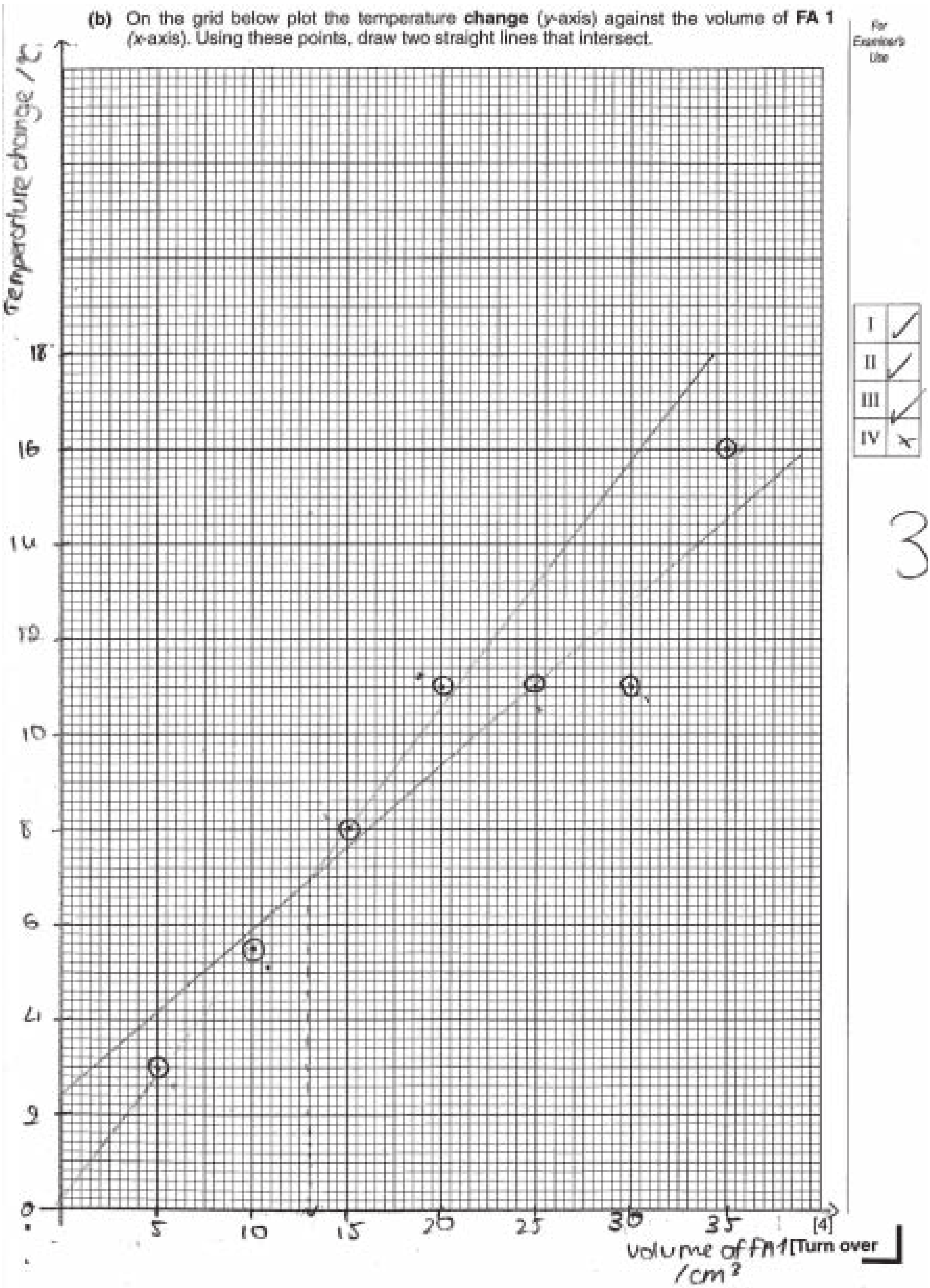
Example candidate response – grade A



Examiner comment – grade A

This excellent answer is typical of many grade A and B candidates. The drawing of a best fit line with positive gradient was made easier by obtaining excellent experimental results.

Example candidate response – grade C



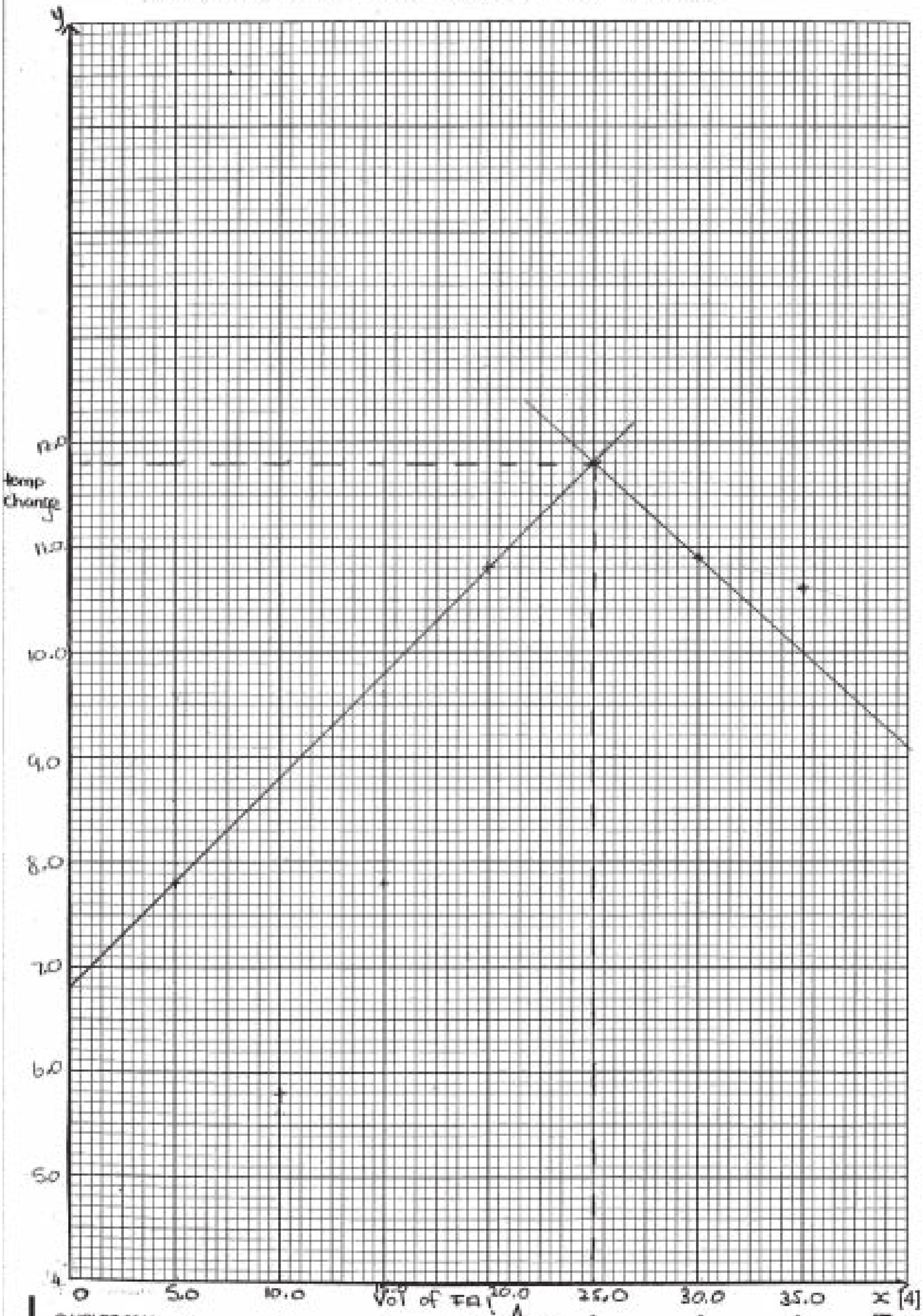
Examiner comment – grade C

Had the anomalous result for experiment 7 been circled or labelled, and omitted from any attempt at a best fit line, the candidate may have been awarded full marks on this section. The line with the higher gradient is almost one of best fit: the candidate would have benefited from using (0,0) and ensuring points were lying either side of the line in equal measure. The line with the smaller gradient is one of best fit but the points are a long way off the line and the constant temperature rise portion has not been recognised.

Example candidate response – grade E

(b) On the grid below plot the temperature **change** (*y*-axis) against the volume of **FA 1** (*x*-axis). Using these points, draw two straight lines that intersect.

For Examiner's Use



[4]

I	X
II	✓
III	✓
IV	X

2 ✓

© UCLES 2011 9701/33/O/N/11 [Turn over

Examiner comment – grade E

The labels for the axes, though correctly placed, do not include units. Both 'best fit' lines have points lying to one side only. By starting the scale at 4.0 °C it was not possible for the candidate to use (0,0).

Question 1(c) and 1(d) – using the graph

(c) Reading from the intersection of the two lines on your graph,

the volume of **FA 1** is .... cm^3,

the temperature change is .... °C. [1]

The volume of **FA 1** at the intersection represents the volume of **FA 1** which neutralised 25.0 cm^3 of **FA 2**.

(d) The reaction between **FA 1** and **FA 2** is shown in the equation below.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This reaction is exothermic.

Use this information to explain the shape of the graph.

....

....

....

.... [2]

Mark scheme

(c)	ACE Interpretation	Reads to nearest ½ square to 1 or 2 dp volume of **FA 1** and temperature rise from intercept. Do **not** award if ΔT at intercept (or point) < max ΔT from table unless candidate has clearly indicated the max ΔT is anomalous.	1	[1]

(d)	ACE Conclusions	**I** The temperature/temperature change increases as **more** reaction/more hydrochloric acid/sodium hydroxide reacts/as more water formed. **II** The temperature/temperature change stays constant/decreases when all acid/limiting reagent has reacted/excess NaOH is added.	1 1	[2]

General comment

Question 1(c)

The most common error in this section was that candidates did not show they had read the intercept to the nearest half square as many answers were given as whole numbers. Some candidates were unable to score the mark as the intercept was less than the maximum temperature rise recorded. However, there were many candidates who correctly gave the values of temperature change and volume to the level of precision shown in the graph.

Question 1(d)

Relatively few candidates gained both marks as the responses tended to describe the shape of the graph or the temperature rise without relating it to any reaction between the acid and alkali. More candidates gained the second mark which involved identifying that excess alkali was being added. A small minority of candidates wrote about bond breaking and making without specifying that more water was formed in successive experiments (until all the limiting reagent had reacted). Very few answered the question incorrectly in terms of equilibria or kinetics.

Example candidate response – grade A

(c) Reading from the intersection of the two lines on your graph,

the volume of **FA 1** is ....20.0.... cm^3,

the temperature change is ..11.0.. °C. ✓ [1]

The volume of **FA 1** at the intersection represents the volume of **FA 1** which neutralised $25.0\,cm^3$ of **FA 2**.

(d) The reaction between **FA 1** and **FA 2** is shown in the equation below.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This reaction is exothermic.

Use this information to explain the shape of the graph.

Since the reaction is exothermic, when the volume of FA1 increases, the temperature rise also increase. But when the minimum volume of FA1 needed to neutralise FA2 is reached, the temperature rise remains constant. [2]

Examiner comment – grade A

(c) The intersection was read correctly and the values recorded to the expected level of precision.

(d) The second mark was awarded as the answer incorporated the ideas of excess **FA 1**, neutralisation and constant temperature rise.

Example candidate response – grade C

(c) Reading from the intersection of the two lines on your graph,

the volume of **FA 1** is .....25...... cm^3,

the temperature change is ....10.... °C. [1]

The volume of **FA 1** at the intersection represents the volume of **FA 1** which neutralised 25.0 cm^3 of **FA 2**.

(d) The reaction between **FA 1** and **FA 2** is shown in the equation below.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This reaction is exothermic.

Use this information to explain the shape of the graph.

When 25 cm^3 of NaOH was added to the solution the (greatest temperature rise) temperature rise of 10 °C. As the volume of NaOH increased the temperature rise also increased. Then the temperature change decreased. This occurred due to bonds being formed. [2]

Examiner comment – grade C

(c) This answer lacked the precision expected from reading values from the graph.

(d) There was no explanation of the positive gradient line in terms of increasing rise in temperature and volume of alkali reacting. The link between bond making and the temperature change decreasing was not logical.

Example candidate response – grade E

(c) Reading from the intersection of the two lines on your graph,

the volume of **FA 1** is ...17.5... cm^3,

the temperature change is ...9... °C. X [1]

The volume of **FA 1** at the intersection represents the volume of **FA 1** which neutralised 25.0 cm^3 of **FA 2**.

(d) The reaction between **FA 1** and **FA 2** is shown in the equation below.

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

This reaction is exothermic.

Use this information to explain the shape of the graph.

Temperature increased slowly because not all the Hcm^3 of HCL had been neutralised. ^ ^ [2]

Examiner comment – grade E

(c) The mark was not awarded as the reported temperature change was not to the expected level of precision although the volume was correct. Also the maximum temperature change had not been considered.

(d) The answer was partly correct but was not sufficiently developed to gain a mark. With two marks allocated to a question, candidates should aim to make two points in their answers. There was no comment made about the horizontal line portion of the graph.

Question 1(e)–(g)

(e) Calculate the amount of heat energy produced in the reaction. Use the temperature change from **(c)** in calculating your answer.

[Assume that 4.3 J are required to raise the temperature of 1 cm^3 of any solution by 1 °C]

heat energy produced = ... J [2]

(f) Calculate how many moles of hydrochloric acid are present in 25 cm^3 of **FA 2**.

mol of hydrochloric acid = ... [1]

(g) Use your answers to **(e)** and **(f)** to calculate the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide.

Give your answer in $kJ\,mol^{-1}$ and include the relevant sign.

Mark scheme

(e)	ACE Interpretation	I	Volume used in calculation is 65 cm^3	1	
		II	Heat energy change calculated using candidate's value for ΔT correct to 3 or 4 sf	1	[2]
(f)	ACE Interpretation		$\frac{25 \times 2}{1000}$ = **0.05**	1	[1]
(g)	ACE Interpretation	I	$\frac{\text{Candidate's answer to (e)}}{\text{Candidate's answer to (f)}}$	1	
	PDO Display	II	Correct calculation, conversion J to kJ and negative sign to 3 or 4 sf	1	[2]

General comment

Question 1(e)

The most common error in this section was using a volume other than 65 cm^3 in the calculation. However, the majority of candidates were able to gain the second mark for the calculation although some gave the answer to an excessive number of significant figures.

Question 1(f)

This section was correctly answered by almost all candidates.

Question 1(g)

Most candidates were able to gain the first mark. However, some could not be awarded the second mark owing to an inappropriate number of significant figures, no conversion of J to kJ, or, more commonly, writing ΔH or + for the sign.

Example candidate response – grade A

(e) Calculate the amount of heat energy produced in the reaction. Use the temperature change from **(c)** in calculating your answer.

[Assume that 4.3 J are required to raise the temperature of 1 cm^3 of any solution by 1 °C]

Energy = $mc\Delta T$
= 65 × 4.3 × 10.7
= 2990.65
= 2990 J (3 s.f.)

heat energy produced = ...2990..... J [2]

(f) Calculate how many moles of hydrochloric acid are present in 25 cm^3 of **FA 2**.

1000 cm^3 of FA2 contains 2.00 mol of HCl
25 cm^3 ———— $\frac{25 \times 2.00}{1000}$ = 0.05 mol

mol of hydrochloric acid = ...0.05..... [1]

(g) Use your answers to **(e)** and **(f)** to calculate the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide.

Give your answer in kJ mol^{-1} and include the relevant sign.

0.05 mol of HCl releases 2.99065 kJ
1 mol ———— $\frac{1 \times 2.99065}{0.05}$
= 59.813
= 59.8 (3 s.f.)

enthalpy change of neutralisation = ...–... (sign) ...59.8... (value) kJ mol^{-1} [2]

Examiner comment – grade A

These answers were clearly set out, using all the correct data, and correcting to a suitable number of significant figures in **(e)** and **(g)**. The value of the heat energy produced used in **(g)** had already been converted into kJ in the first step which was an acceptable alternative to the working shown in the mark scheme.

Example candidate response – grade C

(e) Calculate the amount of heat energy produced in the reaction. Use the temperature change from **(c)** in calculating your answer.

[Assume that 4.3 J are required to raise the temperature of 1 cm^3 of any solution by 1 °C]

1cm^3 = 1g Q = mc ΔT

= 50 x 4.3 x 10 = 2150J

X

✓ecf

heat energy produced = ...2150........ J [2]

(f) Calculate how many moles of hydrochloric acid are present in 25 cm^3 of **FA 2**.

2.00 mol = 1000cm^3

? = 25

$\frac{25 \times 2}{1000}$ = 0.05 mol

✓

mol of hydrochloric acid = ...0.05mol. [1]

(g) Use your answers to **(e)** and **(f)** to calculate the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide.

Give your answer in kJ mol^{-1} and include the relevant sign.

$\frac{2150 \times 1}{0.05}$ = $\frac{43,000J}{1000}$ = 43KJ

✓

enthalpy change of neutralisation = ...–.... ....43.... X kJ mol^{-1}

sign *value* [2]

sf

Examiner comment – grade C

The use of an incorrect total volume of solution heated was a common error in **(e)** (the volume of water was omitted). Showing working is important when carrying out calculations as 'error carried forward' marks can be awarded. This was evident in the second part of **(e)** and the first part of **(g)**. The final answer was only given to two significant figures.

Example candidate response – grade E

(e) Calculate the amount of heat energy produced in the reaction. Use the temperature change from **(c)** in calculating your answer.

[Assume that 4.3 J are required to raise the temperature of 1 cm³ of any solution by 1 °C]

1 cm³ → 4.3 J by 1°C

(25 + 17.5) cm³ → 4.3 J × (25 + 17.5) J by 1°C

1°C → 182.75

9°C → $\frac{182.75 \times 9}{1}$ = 1,644.75

× sf

heat energy produced = 1,644.75 J [2]

(f) Calculate how many moles of hydrochloric acid are present in 25 cm³ of **FA 2**.

1000 cm³ of HCl reacted with 2 moles of FA 2

25 cm³ → $\frac{2}{1000} \times 25$

= 0.05

✓

mol of hydrochloric acid = 0.05 [1]

(g) Use your answers to **(e)** and **(f)** to calculate the enthalpy change of neutralisation of hydrochloric acid by aqueous sodium hydroxide.

Give your answer in kJ mol⁻¹ and include the relevant sign.

0.05 mol of HCl envolved $\frac{1,644.75}{1000}$ KJ

1 mol of HCl will envolve $\left(\frac{1,644.75}{1000} \times \frac{1}{0.05}\right)$ ✓

enthalpy change of neutralisation = ... (sign) 32.895 (value) kJ mol⁻¹ [2]

Examiner comment – grade E

Again, the volume of water added was not used in the first step of **(e)**. The final answers to both **(e)** and **(g)** were given to too many significant figures, and the latter was also missing the negative sign.

Question 1(h)

(h) Explain why the **total** volume of solution used was kept constant in each of the experiments.

....

....

.... [1]

Mark scheme

(h)	ACE Conclusions	So that rise in temperature is proportional to increase in energy produced/change in volume gives different change in temperature for same energy produced/ increase in volume requires increase in energy for same temperature rise.	1	[1]

General comment

The majority of candidates did not appear to understand this question and answered in terms of fair testing, keeping the concentration constant or other responses commonly associated with kinetics experiments. However, there were a few excellent answers where the candidates clearly linked temperature rise to energy produced. The three example candidate responses show typical errors which were made. The grade refers to the overall grade the candidate received for the whole paper.

Example candidate response – grade A

(h) Explain why the **total** volume of solution used was kept constant in each of the experiments.

To ensure uniform distribution of heat during each experiment ✗

.... [1]

Examiner comment – grade A

While this answer involved 'heat' the link between temperature rise and heat energy produced was not made.

Example candidate response – grade C

(h) Explain why the **total** volume of solution used was kept constant in each of the experiments.

Since the volume of solution is directly proportional
to the concentration of the ~~subs~~ solutions used, the concentration of
volume should be kept constant so as not to change the the solutions. [1]

Examiner comment – grade C

This answer was typical of many as, while chemically correct, it only involved the relationship of concentration with volume.

Example candidate response – grade E

(h) Explain why the **total** volume of solution used was kept constant in each of the experiments.

~~so we can vary~~

so no. of moles in the solution were kept constant.

[1]

Examiner comment – grade E

This answer was incorrect and did not involve temperature rise and heat energy.

Question 1(i)

(i) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide, **FA 1**.

concentration of **FA 1** = ... mol dm^{-3} [2]

Mark scheme

(i)	PDO Display	I	Number moles NaOH = number moles HC*l* (stated or clearly shown)	1	
	ACE Interpretation	II	Calculates or expression for Concentration = <u>0.05 (ecf from (f))</u> / answer to **(c)**/1000 If answer only, award mark if correct to 3 or 4 sf	1	[2]

General comment

Many candidates gained both marks in this section though a significant number did not specify the mole ratio of the reactants which was an essential part of their working.

Example candidate response – grade A

(i) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide, **FA 1**.

From eqation HCl : NaOH ✓ ∴ concentration = 2.74 mol dm^{-3}

1 : 1

0.050 : 0.050

18.25 cm^3 of FA1 → 0.05 moles

1000 cm^3 of FA1 → $\frac{0.05}{18.25} \times 1000$ = 2.74 moles

concentration of **FA 1** = ...2.74... mol dm^{-3} ✓ [2]

Examiner comment – grade A

Although the word mole was not used, the ratio was clearly shown, and the expression and calculation were fully correct.

Example candidate response – grade C

(i) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide, **FA 1**.

Since 1 mole of HCl reacts with 1 mole of NaOH ✓

∴ 0.05 moles of NaOH are in 1 dm^3

∴ <u>Concentration in mol dm^{-3}</u> is 0.05 mol dm^{-3}

concentration of **FA 1** = ...0.05 X... mol dm^{-3} [2]

Examiner comment – grade C

The mole ratio was clearly presented. However, no working was shown for the second mark. Additionally, the answer given for the concentration of **FA 1** was incorrect and was not shown to a suitable number of significant figures.

Example candidate response – grade E

(i) Calculate the concentration, in mol dm^{-3}, of the aqueous sodium hydroxide, **FA 1**.

$$\text{conc.} = \frac{\text{no. of moles}}{\text{volume used}}$$

$$= \frac{0.05}{25} = 2\times10^{-3}\ \text{mol/dm}^3$$

concentration of **FA 1** = ...2×10^{-3}...... mol dm^{-3} [2]

Examiner comment – grade E

The mole ratio was not displayed and, while the volume from **(c)** was used in the calculation, the step to change the unit of volume from cm^3 to dm^3 was omitted.

Question 1(j)

(j) A student thought that the experiment was not accurate because the temperature changes measured were small.

Suggest a modification to the experimental method used in order to give larger changes in temperature.

....

.... [1]

Mark scheme

(j)	ACE Improvements	Use more **concentrated** solutions. (allow use ≤ **5** cm^3 water each time) Ignore all references to heat energy losses.	1	[1]

General comment

Only a minority of candidates gained this mark. The majority suggested increasing volumes of reagents, increasing the concentration of just one of the reagents, or gave methods of reducing heat energy losses. As in **1(h)** the three example candidate responses show typical errors which were made. The grade refers to the grade the candidates received for the whole paper.

Example candidate response – grade A

(j) A student thought that the experiment was not accurate because the temperature changes measured were small.

Suggest a modification to the experimental method used in order to give larger changes in temperature.

I would try to titrate HCl with a bigger concentration of NaOH like 4-M ^ .... [1]

Examiner comment – grade A

This answer was partly correct as the need for greater concentration was recognised. However, both solutions would need to have greater concentrations.

Example candidate response – grade C

(j) A student thought that the experiment was not accurate because the temperature changes measured were small.

Suggest a modification to the experimental method used in order to give larger changes in temperature.

A thermometer which can measure temperature to two decimal places can be used. X .... [1]

Examiner comment – grade C

This answer did not address the question as the same temperature rise would have occurred though it might have been recorded to a greater degree of precision.

Example candidate response – grade E

(j) A student thought that the experiment was not accurate because the temperature changes measured were small.

Suggest a modification to the experimental method used in order to give larger changes in temperature.

By not adding any distilled water. X

.... [1]

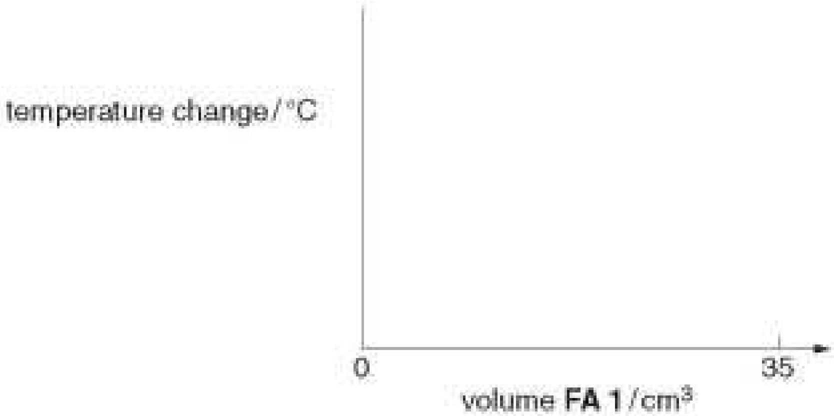
Examiner comment – grade E

Here again there was some understanding shown that greater concentrations would be required. However, more detail of the modification was necessary as the total volume of solution would not have been constant.

Question 1(k)

(k) Experiments **1** to **7** were repeated using 1.00 mol dm^{-3} sulfuric acid, H_2SO_4, instead of the 2.00 mol dm^{-3} hydrochloric acid, HCl.

On the axes below indicate an appropriate temperature scale and sketch the graph for the temperature changes you would expect.



[2]

Mark scheme

(k)	ACE Conclusions	I	Two straight intersecting lines (positive followed by zero gradient).	1	
		II	Same ΔT and V shown as in **(b)**.	1	[2]

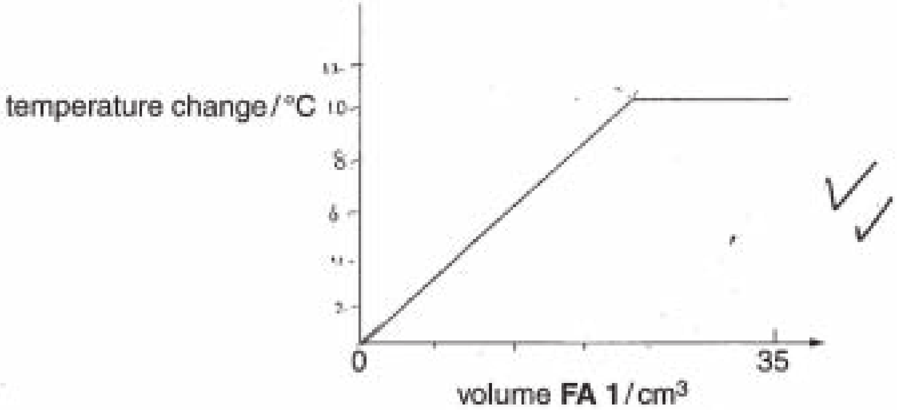
General comment

The majority of candidates gained the first mark in this section though a variety of responses were seen by Examiners including a few curves. Fewer gained the second mark either because there was no temperature scale shown or the intercept was not at the same values as those in **(b)**.

Example candidate response – grade A

(k) Experiments **1** to **7** were repeated using 1.00 mol dm^{-3} sulfuric acid, H_2SO_4, instead of the 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

On the axes below indicate an appropriate temperature scale and sketch the graph for the temperature changes you would expect.



[2]

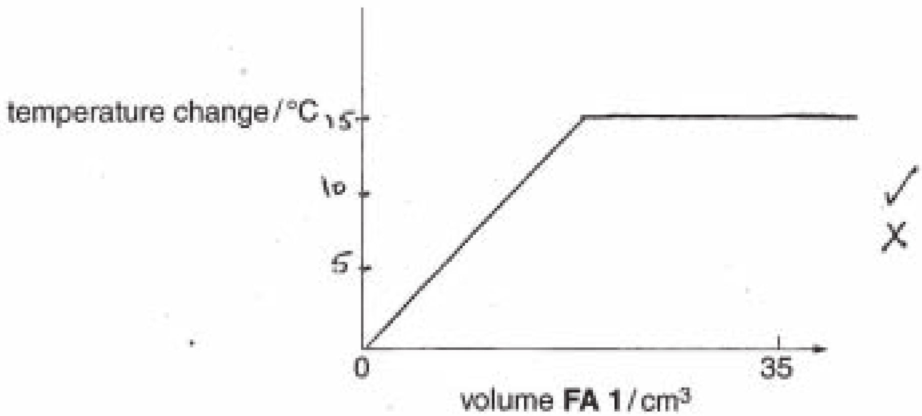
Examiner comment – grade A

This sketch showed the two lines with gradients similar to those in **(b)** and with the appropriate temperature change scale shown in detail.

Example candidate response – grade C

(k) Experiments **1** to **7** were repeated using 1.00 mol dm^{-3} sulfuric acid, H_2SO_4, instead of the 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

On the axes below indicate an appropriate temperature scale and sketch the graph for the temperature changes you would expect.



[2]

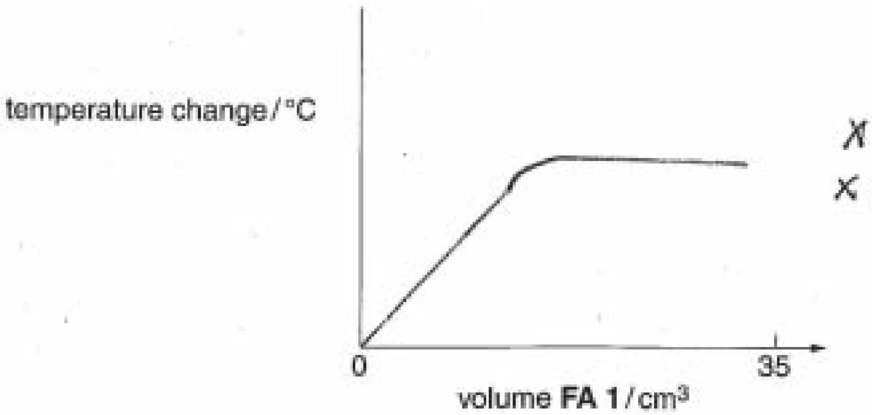
Examiner comment – grade C

The sketch of the two lines was clear and correct. However, the value for the temperature change in **(c)** was 9.0 °C , so the scale on the *y*-axis was incorrect. This implied that the information in the stem of the question allowing the concentration of hydrogen ions to be found had not been correctly used.

Example candidate response – grade E

(k) Experiments **1** to **7** were repeated using 1.00 mol dm^{-3} sulfuric acid, H_2SO_4, instead of the 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

On the axes below indicate an appropriate temperature scale and sketch the graph for the temperature changes you would expect.



[2]

Examiner comment – grade E

Lines with similar gradients to those in **(b)** were drawn but they were not intersecting. There was no scale shown on the *y*-axis.

Question 2(a)

For Examiner's Use

2 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the full name or correct formula of the reagents must be given.

(a) You are provided with three sodium salts **FA 3**, **FA 4** and **FA 5**. Each salt contains **one** of the ions carbonate, CO_3^{2-}, sulfite, SO_3^{2-} or sulfate, SO_4^{2-}.

(i) Using your knowledge of the reactions of these ions, suggest **one** reagent you could add to the solid to find out which ion is present in each of the solids.

....

(ii) Use the reagent you selected in **(i)** to identify which of these ions is present in **FA 3**, **FA 4** and **FA 5**.

Carry out suitable tests on a small amount of each solid and record the results of your experiments in an appropriate form in the space below.

I	
II	
III	
IV	
V	
VI	

Identify the anions in **FA 3**, **FA 4** and **FA 5**.

FA 3 contains the .... ion.

FA 4 contains the .... ion.

FA 5 contains the .... ion. [6]

Mark scheme

FA 3 is $Na_2S_2O_5(s)$; **FA 4** is $Na_2CO_3(s)$; **FA 5** is $Na_2SO_4(s)$; **FA 6** is $Pb(NO_3)_2(s)$ and (aq)				
2 **(a)**	MMO Decisions	(i) I Any named mineral acid or formula or (acidified) potassium dichromate Do **not** allow any reagent suitable for testing cations or more than one reagent.	1	
	PDO Recording	(ii) II Tabulates evidence of 3 tests carried out with no repeat headings. **Only** consider observations with acid or dichromate.	1	
	MMO Collection	III Bubbles/effervescence in **FA 4**.	1	
		IV Slower effervescence in **FA 3** than **FA 4** or **FA 3** turns green **and FA 5** stays orange if dichromate used.	1	
	MMO Decisions	V Appropriate test with positive result used to test for either gas.	1	
	ACE Conclusions	VI All three ions correct from suitable observations. **FA3** is a sulfite. **FA4** is a carbonate. **FA5** is a sulfate. (or correct formulae)	1	[6]

General comment

(a) **(i)** Most candidates selected a suitable reagent with few choosing other than a named mineral acid.

(ii) A large majority set out an appropriate table for their observations and were able to access at least one mark for observations. It is important that candidates appreciate the difference between an observation, ‘effervescence’ and an inference, ‘gas is evolved’. Not all of those using acid as their reagent went on to test the gas(es) produced which meant that there was insufficient evidence for the identification of the anions. However, the most discerning candidates reported the difference in the rate of effervescence when using acid with **FA 3** and **FA 4**.

Example candidate response – grade A

use

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations**.

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the full name or correct formula of the reagents must be given.

(a) You are provided with three sodium salts **FA 3**, **FA 4** and **FA 5**. Each salt contains **one** of the ions carbonate, CO_3^{2-}, sulfite, SO_3^{2-} or sulfate, SO_4^{2-}.

(i) Using your knowledge of the reactions of these ions, suggest **one** reagent you could add to the solid to find out which ion is present in each of the solids.

Dilute hydrochloric acid. ✓

(ii) Use the reagent you selected in **(i)** to identify which of these ions is present in **FA 3**, **FA 4** and **FA 5**.

Carry out suitable tests on a small amount of each solid and record the results of your experiments in an appropriate form in the space below.

Test	Observation with		
	FA 3	FA 4	FA 5
To a portion of the salt, Add 1 cm³ of dilute hydrochloric acid.	A pungent smelling gas is evolved. The gas is SO_2	Rapid effervescence is observed. A gas turning lime water milky is evolved The gas is CO_2 ✓	No visible reaction with dilute HCl. ✓

Table showing results of experiment

I	✓
II	✓
III	✓
IV	✗
V	✓
VI	✓

5

Identify the anions in **FA 3**, **FA 4** and **FA 5**.

FA 3 contains the SO_3^{2-} ion.

FA 4 contains the CO_3^{2-} ion.

FA 5 contains the SO_4^{2-} ion. ✓

[6]

Examiner comment – grade A

This was a good answer including the reporting of slower effervescence in the reaction between **FA 3** and hydrochloric acid than with **FA 4**. Although the gas evolved with **FA 3** was not tested with acidified potassium dichromate, the mark for the identities could be awarded as the choking odour of the gas and the fully correct limewater test with the gas from **FA 4** were clearly reported.

Example candidate response – grade C

2 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the full name or correct formula of the reagents must be given.

(a) You are provided with three sodium salts **FA 3**, **FA 4** and **FA 5**. Each salt contains **one** of the ions carbonate, CO_3^{2-}, sulfite, SO_3^{2-} or sulfate, SO_4^{2-}.

(i) Using your knowledge of the reactions of these ions, suggest **one** reagent you could add to the solid to find out which ion is present in each of the solids.

Add nitric acid to the salt containing CO_3^{2-} ✓
effervescence should be observed and CO_2 released

(ii) Use the reagent you selected in **(i)** to identify which of these ions is present in **FA 3**, **FA 4** and **FA 5**.

Carry out suitable tests on a small amount of each solid and record the results of your experiments in an appropriate form in the space below. ✓

	FA3	FA4	FA5
~~OBSERVATION WITH HNO_3~~	effervescence produced ✓ bubbles of gas observed. The gas SO_2 ~~turns limewater milky white produced~~	Reacts vigorously effervescence produced. A gas which turns lime water milky white produced	~~Does not~~ A white ppt obtained when barium chloride was added. It is insoluble in excess acid

Identify the anions in **FA 3**, **FA 4** and **FA 5**.

~~**FA 3** contains the CO_3^{2-} ion.~~ FA3 contains the SO_3^{2-}

FA 4 contains the CO_3^{2-} ion.

FA 5 contains the SO_4^{2-} ion. [6]

Examiner comment – grade C

Most of this answer was very good as the difference in the rates of effervescence was described as well as a valid test for one of the gases. The error was in using two reagents with **FA 5** contrary to the instruction in part **(ii)**.

Example candidate response – grade E

2 Qualitative Analysis

At each stage of any test you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added

Where gases are released they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the full name or correct formula of the reagents must be given.

(a) You are provided with three sodium salts **FA 3**, **FA 4** and **FA 5**. Each salt contains **one** of the ions carbonate, CO_3^{2-}, sulfite, SO_3^{2-} or sulfate, SO_4^{2-}.

(i) Using your knowledge of the reactions of these ions, suggest **one** reagent you could add to the solid to find out which ion is present in each of the solids.

HCl ✓

(ii) Use the reagent you selected in (i) to identify which of these ions is present in **FA 3**, **FA 4** and **FA 5**.

X Carry out suitable tests on a small amount of each solid and record the results of your experiments in an appropriate form in the space below.

Test	observation
You use FA_3 you add HCl drop by drop till in excess then test gas with lime water on $Cr_2O_7^{2-}/H^+$	Gas given off. Gas turns $K_2Cr_2O_7/H^+$ from orange to green
You use FA_4 you dilute with HCl drop by drop till in excess then test gas with lime water on $Cr_2O_7^{2-}/H^+$	CO_2 given off it turns lime water milky ✓
you use FA_5 you dilute with HCl drop by drop till in excess then test gas with lime water on $Cr_2O_7^{2-}/H^+$	No change

Identify the anions in **FA 3**, **FA 4** and **FA 5**.

FA 3 contains the SO_3^{2-} ion.

FA 4 contains the CO_3^{2-} ion. ✓

FA 5 contains the SO_4^{2-} ion.

[6]

Examiner comment – grade E

A suitable reagent was selected but its formula was repeatedly recorded in the table. There was no observation recorded that would lead to the inference of gas given off and this made two marks unavailable. However, both gas tests were given and the results recorded were correct as were the identities of the sodium salts.

Question 2(b)

(b) (i) You are provided with **FA 6** both as a solid and in aqueous solution. Complete the following table.

For Examiner's Use

test	*observations*
To a small spatula measure of **FA 4** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	
To a small spatula measure of **FA 5** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	
To 1 cm depth of **FA 6** solution in a test-tube, add aqueous sodium hydroxide.	
Carefully heat the solid **FA 6** in the test-tube provided. Note: **two** gases are released.	

I	
II	
III	
IV	
V	
VI	

[6]

(ii) From the results of the tests in **(i)**, identify the cation present in **FA 6**.

Cation present in **FA 6** is .... [1]

(iii) Suggest and use another reagent to confirm the cation present in **FA 6**.

reagent ....

observation..[2]

[Total: 15]

Mark scheme

(b)	MMO Collection	(i) I **FA 4** + **FA 6** white ppt **and** **FA 5** + **FA 6** white ppt. II **FA 6** + NaOH white ppt, soluble in excess sodium hydroxide. III Brown gas IV Gas relights glowing splint. V Yellow residue or crackling/decrepitating.	1	
	ACE Conclusions	VI Gas identified as oxygen or as NO_2 from observations.		[6]
	ACE Conclusions	(ii) Lead/Pb^{2+} provided correct observations with **FA 6** + NaOH **and** **FA 6** + **FA 5** (sulfate).	1	[1]
	MMO Decisions	(iii) I Add HCl / H_2SO_4 / KI / K_2CrO_4 / NH_3*	1	
	MMO Collection	II white ppt/white ppt/yellow ppt/yellow ppt/white ppt insoluble in excess. * If not Pb^{2+} in **(ii)** but one of Al^{3+}, Ba^{2+}, Ca^{2+}, Zn^{2+} allow suitable reagent mark: K_2CrO_4 for Ba^{2+} and NH_3 for the other three. However, observation must be correct for $\mathbf{Pb^{2+}}$.	1	[2]

General comment

(b) (i) The majority of candidates were able to gain at least two marks in this section. The most commonly awarded marks were for the two white precipitates in the first two steps and the white precipitate soluble in excess aqueous sodium hydroxide. However, there are still candidates who report 'white solution' or 'cloudy white' instead of 'white precipitate'. The heating section was not as familiar to candidates and many possible observations were omitted. The mark most commonly awarded was for the brown gas though some were able to identify NO_2 and/or O_2 from a correct test with a positive result. The mark least awarded was for noting the solid turning yellow or for the sound made by the solid as it was heated.

(ii) Pb^{2+} was the cation most commonly identified though a few candidates did not have sufficient correct observations for this conclusion.

(iii) A large majority of candidates selected a suitable reagent, though a small number did not give its full name or formula so were unable to access the first mark. The second mark was frequently awarded as most candidates reported the correct observation for Pb^{2+} with their chosen reagent.

Example candidate response – grade A

(b) (i) You are provided with **FA 6** both as a solid and in aqueous solution. Complete the following table.

test	*observations*
To a small spatula measure of **FA 4** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	~~A white ppt was formed~~ The solid dissolves to give a colourless soln A white ppt was formed ✓
To a small spatula measure of **FA 5** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	~~A white ppt was formed~~ The solid dissolves to give a colourless soln A white ppt was formed ✓
To 1 cm depth of **FA 6** solution in a test-tube, add aqueous sodium hydroxide.	A white precipitate was formed ✓ The precipitate dissolves in excess of aqueous sodium ✓ hydroxide to give a colourless solution.
Carefully heat the solid **FA 6** in the test-tube provided. Note: **two** gases are released.	The solid decompose to give a yellow solid. ✓ A brown gas ✓ was evolved. Gas was NO_2. ✓ A second gas is evolved which bleaches damp red litmus paper. Gas was Cl_2. ✗

[6]

(ii) From the results of the tests in **(i)**, identify the cation present in **FA 6**.

Cation present in **FA 6** is ....Pb^{2+} ✓........ [1]

(iii) Suggest and use another reagent to confirm the cation present in **FA 6**.

reagent ....Dilute sulphuric acid ✓....

observation....A white precipitate was formed. ✓....[2]

Examiner comment – grade A

The observations using solutions in **(i)** are detailed and fully correct. The observations for heating solid **FA 6** were more detailed than seen in many scripts. Although NO_2 will bleach litmus paper so the inference of chlorine as the second gas is understandable, the thermal decomposition of nitrates is covered in the syllabus so should not be unfamiliar. Parts **(ii)** and **(iii)** were fully correct.

Example candidate response – grade C

(b) **(i)** You are provided with **FA 6** both as a solid and in aqueous solution. Complete the following table.

test	*observations*
To a small spatula measure of **FA 4** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	A white ppt is ~~given~~ ~~off~~ formed. ✓
To a small spatula measure of **FA 5** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	A white ppt is formed ✓
To 1 cm depth of **FA 6** solution in a test-tube, add aqueous sodium hydroxide.	A white ppt is formed but in excess of NaOH (aq) the ~~solution~~ solid dissolves and turns colourless ✓
Carefully heat the solid **FA 6** in the test-tube provided. Note: **two** gases are released.	Pop sounds are given off ✓ with a ~~blue~~ brown glow around the test tube. ~~Next~~ It turns blue litmus red.

[6]

(ii) From the results of the tests in **(i)**, identify the cation present in **FA 6**.

Cation present in **FA 6** is Pb^{2+} ✓ [1]

(iii) Suggest and use another reagent to confirm the cation present in **FA 6**.

reagent Aqueous Ammonia (NH_3 (aq)) ✓

observation White ppt [2]

Examiner comment – grade C

The formation of the white precipitates was correctly reported as was the solubility of the hydroxide precipitate in excess sodium hydroxide. ‘Pop sounds given off’ was taken to mean the heated solid was decrepitating and there was no reference to a lighted splint to indicate that it referred to a test for hydrogen gas. The ‘brown glow around the test tube’ was not sufficiently precise to be credited. ‘It’ should not be used as it is imprecise. The observations were used to correctly identify the cation in **(ii)** and the reagent selected was suitable in **(iii)**. However, use of aqueous ammonia involves testing with a small volume and then with excess and the solubility of the lead(II) hydroxide precipitate in excess ammonia was not investigated.

Example candidate response – grade E

(b) **(i)** You are provided with **FA 6** both as a solid and in aqueous solution. Complete the following table.

test	*observations*
To a small spatula measure of **FA 4** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	~~An effulate ppt is~~ solid dissolves and a ~~cream~~ colourless solution is obtained. A white ppt is obtained when FA6 is added.
To a small spatula measure of **FA 5** in a test-tube, add enough distilled water to make a solution. Add 1 cm depth of **FA 6** solution.	solid dissolves to give a colourless solution. A milky white ppt is obtained when FA6 solution is added. ✓
To 1 cm depth of **FA 6** solution in a test-tube, add aqueous sodium hydroxide.	A white ppt is produced which is soluble in excess to form a colourless solution. ✓
Carefully heat the solid **FA 6** in the test-tube provided. Note: **two** gases are released.	Pungent smell of ammonia observed An orange, brownish gas vapour is observed of SO_2. X

[6]

(ii) From the results of the tests in **(i)**, identify the cation present in **FA 6**.

Cation present in **FA 6** is Pb^{2+} ✓ [1]

(iii) Suggest and use another reagent to confirm the cation present in **FA 6**.

reagent Addition of potassium dichromate X

observation A yellow ppt is observed. ✓ [2]

Examiner comment – grade E

Again the observations for the tests on the solution of **FA 6** in **(i)** were fully correct. Candidates should be discouraged from trying to identify gases by smell; a chemical test is safer and is more likely to be credited. The colour of the gas was incorrectly reported and the identity of SO_2 was inconsistent with the observation. The identity of the cation was correct in **(ii)** but the reagent chosen in **(iii)** did not show use of the Qualitative Analysis Notes. However, the observation was correct as the solubility of lead(II) chromate is so low that the equilibrium is shifted from dichromate to chromate.

Paper 4 – Structured questions

Question 1

1 (a) Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$..

Mn^{2+}: $1s^2 2s^2 2p^6$..

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

....

....

....

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$ from .... to ....
- $K_2Cr_2O_7$ from .... to ....

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

....

....

....

(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

....

....

[4]

Mark scheme

1 **(a)** Cr^{3+}: $1s^22s^22p^6$ **$3s^2\ 3p^6\ 3d^3$** [1]
Mn^{2+}: $1s^22s^22p^6$ **$3s^2\ 3p^6\ 3d^5$** [1]
[2]

(b) (i) Any two from
- H^+ is on the oxidant/L.H. side of each of the ½-equations, *or* H^+ is a reactant
- (increasing $[H^+]$) will make $E^⦵$ more positive
- (increasing $[H^+]$) will drive the reaction over to the R.H./reductant side *or* forward direction

[1] + [1]

(ii) $KMnO_4$: Purple/violet to colourless (allow ***very*** pale pink) [1]
$K_2Cr_2O_7$ Orange to green [1]
[4]

(c) (i) $MnO_2 + SO_2 \longrightarrow MnSO_4$ (*or* $Mn^{2+} + SO_4^{2-}$) [1]

manganese changes/is reduced from +4 to +2 [1]
sulfur changes/is oxidised from +4 to +6 [1]

(ii) **No effect**, because H^+ does not appear in the overall equation *or* its effect on the MnO_2/Mn^{2+} change is cancelled out by its effect on the SO_2/SO_4^{2-} change [1]
[4]

(d) (i) $MnO_2 + 4H^+ + Sn^{2+} \longrightarrow Mn^{2+} + 2H_2O + Sn^{4+}$ [1]

(ii) $n(MnO_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4}$ mol [1]
$n(Sn^{2+}) = 3.62 \times 10^{-4} \times 5/2 = 9.05 \times 10^{-4}$ mol [1]
$n(Sn^{2+})$ that reacted with $MnO_2 = (20 - 9.05) \times 10^{-4} = 1.095 \times 10^{-3}$ mol [1]
reaction is 1:1, so this is also $n(MnO_2)$
mass of $MnO_2 = 1.095 \times 10^{-3} \times (54.9+16+16) = 0.0952$ g [1]
$\Rightarrow$ **95% – 96%**; 2 or more s.f. [1]
[6]

[Total: 16]

General comment

This question was designed to be a mostly straightforward starter question to the paper. Part **(a)** involved use of the Periodic Table; part **(b)(ii)** required simple recall and part **(d)** was a standard calculation. Parts **(b)(i)** and **(c)** required a little more thought however.

Common errors seen in scripts included the following:

- miscalculating the number of electrons in the ions in part **(a)**
- not applying le Chatelier's principle in part **(b)(i)**
- not appreciating in **(b)(ii)** the significance of the fact that the overall equation did not involve H^+
- using MnO_4^- rather than MnO_2 as the oxidant in **(d)(i)**
- calculating the percentage of Mn rather than MnO_2 in **(d)(ii)**

Example candidate response – grade A

1 (a) Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$ $3s^2\ 3p^6\ 3d^3$

Mn^{2+}: $1s^2 2s^2 2p^6$ $3s^2\ 3p^6\ 3d^4$

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$, $E^\ominus = +1.52V$ } $[H^+]\uparrow$, $E^\ominus\uparrow$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$, $E^\ominus = +1.33V$ } ∴ more reducing ∴ stronger ox. agent

As $[H^+(aq)]$ increases, by Le Chatelier's principal, equilibrium shifts to RHS as there are more ~~products~~ reactants than products.

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$ from Purple to Colourless
- $K_2Cr_2O_7$ from Orange to Green

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$, $SO_2 + 2H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$

∴ $MnO_2 + SO_2$ ~~+ 2H_2O~~ $\rightarrow Mn^{2+}$ ~~+ 2H_2O~~ $+ SO_4^{2-}$

Ox. state of Manganese reduce from +4 to +2, Ox. state of Sulfur oxidises from +4 to +6

(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

~~(Initial) Rate~~ ~~Rate of reaction would decrease~~ (Initial) Rate of reaction would decrease.

Thus ~~decolourisation~~ dissolving of MnO_2 to colourless would take longer time.

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess Sn^{2+}(aq) ions are titrated with a standard solution of $KMnO_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

The equation for the reaction between Sn^{2+}(aq) and MnO_4^-(aq) is as follows.

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution.

$MnO_2 + 4H^+ + Sn^{2+} \rightarrow Sn^{4+} + Mn^{2+} + 2H_2O$ ✓

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

  $n = cV$
  $= \overset{0.02}{\cancel{2.00 \times 10^{-3}}} \times 0.0181$
  $\therefore n = \cancel{3.62 \times 10^{-5} mol}$ 3.62×10^{-4} mol

- number of moles of Sn^{2+} this MnO_4^- reacted with

  2 mol MnO_4^- : 5 mol Sn^{2+}
  $\therefore n(Sn^{2+}) = \frac{3.62 \times 10^{-4}}{2} \times 5 = 9.05 \times 10^{-4}$ mol

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

  $n = (2.00 \times 10^{-3}) - (9.05 \times 10^{-4}) = 1.095 \times 10^{-3}$ mol
  $\cancel{1.6095 \times 10^{-3} \approx 1.91 \times 10^{-3} mol}$ $\approx 1.10 \times 10^{-3}$ mol

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

  1 mol Sn^{2+} : 1 mol MnO_2 , $\cancel{n(MnO_2) = 1.91 \times 10^{-3} mol}$
  $\therefore n = \cancel{1.91 \times 10^{-3} mol}$ 1.10×10^{-3} mol

- mass of MnO_2 in 0.100 g pyrolusite

  $\cancel{m = 1.91 \times 10}$ $n = \frac{m}{M_r}$
  $m(MnO_2) = n \times M_r = (\overset{1.10 \times 10^{-3}}{\cancel{1.91 \times 10^{-3}}}) \times (86.9)$
  $= \cancel{0.166 g}$ 0.0957 g

- percentage of MnO_2 in pyrolusite

  $\% MnO_2 = \frac{0.0957}{0.1} \times 100 = 95.7\%$

percentage = 95.7 %

[6]

Examiner comment – grade A

(a) The candidate's second thoughts for Cr^{3+} were correct; the $4s^1$ electron is removed first, and then two of the 3d electrons. For Mn^{2+}, however, the candidate removed three rather than two electrons.

(b) The correct half equations were abstracted from the *Data Booklet*, and le Chatelier's principle was applied correctly.

(c) The overall equation and the oxidation number changes for the two reactants were calculated correctly in **(i)**. However, it was not appreciated in **(ii)** that a change in pH would not affect the *extent* of reaction, because H^+ does not appear in the overall equation.

(d) This correct answer was typical of a good candidate.

Example candidate response – grade C

Cr: $1s^2 2s^2 2p^6 3s^2 3p^6$ 4s¹ 3d⁵

Mn: $1s^2 2s^2 2p^6 3s^2 3p^6$ 4s² 3d⁵

1 (a) Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$ $3s^2 3p^6 3d^3$

Mn^{2+}: $1s^2 2s^2 2p^6$ $3s^2 3p^6 3d^5$

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution. H^+

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

$Cr_2O_7^{2-}/Cr^{3+}$ $E^\ominus = +1.33$

MnO_4^-/Mn^{2+} $E^\ominus = +1.67$

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$ from colourless to purple
- $K_2Cr_2O_7$ from orange to green

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

MnO_2: $x + 2(-2) = 0$, $x = +4$

Mn

SO_2: $x + 2(-2) = 0$

SO_4^{-2}: $x + 4(-2) = -2$, $x - 8 = -2$, $x = +6$

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

$\cancel{MnO_2}$ $MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$, $E^\ominus = +1.23$.

$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$, $E^\ominus = +0.17$.

Overall equation:

$MnO_2 + SO_2 \longrightarrow Mn^{2+} + SO_4^{2-}$

Oxidation state of Mn decreases from +4 to +2.

oxidation state of S increases from +4 to +6.

(ii) The pH of the suspension of MnO_2 is reduced.

Explain what effect, if any, this would have on the extent of this reaction.

At lower pH, concentration of H^+ increases. Reaction would go forward.

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess Sn^{2+}(aq) ions are titrated with a standard solution of $KMnO_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

$2\times(MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O)$ $E^\ominus = 1.67$

$3\times(Sn^{4+} + 2e \rightleftharpoons Sn^{2+})$ $E^\ominus = +0.15$

The equation for the reaction between Sn^{2+}(aq) and MnO_4^-(aq) is as follows.

$Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$ $+0.15$

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O$ 1.23

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution. $MnO_2 + 4H^+ + Sn^{2+} \rightarrow Mn^{2+} + 2H_2O + Sn^{4+}$

~~$2MnO_4^- + 8H^+ + 3Sn^{2+} \rightarrow 2MnO_2 + 4H_2O + 3Sn^{4+}$~~

....

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

  0.02 mol : 1000 cm^3

  x : 18.1 cm^3

  $x = \frac{0.02 \times 18.1}{1000}$

  $x = 3.62 \times 10^{-4}$ mol MnO_4^-

- number of moles of Sn^{2+} this MnO_4^- reacted with

  2 mol MnO_4^- : 5 mol Sn^{2+}

  3.62×10^{-4} mol MnO_4^- : x

  $x = \frac{3.62 \times 10^{-4} \times 5}{2}$

  9.05×10^{-4}

  $x =$ ~~5.43×10^{-4}~~ mol Sn^{2+}

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

- mass of MnO_2 in 0.100 g pyrolusite

- percentage of MnO_2 in pyrolusite

percentage = ...%

[6]

Examiner comment – grade C

(a) This candidate scored full marks for correctly deducing the electronic configurations.

(b) In part **(i)** the candidate picked out the correct $E^\ominus$ values, but did not quote the half equations or use le Chatelier's principle to explain the effect of $[H^+]$ on $E^\ominus$. In part **(ii)** the colour change for $KMnO_4$ was reversed, but that for $K_2Cr_2O_7$ was correct.

(c) The overall equation and the oxidation number changes for the two reactants were calculated correctly in **(i)**. However, it was not appreciated in **(ii)** that a change in pH would not affect the *extent* of reaction, because H^+ does not appear in the overall equation.

(d) This candidate realised they had used the incorrect oxidant in **(i)**, and changed the equation accordingly. A good start was made in part **(ii)**, but the rest was left blank.

Example candidate response – grade E

1 **(a)** Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$ ~~4s~~ $3s^2\ 3p^6\ 4s^1\ 3d^5$

Mn^{2+}: $1s^2 2s^2 2p^6$ $3s^2\ 3p^6\ 4s^2\ 3d^5$

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$ $E^\ominus = +0.56$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\ominus = +1.33$

As H^+ increases ~~H⁺ will react~~ equilibrium moves to the ~~right~~ left, causing the $E^\ominus$ to become more negative or decrease.

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$ from purple to colourless
- $K_2Cr_2O_7$ from orange to green

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

$SO_2 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

$SO_2 + H_2O + MnO_2 \rightarrow SO_4^{2-} + Mn^{2+} + 2H_2O$

oxidation state of manganese decreases from +4 to −2. Oxidation state of sulfur increases from +4 to +8

(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

It will take time for solution to be colourless.

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess Sn^{2+}(aq) ions are titrated with a standard solution of $KMnO_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

The equation for the reaction between Sn^{2+}(aq) and MnO_4^-(aq) is as follows.

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution.

~~$MnO_2 + 4H^+ + Sn^{2+} \rightarrow Mn^{2+} + 2H_2O + Sn^{4+}$~~

$2MnO_2 + 4H_2O$ ~~Mn^{2+}~~ $+ 3Sn^{2+} \rightarrow 2MnO_4^- + 8H^+ + 3Sn$ ✗

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

~~$MnO_2 \rightarrow MnO_4$~~ $\quad \frac{0.100}{86.9}$ ~~$\frac{18.1}{1000} \times 0.02$~~ $\frac{18.1}{1000} \times 0.02$

$= 3.62 \times 10^{-4}$ mol ✓

- number of moles of Sn^{2+} this MnO_4^- reacted with

$5Sn^{2+} : 2MnO_4^-$

$5 : 2$

$x : 3.62 \times 10^{-4}$ $\quad x =$ ~~1.448×10^{-4} mol~~ 9.05×10^{-4} ✓

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

$5Sn^{2+} : 2MnO_2$

$5 : 2$

$x : \frac{0.1000}{86.9}$ $\quad x =$ ~~2.88×10^{-3}~~ 1.88×10^{-3} mol ✗

ecf

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

$3Sn^{2+} : 2MnO_2 \rightarrow$

$3 : 2$

$2.88 \times 10^{-3} : x$

$x = 1.92 \times 10^{-3}$ mol

$2MnO_2 :$ ~~$2MnO_4$~~

$x : \frac{0.1}{86.9}$ ~~$x = 1.15 \times 10^{-3}$ mol~~

- mass of MnO_2 in 0.100 g pyrolusite

$n = \frac{m}{Mr}$

~~$m = 1.15 \times 10^{-3} \times 86.9$~~

~~$= 0.1$~~

$m = 1.92 \times 86.9 \times 10^{-3}$

$= 0.167$ g ✓

- percentage of MnO_2 in pyrolusite

~~$\frac{0.167}{0.1} \times 100$~~ $\quad \frac{0.1}{0.167} \times 100\% = 59.9\%$

~~$\frac{0.167}{0.1} \times 100\% = 167$~~ percentage = ~~167~~ 59.9 ✗ %

[6]

Examiner comment – grade E

(a) This candidate quoted the correct electronic configurations for the unionised atoms, but did not show that forming cations involves the removal of electrons from the atoms.

(b) Both half equations needed to be correct to gain credit in **(i)**: candidates should be aware that MnO_4^- is reduced to Mn^{2+} in acidic solution. The candidate's second attempt at specifying the direction of movement of the equilibrium was incorrect. The colour changes in **(ii)** were correct.

(c) A good attempt was made to generate a balanced equation for the overall reaction in **(i)**, but the number of water molecules was not balanced. The oxidation state change for Mn should have been to +2 rather than -2, and that for S should have ended up as +6 rather than +8. The unbalanced equation in **(i)** could still have given the candidate the hint that $[H^+]$ would have no effect on the extent of reaction, but this was not observed.

(d) In part **(i)** this candidate took Sn^{2+} to be an oxidising agent rather than a reducing agent, due to their not appreciating that the reactant with the more positive $E^\ominus$ will oxidise that with the more negative $E^\ominus$. In part **(ii)** the first two lines of the calculation were correct, but in the third bullet point this candidate did not see that the number of moles of Sn^{2+} that had reacted with the pyrolusite is the number of moles first added, minus the number of moles left after the reaction. Rather, the candidate calculated the number of moles of MnO_2 in the 0.100 g of pyrolusite, assuming the pyrolusite was 100% pure MnO_2. Although the number of moles of MnO_2 was incorrectly calculated in the fourth bullet point, an error-carried-forward mark was able to be awarded for the calculation in the fifth bullet point: the multiplication of the incorrect number of moles by the correct M_r of MnO_2. Had the sixth bullet point been calculated correctly, the percentage would have been over 100%.

Question 2

For Examiner's Use

2 **(a)** **(i)** What is meant by the term *ligand* as applied to the chemistry of the transition elements?

....

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

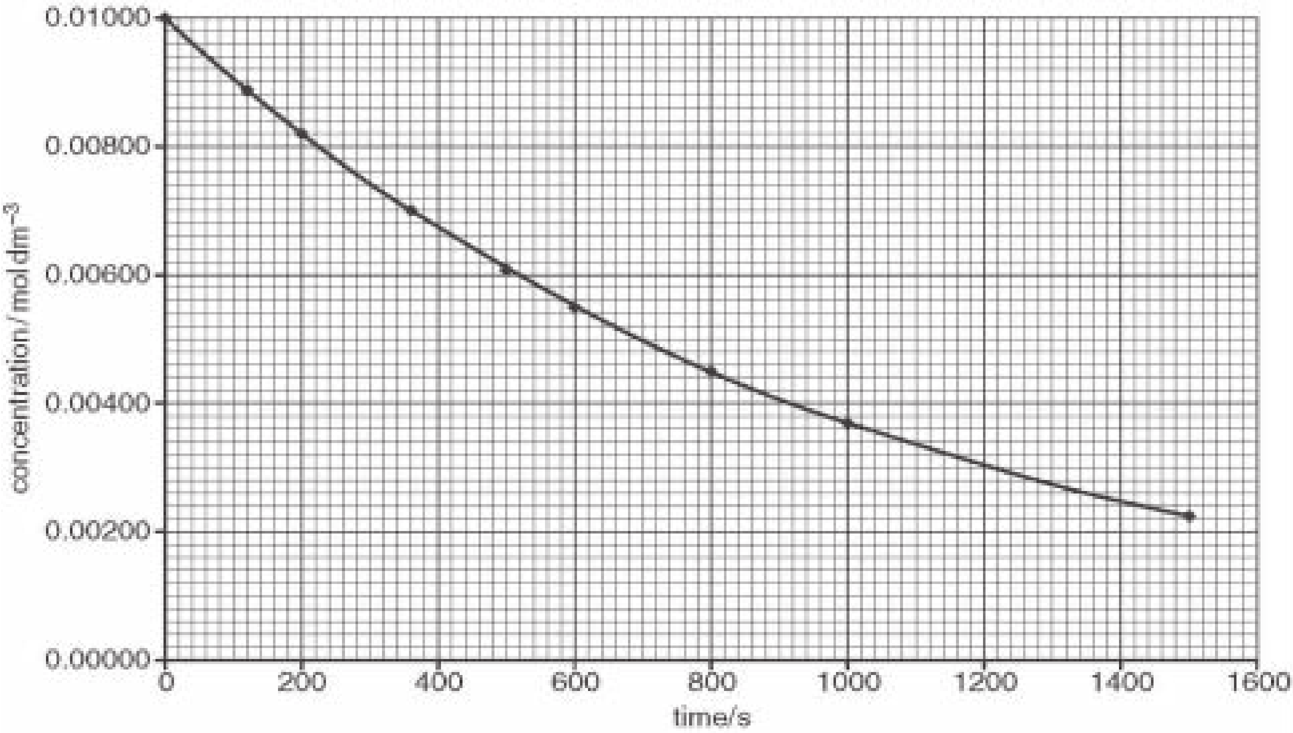
....

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time/s	$[PR_3]$/mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

....

....

PR_3

....

....

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

....

....

....

....

(iv) State the units of the rate constant.

....

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ slow

B $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast

C $Cr(CO)_6 + PR_3 \rightarrow [OC\text{---}Cr(CO)_4\text{---}PR_3] \rightarrow Cr(CO)_5PR_3 + CO$
(transition state)

D $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

....

....

[9]

[Total: 11]

Mark scheme

2 **(a)** **(i)** A molecule/ion/species with a lone pair (of electrons) *or* electron pair donor...
.... that bonds to a metal ion/transition element.... [1]

(ii) ...by means of a dative/coordinate (covalent) bond [1]
[2]

(b) **(i)** straight line from (0, 0.01) to point at (350, 0.0028) with all points on the line [1]

(ii) order w.r.t. $Cr(CO)_6$ is 1 **and** order w.r.t. PR_3 is zero [1]
because **(a)** $Cr(CO)_6$ graph has a constant half-life (which is 700 s)
or construction lines on graph showing this) [1]
because **(b)** PR_3 graph is a straight line (of constant slope) *or* line shows a constant rate of reaction *or* no change in rate *or* shows a linear decrease [1]

(iii) rate = $k[Cr(CO)_6]$ [1]

$k = \mathbf{(0.9 - 1.1) \times 10^{-3}}$ (s^{-1}) (one or more s.f.) [1]

either $rate_0 = 0.01/1020 = 9.8 \times 10^{-6}$ mol sec^{-1} when $[Cr(CO)_6] = 0.01$ mol dm^{-3}
so $k = 9.8 \times 10^{-6}/0.01 = \mathbf{9.8 \times 10^{-4}}$
or $t_{1/2} \approx 700$ sec
$k = 0.693/700 = \mathbf{9.9 \times 10^{-4}}$

(iv) (units of k are) $\mathbf{sec^{-1}}$ [1]

(v) N.B. the chosen mechanism must be consistent with the rate equation in **(iii)**. Thus:
either if rate = $k[Cr(CO)_6]$
mechanism **B** is consistent [1]
because it's the only mechanism that does NOT involve PR_3 in its slow/rate-determining step *or* only $Cr(CO)_6$ is involved in slow step *or* $[PR_3]$ does not affect the rate [1]

or

if rate = $k[Cr(CO)_6][PR_3]$, then
mechanism **A** or **C** or **D** is consistent [1]
because both reactants are involved in slow step [1]
[9]

[Total: 11]

General comment

This question involved a mixture of knowledge recall in part **(a)**, with applying knowledge of reaction rates to the analysis of a concentration-time graph in part **(b)**, along with the understanding of the relationship between mechanism and order of reaction. Many candidates scored well, and even the weaker candidates were able to pick up marks in parts **(a)** and **(b)(i)**.

Example candidate response – grade A

2 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

Ligand is an electron pair donor which forms dative bond with the central transition metal to form complex ion.

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

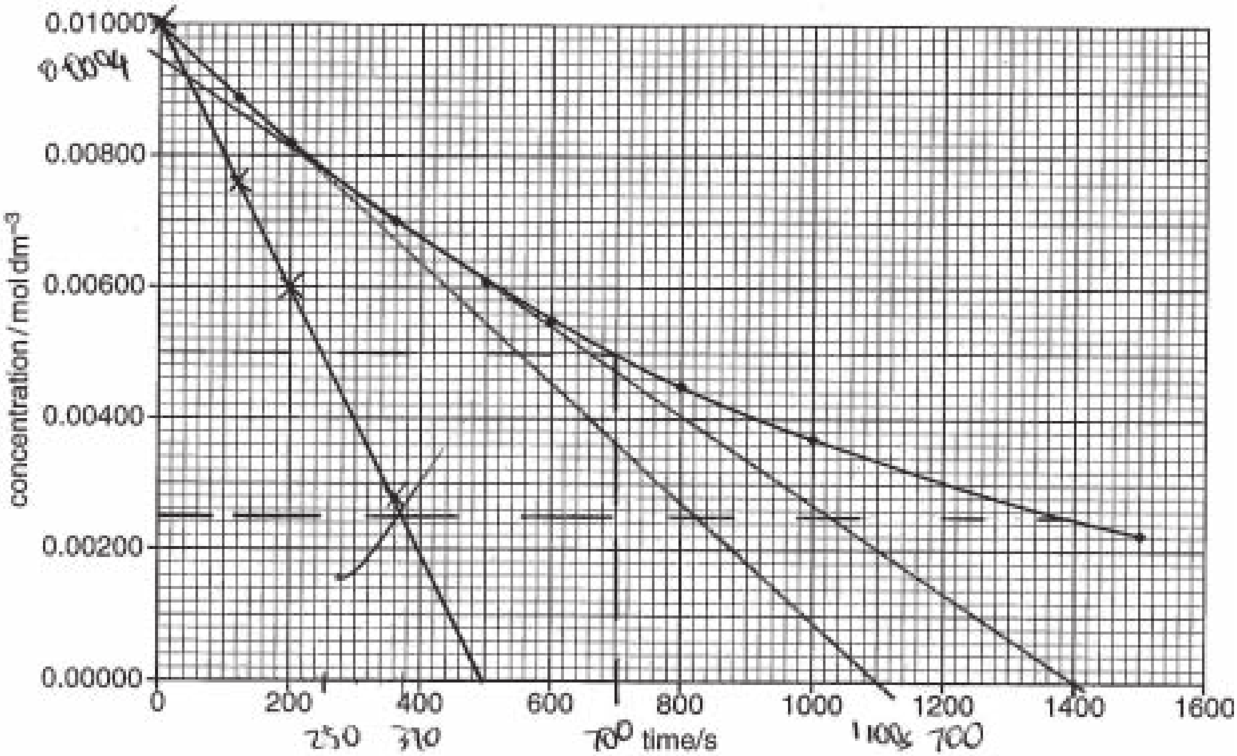
Dative bond

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction. In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

For Examiner's Use

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

It is first order with respect to $Cr(CO)_6$ because its half-life is constant which is 700s

PR_3

It is zero ~~first~~ order with respect to PR_3 because its ~~it is a straight line.~~ half-life is decreasing (from 250s to 120s).

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

$Rate = k[Cr(CO)_6]$ $Rate = \frac{0.0094 \text{ mol dm}^{-3}}{1400\text{s}} = 6.71 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$

$6.71 \times 10^{-6} = k[0.0061]$

$k = 1.1 \times 10^{-3} \text{ s}^{-1}$

(iv) State the units of the rate constant.

s^{-1}

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ slow

B $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast

C $Cr(CO)_6 + PR_3 \rightarrow [OC\text{---}Cr(CO)_4\text{---}PR_3] \rightarrow Cr(CO)_5PR_3 + CO$
(transition state)

D $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

Mechanism B, this is because only $Cr(CO)_6$ involves in the rate equation which means it involves in the rate determining step which is the slowest step in the reaction

[9]

8

[Total: 11]

10

Examiner comment – grade A

(a) This candidate gave a complete answer, typical of a grade A candidate. A ligand needed to be described as containing a lone pair of electrons, which could be donated to a central metal. It was necessary to specify the latter point in order to distinguish a ligand from a *base*, or the more general *nucleophile*. The type of bonding could be described as either *dative* or *co-ordinate*.

(b) The correct plotting of the points and the drawing of the straight line through them allowed this candidate to score the mark in **(i)**. In part **(ii)** the candidate scored the mark for correctly stating both orders, and also gained the mark for the explanation of the first order dependence on $[Cr(CO)_6]$, namely that the half-life was constant. However, the mark available for the explanation of the zero order dependence on $[PR_3]$ was not awarded: reference had to be made to the fact that the rate, i.e. the slope of the concentration-time graph, does not alter with $[PR_3]$. The candidate's phrase 'half life is decreasing' was not an accurate enough description to gain the mark: had the candidate pointed out that successive half lives were each exactly half the previous half life, a mark could have been gained. In part **(iii)** this candidate chose to draw a gradient to the line where $[Cr(CO)_6] = 0.0061$ mol dm^{-3}, rather than the more usual $[Cr(CO)_6] = 0.010$ mol dm^{-3} at t = 0 sec. However, the calculation was performed well, the value of the rate constant *k* was in the acceptable range, and the units were correct in part **(iv)**. In part **(v)** both the mechanism chosen and the explanation fitted with the orders deduced earlier.

Example candidate response – grade C

2 **(a)** **(i)** What is meant by the term *ligand* as applied to the chemistry of the transition elements?

A molecule or ion with lone pair of electron ~~to~~ which forms covalent dative bond with a central metal atom or ion ✓

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

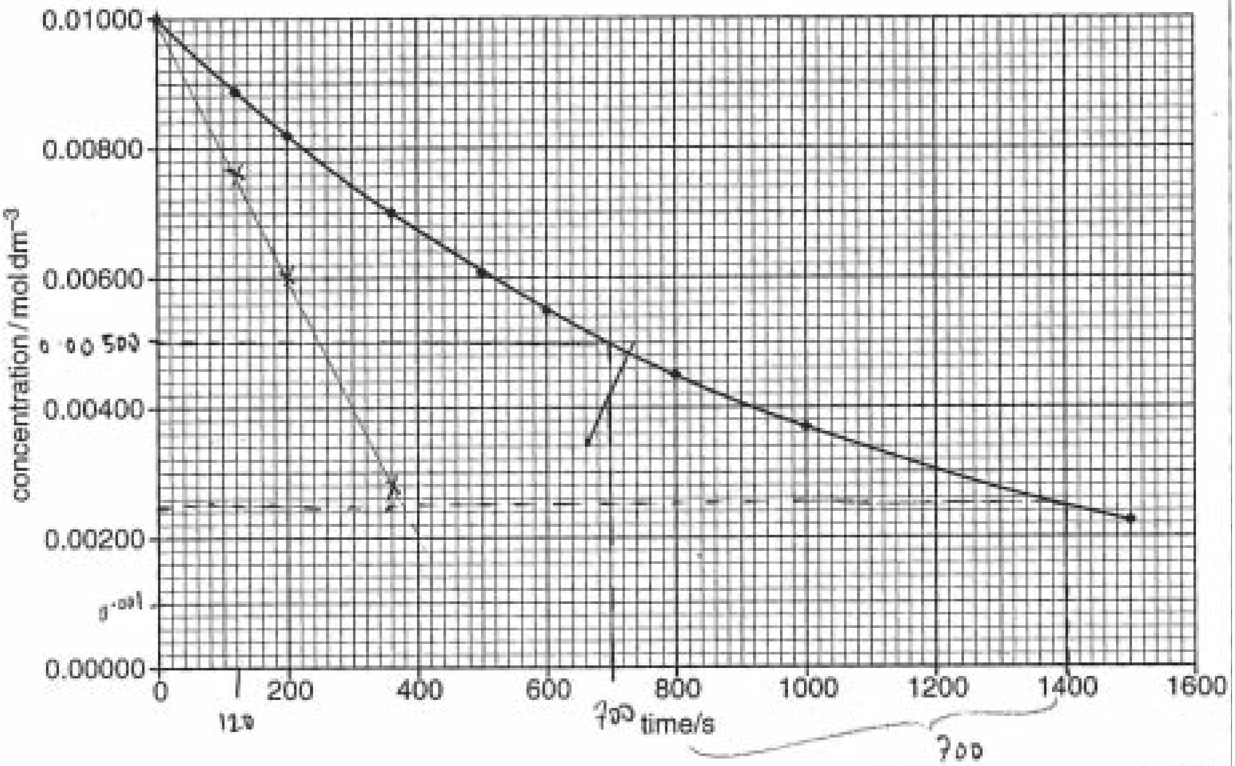
Covalent dative bonding ✓

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

For the concentration of $Cr(CO)_6$ to decrease by half: 700s (from 0.0100 mol dm^{-3} to 0.00500 mol dm^{-3}) and from 0.00500 mol dm^{-3} to 0.00250 mol dm^{-3}) also took 700s. Constant half-life. Therefore ~~rate~~ order of reaction w.r.t. [$Cr(CO)_6$] is 1.

PR_3

Graph of [PR_3] against time is a straight line ~~decreasing~~ (decreasing) therefore order of reaction ~~wrt~~ w.r.t. [PR_3] is 2.

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

rate equation = k [$Cr(CO)_6$] [PR_3]^2 ecf.

For PR_3

(iv) State the units of the rate constant. $k = \dfrac{mol\,dm^{-3}\,s^{-1}}{(mol\,dm^{-3})^3} = \dfrac{mol\,dm^{-3}\,s^{-1}}{mol^3\,dm^{-9}}$

$mol^{-2}\,dm^6\,s^{-1}$.

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ slow

B $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast

C $Cr(CO)_6 + PR_3 \rightarrow [OC\text{---}Cr(CO)_4\text{---}PR_3] \rightarrow Cr(CO)_5PR_3 + CO$
(transition state)

D $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

D. $Cr(CO)_6$ and PR_3 are in the rate equation. Therefore their concentration will determine the rate (in the slow step). $Cr(CO)_6PR_3$ is not in the rate equation. Therefore it should be in the fast step.

[9]

[Total: 11]

Examiner comment – grade C

(a) This candidate also gave a complete answer and gained full credit for this part.

(b) The correct plotting of the points and the drawing of the straight line through them allowed this candidate to score the mark in part **(i)**. In part **(ii)** the explanation for the first order dependence on $[Cr(CO)_6]$ was well expressed, but the logic for $[PR_3]$ was incorrect. In parts **(iii)** and **(iv)**, however, error-carried-forward marks were gained for deducing the correct rate equation and units based on the candidate's incorrect second order dependence on $[PR_3]$. Since none of the four possible mechanisms in part **(v)** were consistent with a second order dependence on $[PR_3]$, it was not possible to award any error-carried-forward marks here to this candidate.

Example candidate response – grade E

2 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

Ligand has a lone pair

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

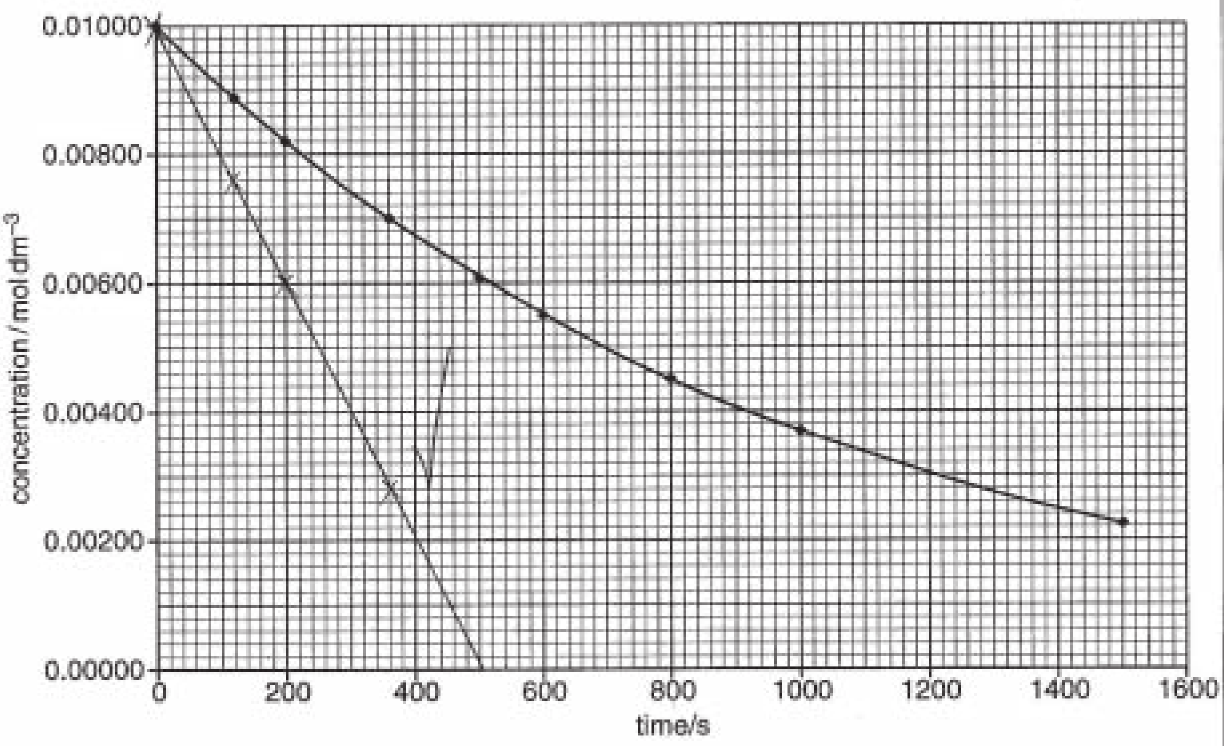
covalent bond.

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

$Cr(CO)_6$

order of reaction is 1. The graphs is inversely proportional.

As time decreases, concentration decreases.

PR_3

Order of reaction is 1. The graphs is inversely proportional.

Concentration is inversely proportional to time.

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

ecf

rate = k[Cr(CO)$_6$][PR$_3$]

k = [Cr(CO)$_6$][PR]$_3$ = [0.01][0.01] = 1×10^{-4}

rate = 1×10^{-4} [0.01][0.01]

= 1×10^{-8}

(iv) State the units of the rate constant.

mol^{4} dm^{-1}

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ slow

B $Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \rightarrow Cr(CO)_5PR_3$ fast

C $Cr(CO)_6 + PR_3 \rightarrow [OC{-}{-}{-}Cr(CO)_4{-}{-}{-}PR_3] \rightarrow Cr(CO)_5PR_3 + CO$
(transition state)

ecf

D $Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \rightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

Because it is a slow reaction.

[9]

Examiner comment – grade E

(a) Both parts **(i)** and **(ii)** had detail missing. In **(i)** the candidate needed to explain that the lone pair of electrons on the ligand was used *for bonding to a central metal atom*, and in **(ii)** the bonding needed to be *dative* or *co-ordinate* as well as covalent.

(b) The plotting of the points and the straight line scored the mark in part **(i)**. In part **(ii)**, although the order with respect to $[Cr(CO)_6]$ was correct, the explanation was not: the graph does not show inverse proportionality, and the second statement is incorrect The first order dependence on $[PR_3]$ was incorrect. However, an error-carried-forward mark was awarded in part **(iii)** for the correct rate equation based on the incorrect orders stated in part **(ii)**, but the units in part **(iv)** were incorrect. Another error-carried-forward mark was awarded in part **(v)**, because any of the mechanisms A, C or D is consistent with the reaction being first order with respect to each reactant.

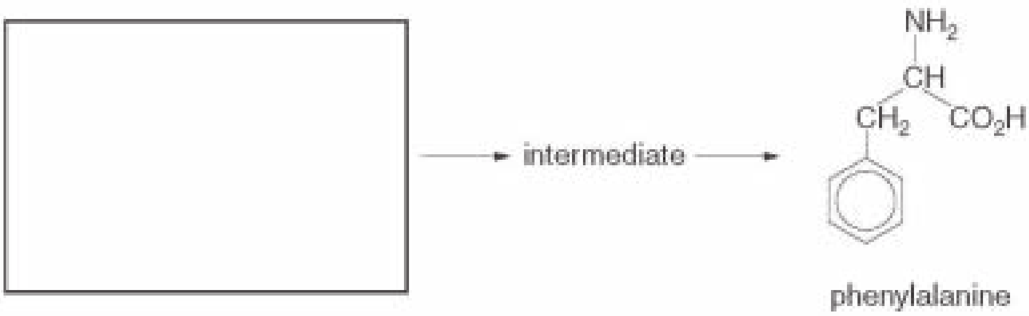
Question 3

3 (a) Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.

$$CH_3CHO \xrightarrow{NaCN\ +\ NH_4Cl} \boxed{\quad \mathbf{E},\ C_3H_6N_2 \quad} \xrightarrow[\text{(ii) neutralise}]{\text{(i) } H_3O^+ \text{ + heat}} \underset{\text{alanine}}{CH_3CH(NH_2)CO_2H}$$

(i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.



phenylalanine

[2]

(b) (i) What is a *protein*?

....

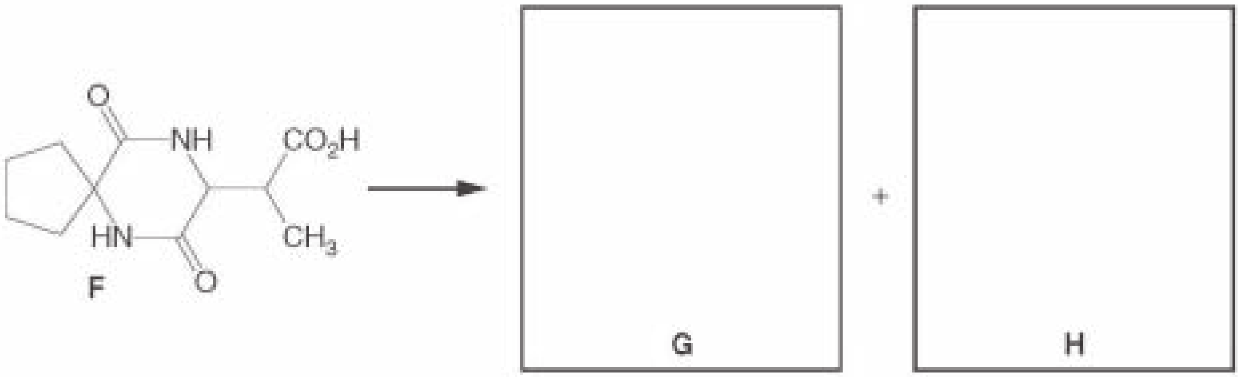
(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.

[3]

For Examiner's Use

For Examiner's Use

(c) The hydrolysis of compound **F** produces two compounds **G** and **H**.



(i) State the reagents and conditions needed for this hydrolysis.

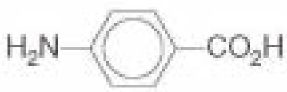
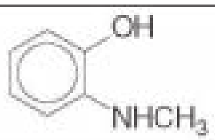
....

(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) (i) Draw the zwitterionic structure of alanine.

(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
	
	
	

[4]

For Examiner's Use

(e) Solutions of amino acids are good buffers.

(i) What is meant by the term *buffer*?

....

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as $HCl(aq)$.

....

(iii) Briefly describe how the pH of blood is controlled.

....

....

....

(iv) Calculate the pH of the buffer formed when $10.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH is added to $10.0\,cm^3$ of $0.250\,mol\,dm^{-3}$ CH_3CO_2H, whose $pK_a = 4.76$.

pH = ...

[7]

[Total: 19]

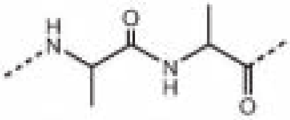
Mark scheme

3 **(a)** **(i)** **E** is $CH_3CH(NH_2)CN$ [1]

(ii) $C_6H_5CH_2CHO$ [1]
[2]

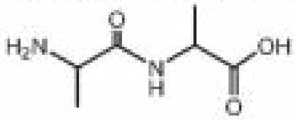
(b) **(i)** a polymer/polypeptide of amino acids, (joined by peptide bonds)
(allow '**chain** of amino acids' but not 'sequence': the idea of 'many' has to be conveyed) [1]

(ii)



peptide bond shown in full (C=O) in an ala-ala fragment in a chain [1]
two repeat units [1]

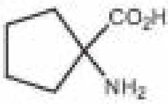
Allow peptide bond shown in full (C=O) in a dipeptide ala-ala for 1 mark



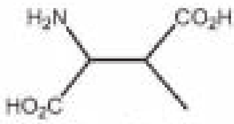
[3]

(c) **(i)** HCl *or* H_2SO_4 *or* NaOH *or* H^+ *or* OH^- reagents [1]
+ heat and H_2O/aq (allow H_3O^+).
If T is quoted, 80 °C < T < 120 °C. NOT warm. conditions [1]

(ii)



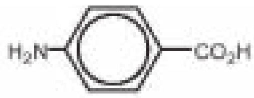
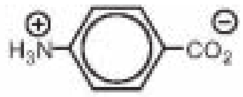
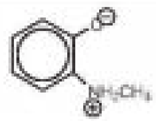
and



(if a structural formula, it must have all H atoms) allow protonated or deprotonated versions [1] + [1]
[max 3]

(d) **(i)** $NH_3^+\text{–}CH(CH_3)\text{–}CO_2^-$ [1]

(ii)

compound	zwitterion
	
	
	

[3]
[4]

(e) **(i)** A buffer is a solution whose pH stays **fairly** constant *or* which maintains **roughly** the same pH *or* which resists/minimises changes in pH [1]
when **small/moderate** amounts of acid/H^+ or alkali/OH^- are added [1]

(ii) $NH_2CH(CH_3)CO_2H + H(Cl) \longrightarrow {}^+NH_3CH(CH_3)CO_2H\ (+\ Cl^-)$ [1]

(iii) blood contain $\mathbf{HCO_3^-}$ (*or* in an equation) [1]
which absorbs H^+ *or* equn $H^+ + HCO_3^- \longrightarrow H_2CO_3\ (H_2O + CO_2)$
or absorbs OH^- *or* equn $OH^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2O$ [1]

(iv) $[CH_3CO_2Na] = 0.05\ [CH_3CO_2H] = 0.075$ [1]
pH = 4.76 + log (0.05/0.075) = **4.58** *or* **4.6** [1]
[7]

[Total: 19]

General comment

This question covered a wide range of topics, from the hydrolysis of nitriles and amides to the structures of proteins and zwitterions, and the calculation of buffer pH. Because of the range of topics covered, full marks were obtained only rarely, but many candidates scored 16–18 out of 19. Part **(a)** required enough understanding of the synthesis of carboxylic acids by the hydrolysis of nitriles to be able to work backwards to deduce the structures of starting materials and intermediates. Part **(b)** started with a definition of a protein, followed by their typical structure. In part **(c)**, knowledge of amide hydrolysis needed to be applied to a cyclic bis-amide, and part **(d)** involved the application of knowledge of the structures of zwitterions to some unusual compounds. Part **(e)** started with a straightforward definition of a buffer, continued with knowledge recall of blood buffers, and finished with a fairly simple calculation of buffer pH, which, however, caught out many candidates.

The most challenging parts were **(a)(ii)**, **(c)**, **(e)(iii)** and **(e)(iv)**.

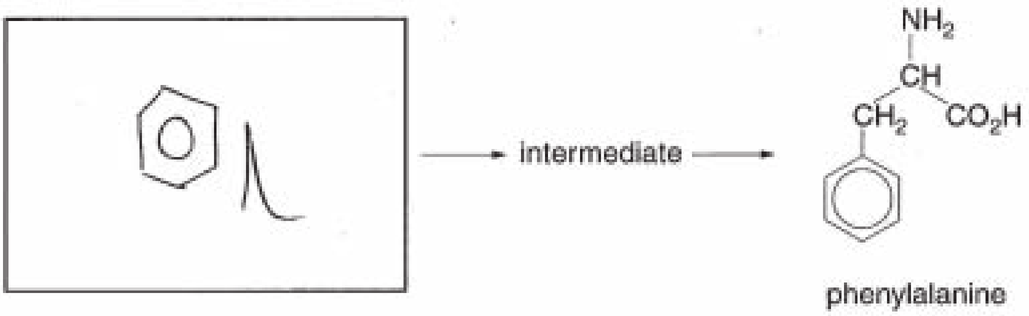
Example candidate response – grade A

3 **(a)** Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.

$$CH_3CHO \xrightarrow{NaCN + NH_4Cl} \boxed{\begin{array}{c} CH_3CH(NH_2)CN \\ \mathbf{E},\ C_3H_6N_2 \end{array}} \xrightarrow[\text{(ii) neutralise}]{\text{(i) } H_3O^+ + \text{heat}} \begin{array}{c} CH_3CH(NH_2)CO_2H \\ \text{alanine} \end{array}$$

(i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.

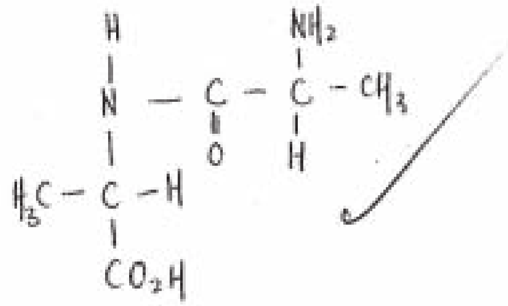


[2]

(b) (i) What is a *protein*?

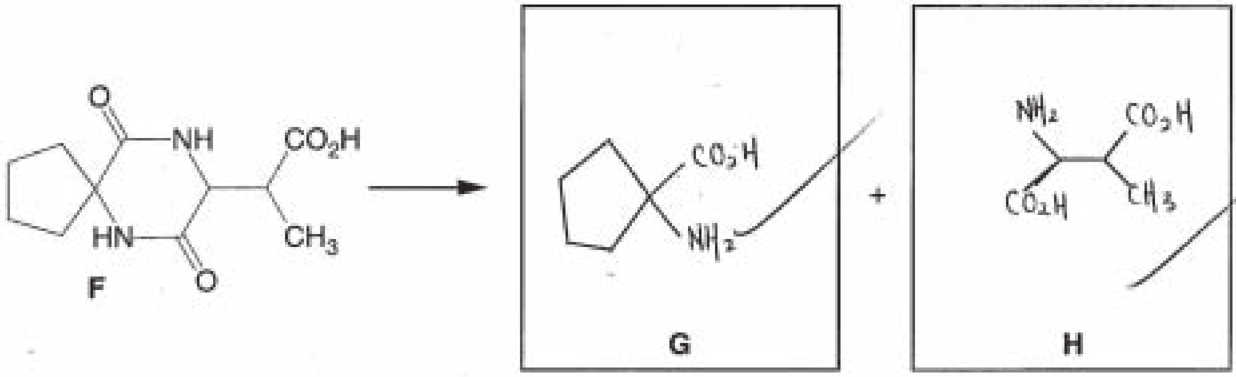
Protein is the polymer of amino acids.

(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.



[3]

(c) The hydrolysis of compound **F** produces two compounds **G** and **H**.



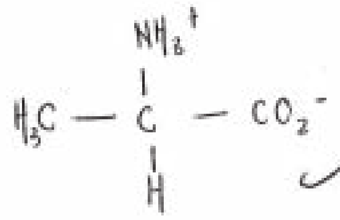
(i) State the reagents and conditions needed for this hydrolysis.

HCl (aq) and heat

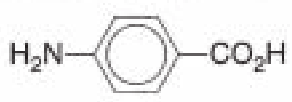
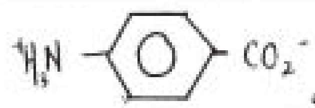
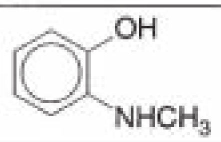
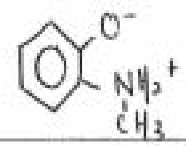
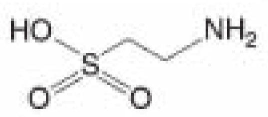
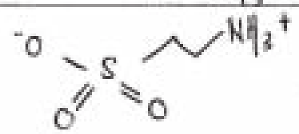
(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) **(i)** Draw the zwitterionic structure of alanine.



(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
	
	
	

[4]

(e) Solutions of amino acids are good buffers.

(i) What is meant by the term *buffer*?

A solution that resist changes in pH when small amount of acid or base are added to it.

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as HCl(aq).

$CH_3CH(NH_2)CO_2H + HCl \longrightarrow CH_3CH(NH_3^+Cl^-)CO_2H$

(iii) Briefly describe how the pH of blood is controlled.

pH of blood is controlled by haemoglobin molecules which combines with H^+ forming haemoglobinic acid therefore act as a buffer in the blood.

(iv) Calculate the pH of the buffer formed when $10.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH is added to $10.0\,cm^3$ of $0.250\,mol\,dm^{-3}$ CH_3CO_2H, whose $pK_a = 4.76$.

$[salt] = 10\times10^{-3} \times 0.10$

$= \dfrac{1\times10^{-3}}{10\times10^{-3}} = 0.10\ mol\,dm^{-3}$

$[acid] = 0.25 \times 10\times10^{-3}$

$= 2.5\times10^{-3} - (10\times10^{-3}\times0.10)$

$= \dfrac{1.5\times10^{-3}}{10\times10^{-3}} = 0.15\ mol\,dm^{-3}$

$pH = pK_a + \left(\log_{10}\dfrac{[salt]}{[acid]}\right)$

$= 4.76 + \left(\log_{10}\dfrac{0.10}{0.15}\right)$

$= 4.76 + (-0.17)$

$pH = 4.59$ #

pH = 4.59

[7]

Examiner comment – grade A

(a) This candidate correctly worked out that the intermediate in part **(i)** was $CH_3CH(NH_2)CN$, but did not deduce that the starting material in part **(ii)** was $C_6H_5CH_2CHO$.

(b) This candidate clearly stated the key point in part **(i)**, that proteins are polymers of amino acids. In part **(ii)** this candidate scored one out of the possible two marks: the structure drawn was the correct structure of the dipeptide ala-ala, rather than two repeat units in a polypeptide chain, as the question asked.

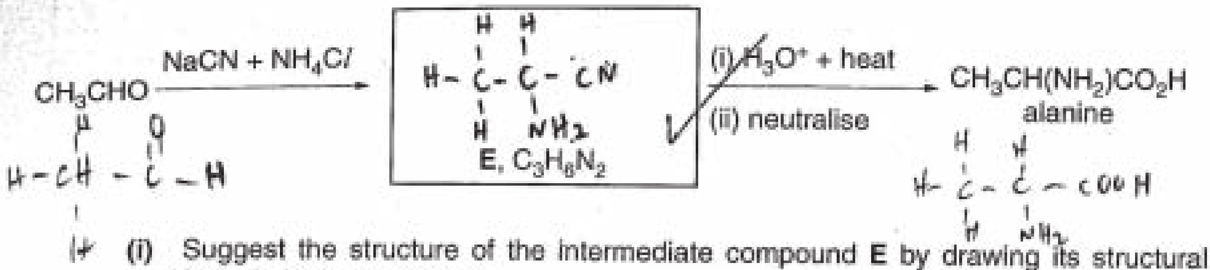
(c) The correct reagents and conditions were stated for the hydrolysis, and this candidate correctly worked out the hydrolysis products.

(d) The principle behind zwitterion formation was clearly understood, so all structures were correct.

(e) The two important features of buffers: that they *resist*, rather than totally prevent, changes in pH and that they are only effective if *small amounts* of acids or bases are added, were well explained by this candidate. In addition, a correct equation was offered in part **(ii)**. Part **(iii)** illustrated a gap in this candidates knowledge of blood buffers: HCO_3^- ions are the main agent, reacting with H^+ to give H_2CO_3 (or $H_2O + CO_2$) and with OH^- to give CO_3^{2-} ions. However, this candidate was one of a fairly rare number who scored the full two marks for a totally correct answer in part **(iv)**.

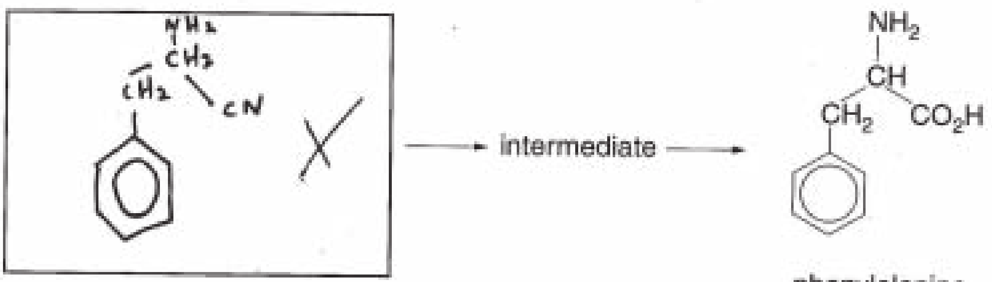
Example candidate response – grade C

3 (a) Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.



(i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.



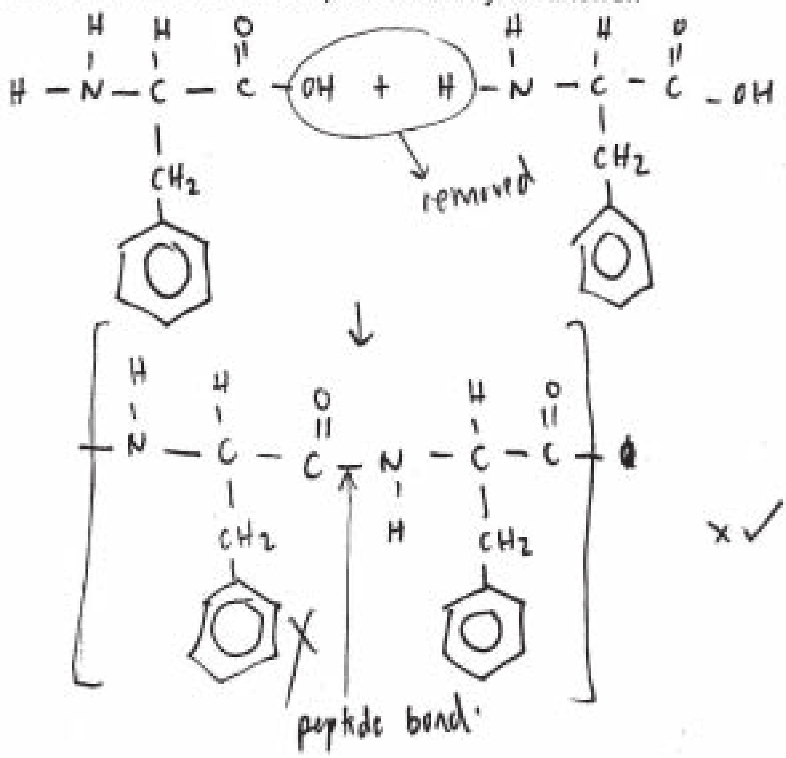
phenylalanine

[2]

(b) (i) What is a *protein*?

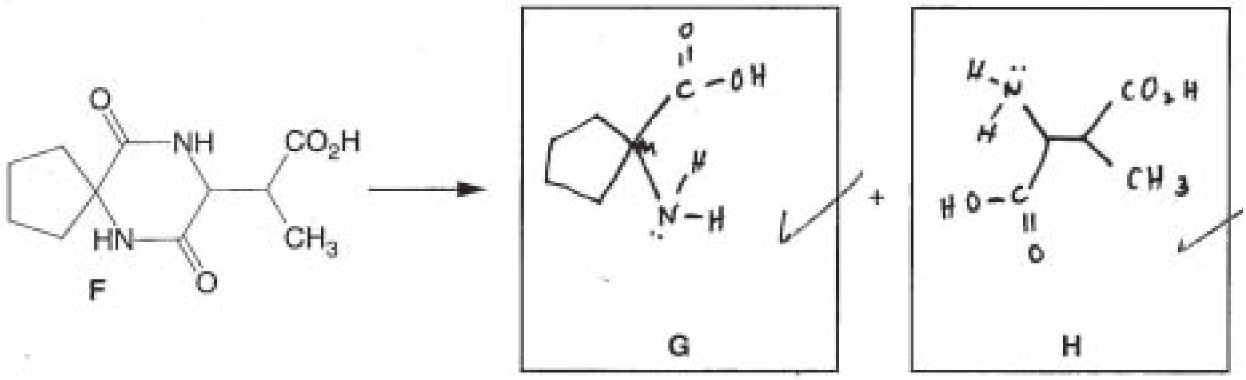
~~poly~~ long chains of amino acids.

(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.



[3]

(c) The hydrolysis of compound **F** produces two compounds **G** and **H**.



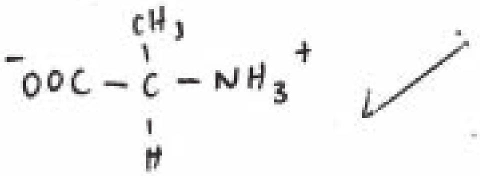
(i) State the reagents and conditions needed for this hydrolysis.

~~alkaline~~ H^+, water + heat

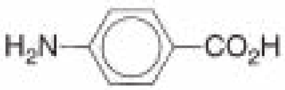
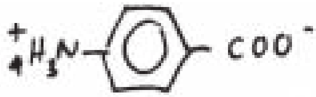
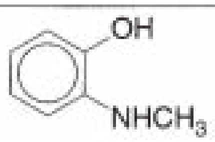
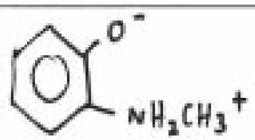
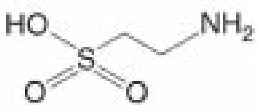
(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) (i) Draw the zwitterionic structure of alanine.



(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
	
	 Bod
	

[4]

(e) Solutions of amino acids are good buffers.

(i) What is meant by the term *buffer*?

solution that prevents any changes of pH.

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as HC*l*(aq).

~~by using~~ $CH_3CH(NH_2)COO^- + H^+ \rightarrow CH_3CH(NH_2)COOH$

(iii) Briefly describe how the pH of blood is controlled.

by presence of hydrogen carbonic ~~acid~~ ion, HCO_3^-

when H^+ is present, $HCO_3^- + H^+ \rightleftharpoons H_2CO_3$

(iv) Calculate the pH of the buffer formed when $10.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH is added to $10.0\,cm^3$ of $0.250\,mol\,dm^{-3}$ CH_3CO_2H, whose $pK_a = 4.76$.

$\cancel{pH = pka + \log\left(\frac{acid}{base}\right)}$ $\left(\frac{\cancel{base}}{acid}\right)$ $pH = pka + \log\left(\frac{acid}{base}\right)$

$pH = 4.76 + \log\left(\frac{[0.250]}{[0.100]}\right)$

$pH = 4.76 + 0.397$

$pH = 5.16$

pH = 5.16

[7]

[Total: 19]

Examiner comment – grade C

(a) This candidate correctly worked out the intermediate in part **(i)**. In part **(ii)** the correct intermediate was shown, but the candidate had not read the question correctly so drew the intermediate's structure in the box rather than that of the starting material.

(b) A mark was gained for 'long chains of amino acids' in part **(i)**, but in part **(ii)** one of the two marks was lost because the candidate drew two repeat units of poly-phenylalanine, rather than poly-alanine, as asked for in the question.

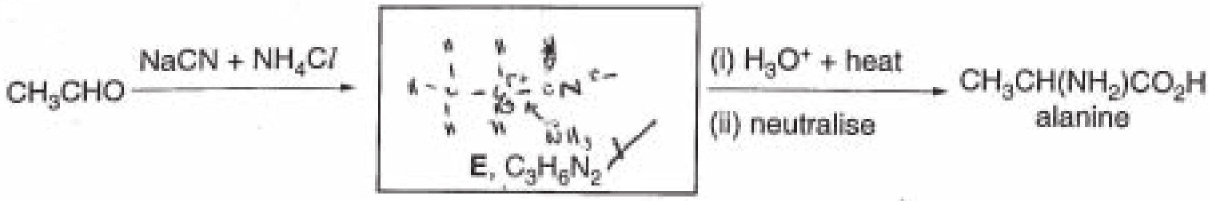
(c) The reagents were correct in part **(i)**, and correct hydrolysis products were given in part **(ii)** .

(d) The principle behind zwitterion formation was understood, so all structures were correct.

(e) The buffer definition was incorrect: it is important to remember that buffers do not *prevent* changes in pH, but merely minimise them. Secondly, buffers can only do this if only *small amounts* of H^+ or OH^- ions are added. In part **(ii)** this candidate incorrectly used the anion of alanine to react with H^+, rather than the unionised acid (or its zwitterion). In contrast, this candidate's answer to part **(iii)** was excellent. An equation showing how HCO_3^- reacts with *either* OH^- *or* with H^+ was required as part of the answer. Two errors were made in part **(iv)**, and so no marks were obtained. The first was not to appreciate that when 0.001 mol of NaOH is added to 0.0025 mol of CH_3CO_2H, not only will 0.001 mol of CH_3CO_2Na be formed, but 0.001 mol of CH_3CO_2H will have been used up, leaving only 0.0015 mol to contribute to the buffer. The second error was to invert the (0.1/0.25) ratio in the Henderson-Hasselbach equation, thus making the buffer pH more acidic than the pK_a, rather than less so.

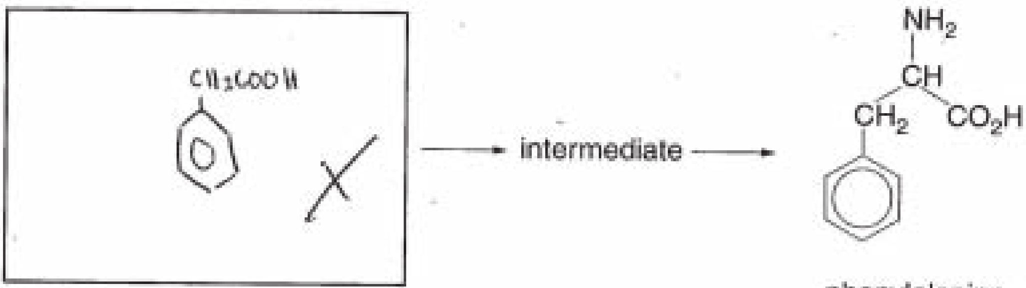
Example candidate response – grade E

3 (a) Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.



(i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.



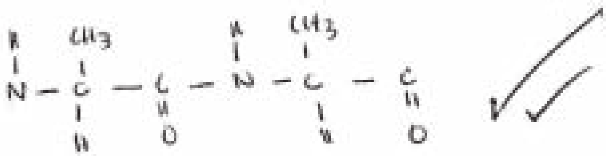
phenylalanine

[2]

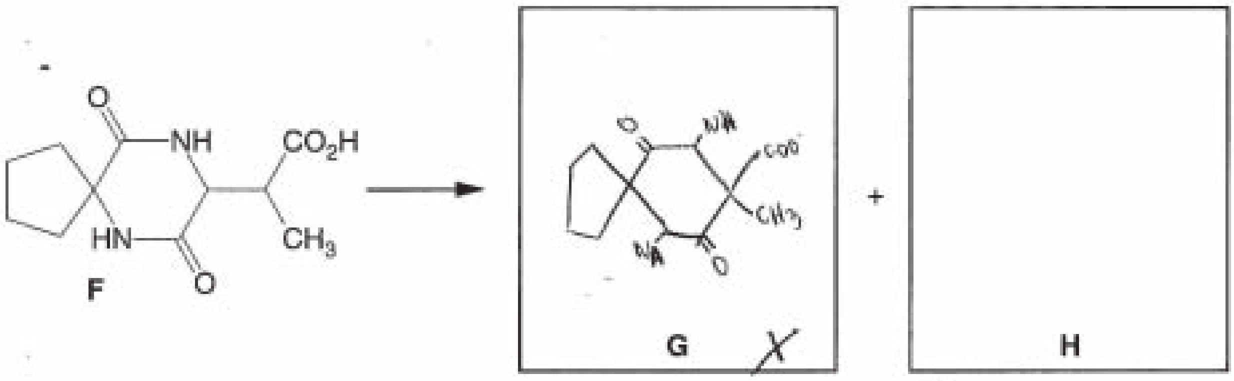
(b) (i) What is a *protein*?

a sequence of amino acids

(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.



(c) The hydrolysis of compound **F** produces two compounds **G** and **H**.



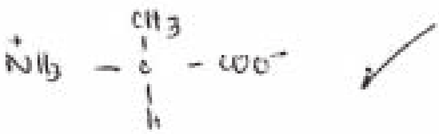
(i) State the reagents and conditions needed for this hydrolysis.

conc H_2SO_4 + heat

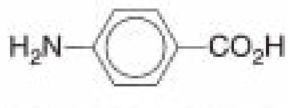
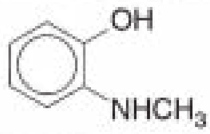
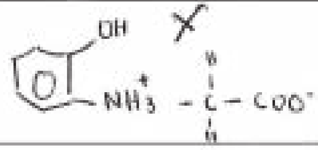
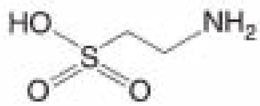
(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) (i) Draw the zwitterionic structure of alanine.



(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
	
	
	NH_3^+

[4]

(e) Solutions of amino acids are good buffers.

(i) What is meant by the term *buffer*?

A solution that resist changes in pH when small amount of acid or alkali is added.

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as HCl(aq).

$CH_3CH(NH_2)COOH + HCl \rightarrow CH_3CH(NH_2)COOCl + H_2O$

(iii) Briefly describe how the pH of blood is controlled.

....

....

....

(iv) Calculate the pH of the buffer formed when $10.0\,cm^3$ of $0.100\,mol\,dm^{-3}$ NaOH is added to $10.0\,cm^3$ of $0.250\,mol\,dm^{-3}$ CH_3CO_2H, whose $pK_a = 4.76$.

$\cancel{Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}}$

~~$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$~~

1 : 1

pH = ...

[7]

[Total: 19]

$pKa = 4.76$

$Ka = 1.74 \times 10^{-5}$

$Ka = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

$1.74 \times 10^{-5} = \frac{[CH_3COO^-][H^+]}{0.250}$

Examiner comment – grade E

(a) The intermediate **E** was drawn as the second stage of an S_N1 reaction, rather than the stable amino-nitrile. In part **(ii)** the starting material was incorrectly deduced, in which the corresponding carboxylic acid was drawn instead of the aldehyde.

(b) The term 'sequence' was not accepted as suggesting a large polymeric chain, but this candidate did score the full two marks for correctly drawing two repeat units.

(c) A mark was gained in part **(i)** for H_2SO_4, but the 'conditions' mark was not awarded: the H_2SO_4 had to be dilute, or 70%, rather than conc.

(d) Although this candidate understood the idea of zwitterions in part **(i)**, in part **(ii)** the more unusual structures were incorrectly completed.

(e) This candidate scored well on the 'recall' marks in part **(i)**, but suggested the acid (peroxy) chloride as a product of the reaction with HCl in part **(ii)**. Knowledge of blood buffers was unanswered in part **(iii)**, and in part **(iv)** the candidate did not correctly complete the buffer calculation.

Question 4

4 (a) Write an equation representing the action of heat on calcium nitrate, $Ca(NO_3)_2$.

.... [1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

....

....

....

....

.... [3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces $CO_2(g)$.

(i) Suggest an equation for the action of heat on lithium carbonate.

....

(ii) Suggest a reason for the difference in reactivity of these two carbonates.

....

....

(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

....

....

.... [4]

[Total: 8]

Mark scheme

4 **(a)** $Ca(NO_3)_2 \longrightarrow CaO + 2NO_2 + \frac{1}{2} O_2$ [1]
[1]

(b) (down the group) nitrates become **more stable** *or* require a higher temperature to decompose [1]
as size/radius of (cat)**ion** increases *or* charge density **of ion** decreases [1]
so polarisation/distortion of **anion/nitrate** decreases [1]
[3]

(c) **(i)** $Li_2CO_3 \longrightarrow Li_2O + CO_2$ [1]

(ii) radius of Li ion/Li^+ is less than that of Na ion/Na^+ (or polarising power of M^+ is greater) [1]

(iii) Brown/orange fumes/gas would be evolved *or* glowing splint relights [1]
Since the nitrate is likely to be thermally unstable *or* decomposes (just like the carbonate) *or* the balanced equation: $2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$ [1]
[4]

[Total: 8]

General comment

This short question tested knowledge of the thermal decomposition of Group II nitrates, and the application of that knowledge to the decomposition of Group I nitrates and carbonates. Most candidates did well on the knowledge recall of part **(b)**, but the application of knowledge in part **(c)** caused some difficulties. Quite a number of candidates – of all abilities – lost a mark through not checking the balancing of their equation in part **(a)**.

Example candidate response – grade A

4 **(a)** Write an equation representing the action of heat on calcium nitrate, $Ca(NO_3)_2$.

$Ca(NO_3)_2 \xrightarrow{heat} CaO + 2NO_2 + \frac{1}{2}O_2$

[1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

Down Gp II, thermal stabilities of nitrates increases. This is because down the gp., charge of cation is the same, ionic radius increases, ∴ charge density decreases. Hence down the gp., lesser polarization of the anion NO_3^-. Above the group, high charge density thus polarise and would weaken anion.

[3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces $CO_2(g)$.

(i) Suggest an equation for the action of heat on lithium carbonate.

$Li_2CO_3 \xrightarrow{heat} 2Li + CO_2 + \frac{1}{2}O_2$.

(ii) Suggest a reason for the difference in reactivity of these two carbonates.

Li^+ has a higher charge density than Na^+ thus polarise anion CO_3^{2-} and weaken C=O bond more. ∴ C=O breaks more easily.

(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

$LiNO_3$ would decompose to NO_2 and Li_2O. A brown gas would be observed. This is due to diagonal relationship with Mg^{2+} and Li^+. Thus having similar trend in properties of thermal stabilities as noted in b).

[4]

High charge density, polarisation of anion thus weaken bonds within causing Ea to be low.

[Total: 8]

Examiner comment – grade A

(a) One mark was gained for the standard balanced equation.

(b) The three points required were described well here: thermal stability increases, due to the ionic radius increasing, thus causing less polarisation of the nitrate anion.

(c) Instead of suggesting in part **(i)** an equation analogous to that for the decomposition of Group II carbonates, this candidate incorrectly deduced that the metal oxide would decompose further into the alkali metal and oxygen gas. The reasoning in part **(ii)** was sound and the prediction and explanation in part **(iii)** formed an excellent answer.

Example candidate response – grade C

$Ba(NO_3)_2 \rightarrow BaO + 2NO + O_2$

$CaCO_3 \rightarrow CaO + CO_2$

9

$Ca(NO_3)_2 \rightarrow CaO + NO_2 + O_2$

4 **(a)** Write an equation representing the action of heat on calcium nitrate, $Ca(NO_3)_2$.

$Ca(NO_3)_2 \rightarrow CaO + 2NO_2 + O_2$

[1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

The thermal stabilities increase down Group II. The cationic size increased down the group, has low charge density and thus has low polarising power. The NO_3^- is less distort. More energy needed to break the bond.

[3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces CO_2(g).

(i) Suggest an equation for the action of heat on lithium carbonate.

$Li_2CO_3 \rightarrow Li_2O + CO_2$

(ii) Suggest a reason for the difference in reactivity of these two carbonates.

Li_2CO_3 is more reactive than Na_2CO_3 because the cationic size of Li^+ is smaller than Na^+. Thus less energy needed to break the bond.

(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

$LiNO_3 \rightarrow Li_2O + NO_2$

Black solid is formed and gas evolved.

The black solid is lithium oxide while the gas evolved is NO_2

[4]

Examiner comment – grade C

(a) This candidate lost the mark here through not checking the atom balance in the chemical equation.

(b) The full three marks were awarded for the accurate recall of this area of knowledge.

(c) The equation in part **(i)** and the reason in part **(ii)** demonstrated a good understanding of the application of knowledge of Group II reactivity to these Group I compounds. No marks were gained in part **(iii)**, however: the colour of NO_2 gas was not stated, and no explanation for the decomposition of the nitrate was given.

Example candidate response – grade E

4 **(a)** Write an equation representing the action of heat on calcium nitrate, $Ca(NO_3)_2$.

$2Ca(NO_3)_2\,(s) \rightleftharpoons 2CaO\,(g) + 4NO_2\,(g) + O_2\,(g)$ ✓ [1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

Down the group, cation size increases, ionic charge density decreases, polarising power decreases ✓ Therefore it is more thermally stable and requires high energy to decompose it ✓

[3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces CO_2(g).

Li^{+} CO_3^{2-}

(i) Suggest an equation for the action of heat on lithium carbonate.

$Li_2CO_3\,(s) \rightleftharpoons 2LiO\,(g) + CO_2\,(g)$ ✗

(ii) Suggest a reason for the difference in reactivity of these two carbonates.

(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

[4]

Examiner comment – grade E

This candidate was typical of the less able candidates in scoring well on the straightforward parts **(a)** and **(b)**, but not on the more demanding part **(c)**.

(a) A mark was gained for the balanced equation. Equations including either 1 or 2 moles of $Ca(NO_3)_2$ were accepted.

(b) The trend was described correctly, and the explanation was correct, but there was no indication in this answer of how the nitrates decompose, i.e. that the nitrate ion is distorted by the cation's electric field.

(c) A common error was to give the formula of lithium oxide as LiO rather than Li_2O.

Question 5

For Examiner's Use

5 Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(a) Suggest a reason why these reagents **do not** attack an alkane such as CH_4.

.... [1]

(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction.
Under more controlled conditions, however, the following reaction occurs.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) What is the name of this type of reaction?

....

(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

....

....

....

....

....

....

(iii) This reaction can produce organic by-products, in addition to C_2H_5Cl.
Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule.
Briefly describe how each by-product could be formed.

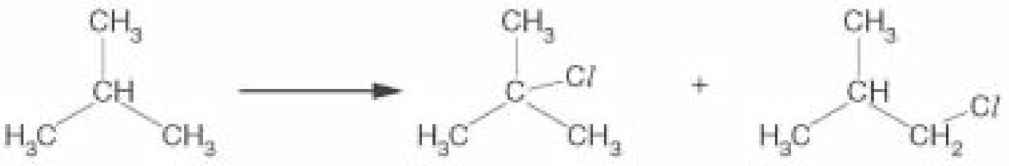
structural formula of by-product	formed by

For Examiner's Use

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **J** and **K** from the chlorination of 2-methylpropane. Explain your answer.



2-methylpropane **J** **K**

ratio **J** / **K** = ...

explanation:

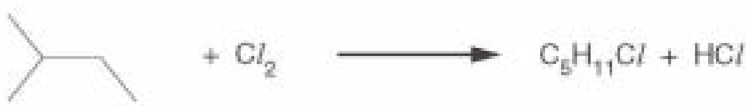
....

....

....

[10]

(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).



2-methylbutane

[5]

[Total: 16]

Mark scheme

5 **(a)** Alkanes are non-polar *or* have no dipole *or* C–H bonds are strong *or* C and H have similar electronegativities [1]
[1]

(b) **(i)** (free) radical substitution *or* substitution by homolytic fission [1]

(ii) initiation: $Cl_2 \longrightarrow 2Cl^{\bullet}$ [1]

propagation: $Cl^{\bullet} + C_2H_6 \longrightarrow C_2H_5^{\bullet} + HCl$

$C_2H_5^{\bullet} + Cl_2 \longrightarrow C_2H_5Cl + Cl^{\bullet}$ [1]

termination: $C_2H_5^{\bullet} + Cl^{\bullet} \longrightarrow C_2H_5Cl$

or $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$ etc [1]

all 3 names [1]

(iii)

structural formula of by-product	formed by
$CH_2Cl–CH_2Cl$ (or isomer)	**further substitution**
$CH_3CH_2CH_2CH_3$	**(termination of 2 ×) $C_2H_5^{\bullet}$**
$CH_3CH_2CH_2CH_2Cl$ (or isomer)	**substitution of C_4H_{10} by-product**

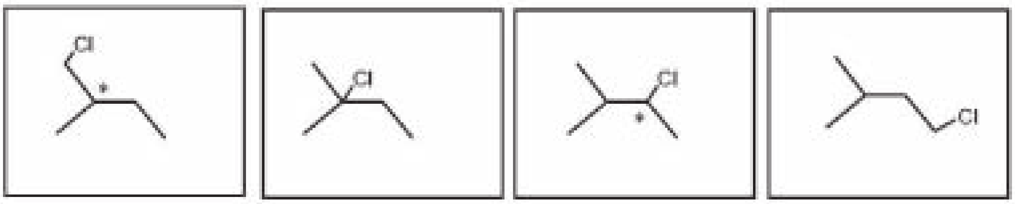
[3]

accept in the "formed by" column the formulae of radicals that will produce the compound in the "by-product" column, or the reagents, e.g. $C_4H_9^{\bullet} + Cl_2$ *or* $C_4H_9^{\bullet} + Cl^{\bullet}$ *or* $C_4H_{10} + Cl_2$ (giving $CH_3CH_2CH_2CH_2Cl$).
do not allow anything more *Cl*-substituted than **di**chlorobutane.
N.B. C_2H_5Cl is the **major** product, not a **by**-product, so do not allow C_2H_5Cl.

(iv) J/K = **2.3 : 1** *or* 7:3 *or* 21:9 [2]
(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)
allow [1] mark if J/K ratio is given as 21:1;

[10]

(c)



4 isomers 4 × [1]

2 chiral atoms identified correctly, even in incorrect structures [1] + [1]

[max 5]

[Total: 16]

General comment

This question concerned itself with the free radical substitution of alkanes. It proved to be the most difficult question of the whole paper, involving one of the less easy knowledge recall topics (the mechanism of the reaction), some tricky comprehension of data, and skeletal formulae which candidates often find difficult.

Example candidate response – grade A

5 Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(a) Suggest a reason why these reagents **do not** attack an alkane such as CH_4.

Alkanes are non - polar molecules.

[1]

(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction.
Under more controlled conditions, however, the following reaction occurs.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) What is the name of this type of reaction?

Free - radical substitution.

(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

① $Cl_2 \xrightarrow{u \cdot v} 2Cl\cdot$ ① Sunlight splits a chlorine molecule into two chlorine free radicals. This is the initiation step.

② The chlorine free radical attack ethane molecule. The H atom ~~substituted~~ combines with ~~another~~ the Cl, forming HCl, leaving $C_2H_5\cdot$ free radical.

② $C_2H_6 + Cl\cdot \rightarrow C_2H_5\cdot + HCl$

③ $C_2H_5\cdot + Cl\cdot \rightarrow C_2H_5Cl$ This is known as the propagation step.

③ When the $Cl\cdot$ and $C_2H_5\cdot$ free radicals ~~meet~~ combine, it is known as the termination step.

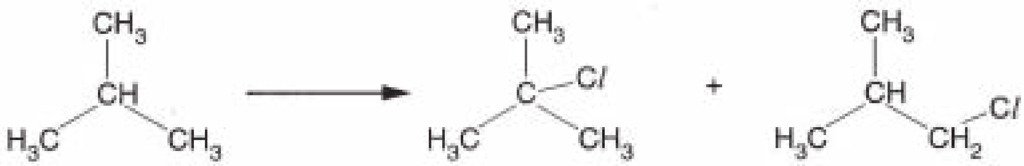
(iii) This reaction can produce organic by-products, in addition to C_2H_5Cl.
Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule.
Briefly describe how each by-product could be formed.

structural formula of by-product	formed by
CH_3CHCl_2	Another Cl free radical attack the C_2H_5Cl molecule
$CH_3CH_2CH_2CH_3$	Two $C_2H_5\cdot$ free radicals combine.
$CH_2ClCH_2CH_2CH_2Cl$	Two $C_2H_4Cl\cdot$ free radicals combine.

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **J** and **K** from the chlorination of 2-methylpropane. Explain your answer.



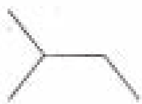
2-methylpropane **J** **K**

ratio **J**/**K** = 21 : 1

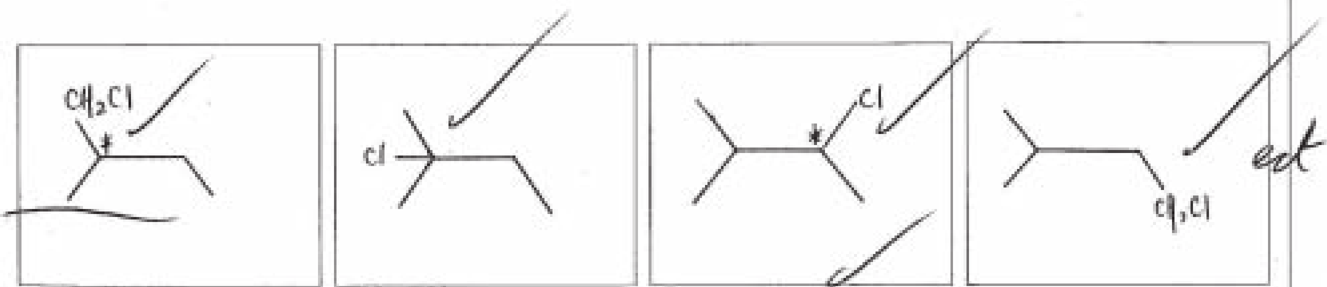
explanation:

In J, the ~~cl~~ chlorine atom replaced H atom on the R_3CH site, which has relative rate of 21. In K, the chlorine atom replace H atom on the RCH_3 site, which has relative rate of 1. Therefore, the ratio of J : ~~K should be~~ 21 : 1. [10]

(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).

 $+ Cl_2 \longrightarrow C_5H_{11}Cl + HCl$

2-methylbutane



Examiner comment – grade A

(a) Either the non-polar nature of alkanes or the high strength of the C-H bond could have been mentioned here.

(b) This was an excellent answer to this question, showing a comprehensive understanding of the mechanism of free radical substitution, as well as an ability to apply these ideas. Apart from the naming of the three steps, the verbal commentary by the side of the equations in part **(ii)** was not required, but was nevertheless correct. The formation of the three chosen by-products in part **(iii)** was well explained. In part **(iv)** the candidate correctly recognised that 2-methylpropane contained both primary and tertiary C–H bonds, but did not appreciate that statistically the 9:1 ratio of primary:tertiary C–H bonds would change the **J:K** ratio from 21:1 to 21:9.

(c) Most of these skeletal formulae were correct: the drawing of the CH_2Cl group in full in the first and last formulae was penalised only once. This candidate also correctly assigned the two chiral centres.

Example candidate response – grade C

5 Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(a) Suggest a reason why these reagents **do not** attack an alkane such as CH_4.

Alkanes are not polar molecules. ✓

[1]

(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction.
Under more controlled conditions, however, the following reaction occurs.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) What is the name of this type of reaction?

Free radical substitution ✓

(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

Initiation, $Cl-Cl \rightarrow Cl^{\bullet}\ \ Cl^{\bullet}$ ✓

Propagation, $C_2H_6 + Cl^{\bullet} \rightarrow C_2H_5Cl + HCl$

Termination, $C_2HCl_5 + Cl^{\bullet} \rightarrow C_2Cl_6 + HCl$

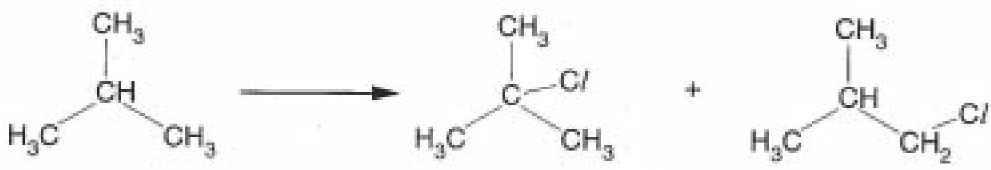
(iii) This reaction can produce organic by-products, in addition to C_2H_5Cl.
Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule.
Briefly describe how each by-product could be formed.

structural formula of by-product	formed by

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **J** and **K** from the chlorination of 2-methylpropane. Explain your answer.



2-methylpropane — **J** — **K**

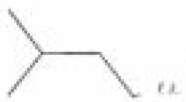
ratio **J** / **K** = 21 : 1

explanation:

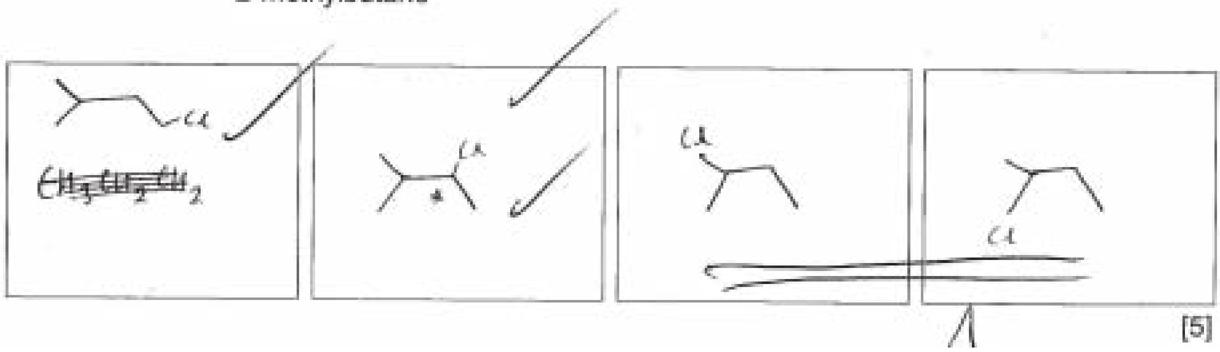
In J, the hydrogen to be replaced has ~~an~~ no neighbouring hydrogen atoms, thus reaction favours this way. However in K, the hydrogen to be replaced has two neighbour hydrogen atoms

[10]

(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).

 + Cl_2 ⟶ $C_5H_{11}Cl$ + HCl

2-methylbutane



[5]

Examiner comment – grade C

(a) A mark was gained for pointing out alkanes' non-polar nature.

(b) Both the name of the reaction type and the names of the steps involved were correct, as was the equation showing the initiation step. However, the answer did not show that in each propagation step a radical reacts with a complete molecule to form another radical and complete molecule pair, or that the termination steps involve the joining of two radicals to form a complete molecule. As with many of the less able candidates, part **(iii)** was not attempted, but a mark was gained for the partially correct 21:1 ratio in part **(iv)**.

(c) The first two skeletal formulae were correct, but the last two, which represented identical compounds, were missing a carbon atom. A correct chiral centre was identified.

Example candidate response – grade E

5 Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(a) Suggest a reason why these reagents **do not** attack an alkane such as CH_4.

strong C - H bonds

[1]

(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction.
Under more controlled conditions, however, the following reaction occurs.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) What is the name of this type of reaction?

Free radical substitution

(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

initiation : $Cl_2 \rightarrow Cl^{\bullet} + Cl^{\bullet}$ ~~Cl + Cl → Cl₂~~

propagation : $C_2H_6 + 2Cl^{\bullet} \rightarrow C_2H_5Cl^{\bullet} + HCl^{\bullet}$

$C_2H_5Cl^{\bullet}$ +

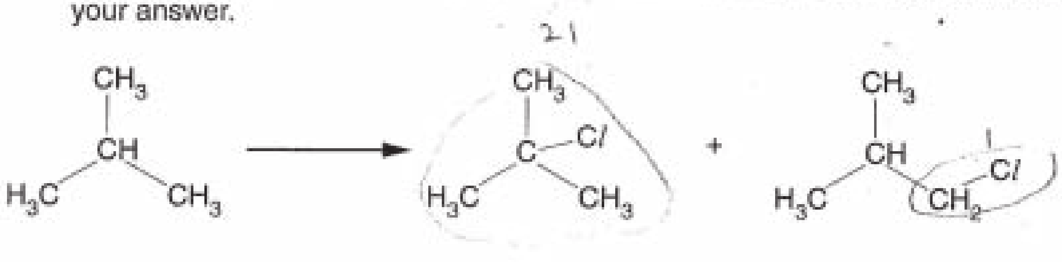
(iii) This reaction can produce organic by-products, in addition to C_2H_5Cl.
Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule.
Briefly describe how each by-product could be formed.

structural formula of by-product	formed by

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **J** and **K** from the chlorination of 2-methylpropane. Explain your answer.



2-methylpropane **J** **K**

ratio **J** / **K** = 21 : 1

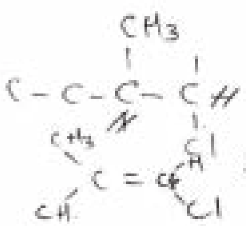
explanation:

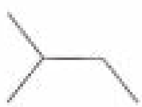
J falls under the reaction $R_3CH \rightarrow R_3CCl$

k fall under $RCH_3 \rightarrow RCH_2Cl$ (the R being $-CH(CH_3)CH_3$)

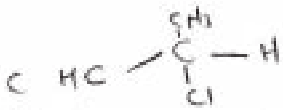
[10]

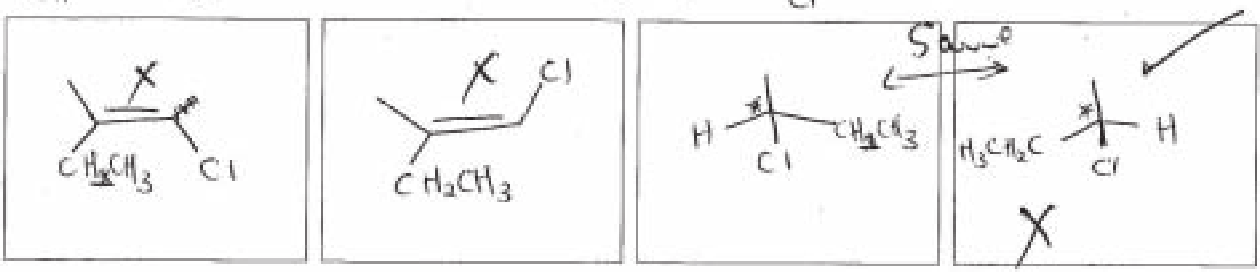
(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).



 $+ Cl_2 \longrightarrow C_5H_{11}Cl + HCl$

2-methylbutane





Examiner comment – grade E

(a) The strong C-H bond was an alternative reason accepted for the unreactivity of alkanes towards common reagents.

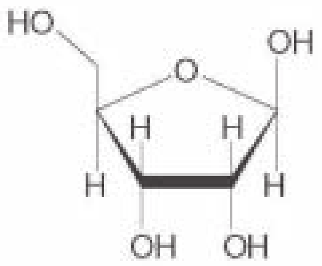
(b) Both the name of the type of reaction and the equation for the initiation step were correct. All three steps needed to be named to attract the 'naming' mark. Part **(iii)** was not attempted, but a mark was gained for the partially correct 21:1 ratio in part **(iv)**.

(c) The first two formulae – part skeletal, part structural – showed incorrect alkene products, whilst the last two showed the formulae (again part skeletal, part structural) of 2-chlorobutane, another incorrect product. A mark was gained, however, for correctly identifying the chiral carbon atom in this incorrect product.

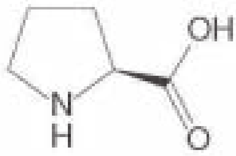
Question 6

6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

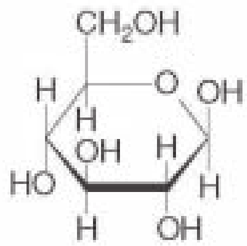
(a) **(i)** Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.



J



K



L

Which of the three could be a building block for a protein? Explain your answer.

....

....

(ii) For which biological polymer could **one** of the other molecules form a building block?

molecule .... **polymer** ....

[2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?

....

(ii) What type of bonding can exist in **all** of the other types of structure?

....

(iii) Name one type of bonding that does **not** occur in the primary or secondary structure of the protein.

....

[3]

For Examiner's Use

(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

(i) What name is given to these catalysts?

....

(ii) Give **two** changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.

....

....

....

....

....

....

[4]

[Total: 9]

Mark scheme

6 **(a)** **(i)** **K**, because it is the (only) one to contain nitrogen *or* it's an amino acid *or* because it contains CO_2H *or* NH groups [1]

(ii) molecule: **J**, polymer: RNA (**not** DNA) [1]
or molecule: **L**, polymer: starch, cellulose, glycogen or polysaccharide (**not** carbohydrate)

[2]

(b) **(i)** Covalent bonding [1]

(ii) Hydrogen bonding [1]

(iii) Ionic/electrovalent bonding *or* disulphide/–S–S– bonding *or* van der Waals' forces [1]

[3]

(c) **(i)** Enzymes [1]

(ii)
- change in pH
- increase in T (NOT decrease; T > 40 °C or "too high" are OK)
- addition of heavy metal ions *or* specific, e.g. Hg^{2+}, Ag^{+}. Pb^{2+} etc.

any two bullet points [1] + [1]

change in pH disrupts ionic bonds
or metal ions disrupt ionic bonds
or metal ions disrupt –S–S– bonds
or heating disrupts hydrogen bonds

any one [1]

This changes: the 3D structure *or* shape of the enzyme *or* the active site [1]

[max 4]

[Total: 9]

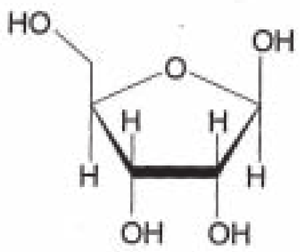
General comment

This question concerned itself with proteins. Although parts **(b)** and **(c)** were mainly recall items, care had to be taken to make sure the wording of answers was accurate and unambiguous. The question proved to be a fairly easy one for candidates, the majority of whom scored over half marks.

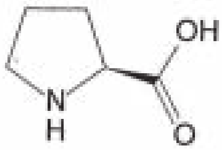
Example candidate response – grade A

6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

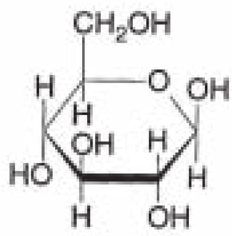
(a) **(i)** Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.



J



K



L

Which of the three could be a building block for a protein? Explain your answer.

J. A protein consist of a 5-carbon sugar, ~~p~~ ribose, ~~a~~ phosphate group and a nitrogenous base.

(ii) For which biological polymer could **one** of the other molecules form a building block?

molecule ....L........ **polymer** ....starch........

[2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?

bod

Peptide bonds which are covalent bonds

(ii) What type of bonding can exist in **all** of the other types of structure?

Hydrogen bonds

(iii) Name one type of bonding that does **not** occur in the primary or secondary structure of the protein.

Disulphide bonds.

[3]

(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

(i) What name is given to these catalysts?

Enzymes

(ii) Give **two** changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.

one condition is in high temperature where the high temperature may distrupt the bonding of the enzymes such as hydrogen bonds, causing them to change shape and altering the shape of their active site. Therefore will not be able to function properly anymore. Another condition is in high pH. High pH will also distrups the bondings in the protein structure such as hydrogen bonds, causing them to change the ~~acti~~ shape of their active site therefore denaturing the enzyme. [4]

[Total: 9]

Examiner comment – grade A

(a) Unusually for a grade A candidate, this candidate incorrectly selected a ribonucleotide instead of the amino acid. This was the only error in the answer to this question, however. Part **(ii)** was well answered: amylose, glycogen or cellulose were all acceptable alternatives to starch as the glucose polymer.

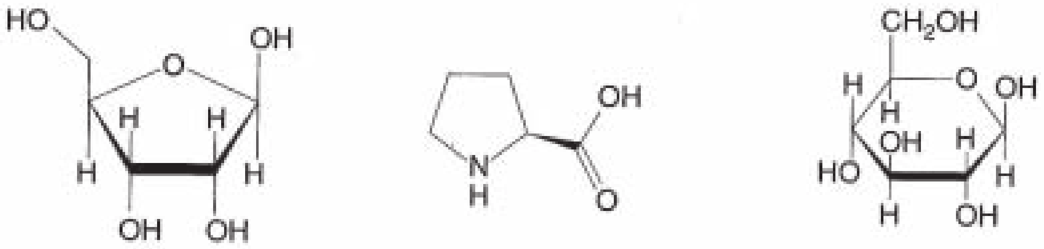
(b) The 'type of bonding' needed to specify *covalent* in part **(i)**: 'peptide bonds' on its own did not receive credit. In part **(ii)** 'hydrogen bonds' needed to be *uniquely* specified, but in part **(iii)** any one of ionic, disulfide or van der Waals would have gained the mark.

(c) This was an excellent answer to this question: high temperature and a change (increase *or* decrease) in pH were two of the three possible conditions which could be changed (the other one accepted was the presence of heavy metal ions). The disruption of hydrogen bonds on heating gained this candidate the 'reason' mark.

Example candidate response – grade C

6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

(a) **(i)** Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.



J **K** **L**

Which of the three could be a building block for a protein? Explain your answer.

K because it has amine and carboxylic group.

(ii) For which biological polymer could **one** of the other molecules form a building block?

molecule L **polymer** galactose

[2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?

Peptide bond

(ii) What type of bonding can exist in **all** of the other types of structure?

Hydrogen bond

(iii) Name one type of bonding that does **not** occur in the primary or secondary structure of the protein.

Disulphide bond.

[3]

(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

(i) What name is given to these catalysts?

Homogenious catalyst bod

(ii) Give **two** changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.

The increase or decrease of temperature and the increase of pH level.

3D

The shape of enzyme will distorted and the substrate cannot bind to active site. ~~They~~ The hydrogen bond, ionic bond and disulphide bonds are broken

High temperature and high pH will break the bondings in enzyme.

[4]

Examiner comment – grade C

(a) This candidate correctly identified **K** as an amino acid, and hence a building block for protein. In part **(ii)**, in common with many candidates, the name of the glucose polymer was incorrect, galactose being an isomer of glucose.

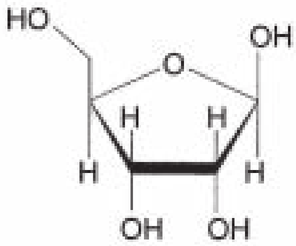
(b) 'Covalent' was a required part of the answer to part **(i)** but was not given in this case.

(c) Although the word 'enzyme' did not appear in part **(i)**, it was read into this part from the candidate's answer to part **(ii)**. In part **(ii)** the temperature change had to be specified as an increase (only), to cause denaturation.

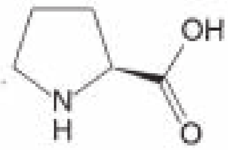
Example candidate response – grade E

6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

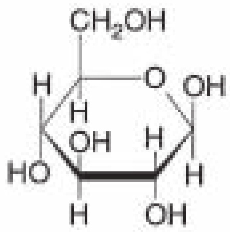
(a) (i) Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.



J



K



L

Which of the three could be a building block for a protein? Explain your answer.

K, because it has amide and carboxylic group

(ii) For which biological polymer could **one** of the other molecules form a building block?

molecule J **polymer** L

[2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?

peptide bond

(ii) What type of bonding can exist in **all** of the other types of structure?

hydrogen bond

(iii) Name one type of bonding that does **not** occur in the primary or secondary structure of the protein.

disulfide bond.

[3]

(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

(i) What name is given to these catalysts?

~~homogeneous~~ heterogeneous ✗

(ii) Give **two** changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.

pH and temperature.

It only activated in specific pH and temperature.

The most reactive rate is at optimum.

[4]

Examiner comment – grade E

(a) Although this candidate correctly chose **K** as the building block, the mark was not gained because the answer stated that **K** contained an amide group, rather than containing an amine group. In part **(ii)** the candidate incorrectly stated that the ribose **J** would form glucose, **L**, as a polymer.

(b) 'Covalent' was a required part of the answer to part **(i)** but was not given in this case.

(c) The term 'enzyme' had to be stated to gain the mark in part **(i)**. In part **(ii)** the candidate gained a mark for suggesting that a change in pH would inactivate the enzyme, but no indication was given that the change in temperature that was suggested was an *increase*.

Question 7

For Examiner's Use

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	
chemical environment of protons in a molecule	
identity of amino acids present in a polypeptide	

[3]

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

....

....

....

(ii) thin-layer chromatography

....

....

....

[2]

For Examiner's Use

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

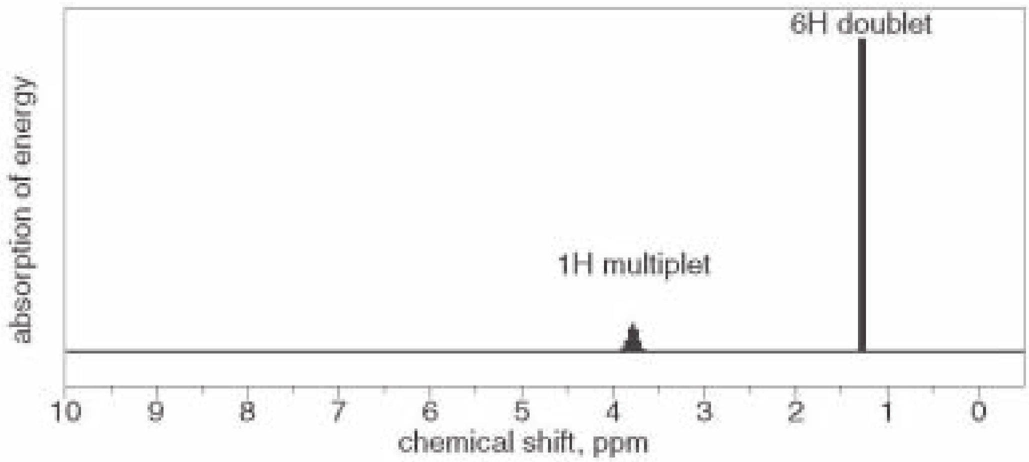
....

(iii) Explain how many atoms of this element are present in one molecule of **N**.

....

....

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

[6]

[Total: 11]

Mark scheme

7 **(a)**

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray crystallography/diffraction
chemical environment of protons in a molecule	NMR (spectroscopy) **only**
identity of amino acids present in a polypeptide	Electrophoresis / chromatography / mass spectrometry

[1] + [1] + [1]
[3]

(b) **(i)** **paper chromatography;**
The components **partition** between the solvent/moving phase and the water/liquid stationary phase *or* separation relies on different solubilities (of components) in the moving solvent and the stationary water phase. [1]

(ii) **thin-layer chromatography.**
Separation depends on the differential **adsorption** of the components onto the solid particles/phase *or* Al_2O_3 *or* SiO_2. [1]
[2]

(c) **(i)** No. of carbon atoms present = $\frac{0.2 \times 100}{5.9 \times 1.1}$ = 3.08 hence 3 carbons [1]

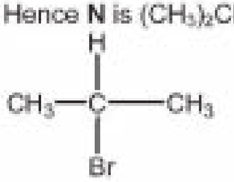
(ii) Bromine [1]

(iii) **One** bromine is present as there is only an M+2 peak / no M+4 peak *or* the M and M+2 peaks are of similar height [1]

(iv) *NMR spectrum shows a single hydrogen split by many adjacent protons and 6 protons in an identical chemical environment. This suggests...*
two $-CH_3$ groups and a lone proton attached to the central carbon atom [1]

Empirical formula of **N** is C_3H_7Br [1]

Hence **N** is $(CH_3)_2CHBr$ *or*



[1]
[6]

[Total: 11]

General comment

This question covered analysis, chromatography and spectroscopy. Parts **(a)** and **(b)** were concerned with recall of knowledge, whereas part **(c)** involved application skills. Most candidates scored at least two marks on part **(a)**, but the chemical principles involved in part **(b)** were often ignored: many candidates merely gave a description of how the techniques were carried out. The last part of **(c)** seemed only to be accessible to the more able candidates.

Example candidate response – grade A

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray crystallography
chemical environment of protons in a molecule	Nuclear Magnetic Reconance (NMR)
identity of amino acids present in a polypeptide	Electrophoresis

[3] 3

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

Paper chromatography uses partition coefficient principle as the stationary phase is liquid (water) and the mobile phase is liquid (solvent), hence the separation of the component of the mixture is due to ~~the~~ different solubility of substance in the stationary and mobile phase.

(ii) thin-layer chromatography

Thin-layer chromatography uses absorption coefficient principle as the stationary phase is solid (~~silica~~ alumina) on a thin sheet of plastic and the mobile phase is liquid (solvent), hence the separation of the substance is due to different adsorption ~~of~~ between the substance and the stationary phase relative to their solubility in the solvent.

[2] 2

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

$n = \frac{100}{1.1}\left(\frac{0.2}{5.9}\right) = 3.08 = 3$ carbons

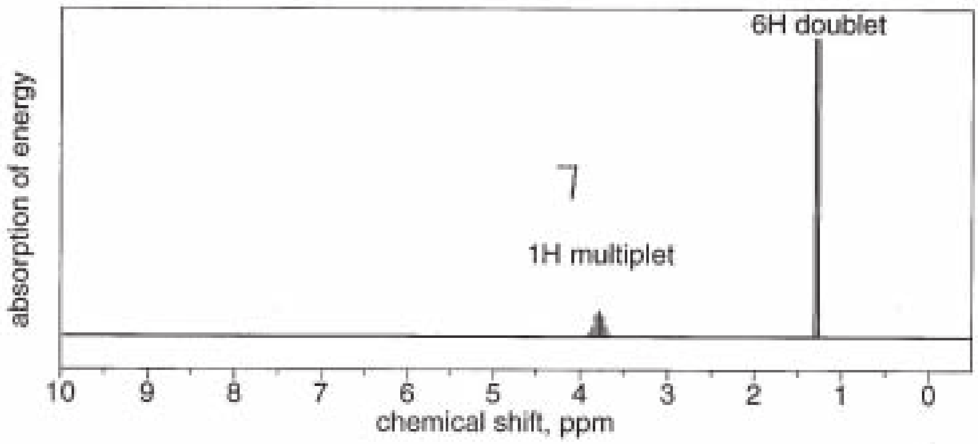
(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

bromine

(iii) Explain how many atoms of this element are present in one molecule of **N**.

Only one atom because the ratio of $^{79}Br : ^{81}Br$ is 1:1.

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

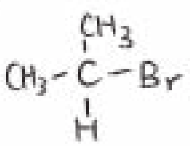
Empirical formula is C_3H_7Br

There are two peaks which show two different chemical environments.
~~The 1H multiplet~~

The 6H doublet shows ~~that~~ the presence of two CH_3 groups due to ~~similar~~ their high intensities

The 1H multiplet shows the CH group due to the presence of two similar chemical environment. [6]

[Total: 11]



Structural formula is $CH_3CH(CH_3)Br$.

Examiner comment – grade A

(a) Like this candidate, many scored all three marks here. For the first box, 'X-Ray' had to be coupled with 'crystallography' or 'diffraction' to gain the mark. There were three acceptable techniques for the last box: electrophoresis, chromatography or mass spectrometry.

(b) This candidate clearly described the differences between the two techniques: paper chromatography relies of the partition of the components between the stationary and the mobile phases, whereas thin-layer chromatography uses the differential adsorption of the components on the solid phase, coupled with their solubilities in the moving solvent.

(c) The calculation in part **(i)** was clearly set out. Although this candidate correctly deduced that bromine was present, the explanation in part **(iii)** was incomplete: the 1:1 ratio of ^{79}Br : ^{81}Br needed to be related to the 1:1 ratio of the M:M+2 peaks. Although the interpretation of the NMR spectrum in part **(iv)** was not a full one, this candidate deduced the correct empirical and structural formulae.

Example candidate response – grade C

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray.
chemical environment of protons in a molecule	nuclear ~~mass~~ magnetic ~~sa~~ resonance
identity of amino acids present in a polypeptide	electrophoresis

[3]

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

The organic molecules are separated in different length using a suitable solvent such as alcohol.

(ii) thin-layer chromatography

particiant coefficient that the ratio of dissolves solutes between two immicible liquid.

[2]

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

$$\text{no. of C} = \frac{100}{1.1} \times \frac{0.20}{5.9}$$

≈ 3 carbon atom

(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

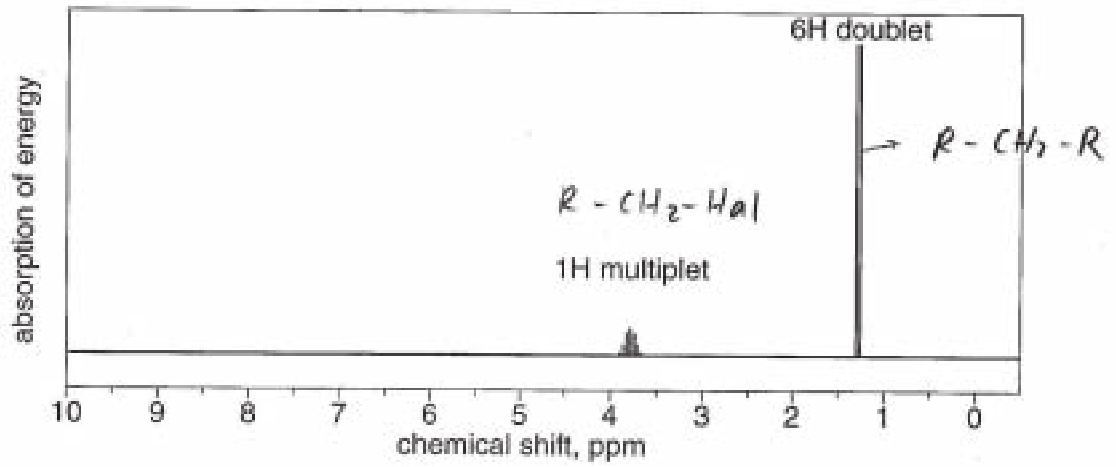
Bromine.

(iii) Explain how many atoms of this element are present in one molecule of **N**.

~~altogether there are 7 hydrogen, the ratio~~ peak M+2 similar height to the M peak $\therefore$ 1 bromine atom.

~~$\therefore$ 6 carbon + 7 hydrogen + 1 Br = 14 atoms.~~

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

= C_3H_7Br //

$R-CH_2-R$: 1.3 ppm

$R-CH_2-Hal$: 3.2 – 3.7 ppm

the halogen is Br. $\therefore$

$CH_3CH_2CH_2Br$

[6]

Examiner comment – grade C

(a) The first mark was lost through the omission of 'crystallography'.

(b) This answer did not explain the chemical principles behind paper chromatography. Had the description of thin-layer chromatography been included in part **(i)** rather than part **(ii)**, it might have been awarded a mark.

(c) There were clear and correct answers to parts **(i)**, **(ii)** and **(iii)**. In part **(iv)** the empirical formula was correct, but the interpretation of the NMR spectrum looked only at the chemical shift values, and ignored both the integration values and the splitting pattern.

Example candidate response – grade E

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	X-ray ~~crystallisation~~ crystalisation bod
chemical environment of protons in a molecule	NMR.
identity of amino acids present in a polypeptide	electrophoresis.

[3]

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

Put in an ~~[illegible]~~ medium.
The medium is ionic. ~~thus~~ ~~those~~
If the medium is cation, cation will be repel.

(ii) thin-layer chromatography

Place a ~~a~~ wire connecting to a electric supply.
~~the~~ Those cation are attracted to cathode
Those anion are attracted to anode.

[2]

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

(i) Calculate how many carbon atoms are present in one molecule of **N**.

$n_c = \frac{100}{1.1}\left(\frac{0.20}{5.9}\right)$ ∴ 3 carbons.

$= 3.1$

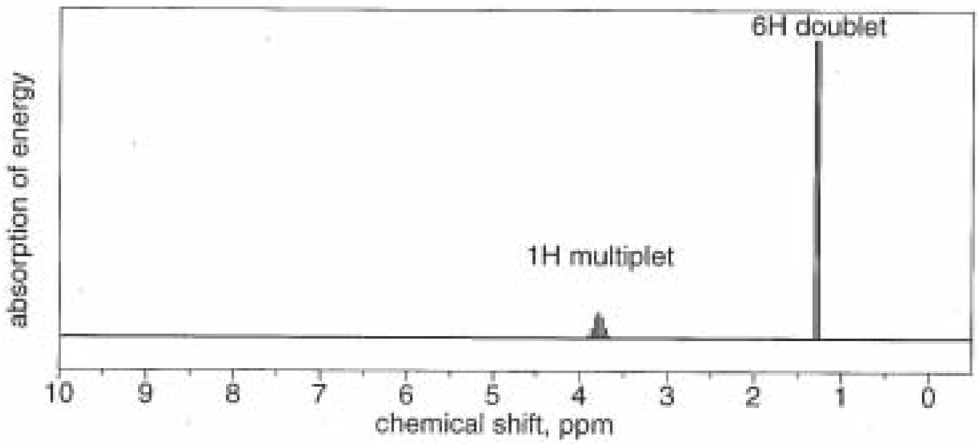
(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

Oxygen.

(iii) Explain how many atoms of this element are present in one molecule of **N**.

2 atoms.

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

empirical formula : C_3H_8O

∴ At 6H doublet, the chemical shift is around 1.3 ppm $R-CH_2-R$

$R-O-CH_3$.

∴ At 1H multiplet, the chemical shift is around 3.3 – 4.0

The structural formula of N is $CH_3-CH_2O-CH_3$ #

[6]

[Total: 11]

Examiner comment – grade E

(a) Bearing in mind that there is little detail on this technique in the syllabus, the word 'crystallisation' was accepted as being near enough to 'crystallography' to gain the mark.

(b) This candidate had poor understanding of the principles behind paper chromatography. The description of thin-layer chromatography seemed more appropriate to that for electrophoresis.

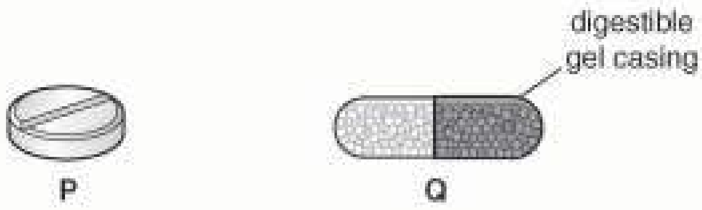
(c) The standard calculation in part **(i)** was shown clearly. This candidate did not show an understanding of the significance of the M+2 peak in the mass spectrum: the answers to parts **(ii)** and **(iii)** were incorrect. The interpretation of the NMR spectrum relied on chemical shift values, ignoring both the integration (total H = 7H, whereas the candidate's empirical formula contained 8H) and the splitting pattern.

Question 8

For Examiner's Use

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

(a) Many common drugs are taken by mouth in forms similar to those shown.



(i) Some drugs are available in solution. How would the speed of action of this form compare with **P** and **Q**? Explain your answer.

....

....

(ii) Explain which of the two forms, **P** or **Q**, would act the most rapidly when taken by mouth.

....

....

(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of **Q** prevents this.

....

....

[3]

(b) After an abdominal operation drugs are often delivered by means of a 'drip' inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

....

....

....

[2]

For Examiner's Use

(c) One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, $HOCH_2CH_2OH$.

$$2n\ HOCH_2CH_2OH \rightarrow H{-}(OCH_2CH_2OCH_2CH_2)_n{-}OH + (2n{-}1)\ H_2O$$

(i) What type of reaction is this?

....

Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

....

(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

....

....

....

(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

....

[5]

[Total: 10]

Mark scheme

8 **(a)** **(i)** Soluble form would be most effective [1]

(ii) **Q**, since the 'mini-pills'/granules/powder have a larger surface area
or **P**, because it has no protective casing [1]

(iii) The gel coat stops it being broken down while passing through the upper part of the digestive system/stomach
or the gel coat is stable to stomach acid. [1]
[3]

(b) The drug is taken quickly/directly to the target
or more accurate dosing can be achieved [1]

When the drug is taken by mouth it has to pass through the stomach/intestine wall to get into the bloodstream. *or* some is digested/lost to the system [1]
[2]

(c) **(i)** condensation (polymerisation) [1]

(ii) hydrogen bonds *or* van der Waals' [1]

(iii) It would change the overall shape of the (drug) molecule
The 'fit' into the active site would be less effective [1] + [1]

(iv) Hydrolysis [1]
[5]

[Total: 10]

General comment

The question involved little knowledge recall; its successful answering lay in the careful reading of the stem of the question of each part, before putting pen to paper. Many candidates wrote answers to what they thought the question was, rather than considering what the question actually asked. Most candidates managed to score at least five marks, however, but few scored more than eight.

Example candidate response – grade A

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

(a) Many common drugs are taken by mouth in forms similar to those shown.

(i) Some drugs are available in solution. How would the speed of action of this form compare with **P** and **Q**? Explain your answer.

Drugs in solution will be faster because the ~~digestion~~ break down of casing of P and Q takes time.

(ii) Explain which of the two forms, **P** or **Q**, would act the most rapidly when taken by mouth.

Q, this is because the drugs inside Q ~~has~~ are smaller and thus larger surface area exposed to the environment.

(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of **Q** prevents this.

Q has a digestible gel casing which prevent the drugs from breaking in the stomach due to acidic condition before it reaches the intestine, as the HCl in the stomach need to break down the casing first. [3]

(b) After an abdominal operation drugs are often delivered by means of a 'drip' inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

Smaller dose can be used and hence more economic and causes less side effects. The response will be much faster also. And the patient does not have to be conscious. [2]

(c) One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, $HOCH_2CH_2OH$.

$$2n\ HOCH_2CH_2OH \rightarrow H{-}(OCH_2CH_2OCH_2CH_2)_n{-}OH + (2n-1)\ H_2O$$

(i) What type of reaction is this?

Condensation polymerisation

Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

Hydrogen bond

(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

This is because the enzymes need to break down the hydrogen bonds between the PEG molecules. ~~bef~~ before it can break down the drug. Thus, the drug is shielded ~~pe~~ temporaly from the enzymes.

(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

Hydrolysis

[5]

Examiner comment – grade A

(a) Careful reading of the stem of each of the three parts to this question allowed this candidate to score all three marks, for recognising that both **P** and **Q** will first need to be dissolved to allow them to act, for being aware that once the gel casing has been digested the smaller particles in **Q** will react/dissolve more quickly than the bulky **P** and for taking the hint from the stem in part **(iii)** that the capsule can pass through the stomach unchanged.

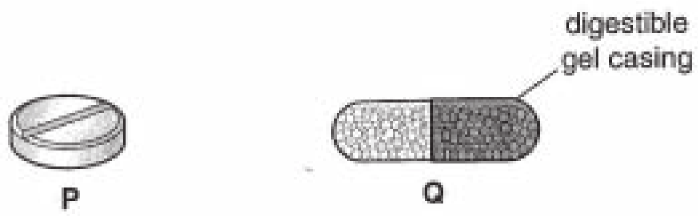
(b) This candidate picked up the idea that the dosage in a drip can be more closely adjusted and monitored, but did not address the problems of oral administration: that some of the drug is likely to be lost through hydrolysis or excretion.

(c) This candidate showed good ability in applying knowledge of the core syllabus to the structure and role of the PEG molecule. The word 'condensation', needed for the mark in part **(i)**, was included; 'van der Waals' was a possible alternative to 'hydrogen bonding' in part **(ii)**. This candidate appreciated that the key point in part **(iii)** was that coupling the drug molecule to PEG made it more difficult for the enzyme to fit around it. Mention of active site bonding, or changing the overall shape of the molecule, would have gained the second mark.

Example candidate response – grade C

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

(a) Many common drugs are taken by mouth in forms similar to those shown.



(i) Some drugs are available in solution. How would the speed of action of this form compare with **P** and **Q**? Explain your answer.

Drugs in solution has a faster speed of action, as they are not enclosed by capsule, and not in solid form.

(ii) Explain which of the two forms, **P** or **Q**, would act the most rapidly when taken by mouth.

P would act most rapidly. It is not enclosed in gel. Therefore it can directly dissolve in water to react.

(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of **Q** prevents this.

Gel casing prevent drug to be released too early. It has very small (nano-sized holes) which slowly enlarges only in the presence of water to enable release of drug. [3]

(b) After an abdominal operation drugs are often delivered by means of a 'drip' inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

If taken by mouth, drug may get destroyed by pH in stomach and it ~~is~~ reacts too early, before even reaching the target organs. [2]

(c) One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, $HOCH_2CH_2OH$.

$$2n\ HOCH_2CH_2OH \rightarrow H{-}(OCH_2CH_2OCH_2CH_2)_n{-}OH + (2n-1)\ H_2O$$

(i) What type of reaction is this?

~~Hydrolysis~~ Condensation. (dehydrolysis).

Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

Hydrogen bond (with the ~~O-H~~ O-H part of PEG).

(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

Because the ~~H~~ Hydrogen bond formed between PEG molecule and drug molecule is very strong and can only be broken in highly acidic or highly alkaline (extreme conditions).

(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

hydrolysis.

[5]

Examiner comment – grade C

(a) In part **(i)** this candidate understood that if the drug was already in solution it would act more quickly. The mark scheme for part **(ii)** allowed the candidate to choose either **P** or **Q**: the mark being awarded for a coherent and logical explanation of the choice. This candidate explained clearly why they thought that **P** would act more rapidly. In part **(iii)**, however, the candidate did not address the different chemical environments of the mouth, stomach and intestine: if the gel casing is digestible, but yet protects the drug inside from reacting before it reaches the intestine, it must be inert to stomach acid, but reactive towards the conditions (enzyme or higher pH) inside the intestines.

(b) This candidate correctly pointed out the problems of loss through digestion in the stomach, but did not mention the advantages of the intravenous route.

(c) Full marks were gained for the answers to parts **(i)**, **(ii)** and **(iv)**. The answer to part **(iii)**, however, did not address the two important features of coupling the drug molecule to PEG: it will change the overall shape of the molecule, and thus will not allow as good a fit into the active site.

Example candidate response – grade E

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

(a) Many common drugs are taken by mouth in forms similar to those shown.

(i) Some drugs are available in solution. How would the speed of action of this form compare with **P** and **Q**? Explain your answer.

Speed of action of Q is faster than P. It use nanotechnology. It coat with digestible gel casing.

(ii) Explain which of the two forms, **P** or **Q**, would act the most rapidly when taken by mouth.

P because it does not have coat with digestible gel casing.

(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of **Q** prevents this.

The digestible gel casing only react with acid. It does not react rapidly with saliva. Thus not easily broken down by enzyme.

[3]

(b) After an abdominal operation drugs are often delivered by means of a 'drip' inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

No any side effect. The drugs can be absorb efficiently and directly by the blood.

[2]

(c) One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, $HOCH_2CH_2OH$.

$$2n\ HOCH_2CH_2OH \rightarrow H{-}(OCH_2CH_2OCH_2CH_2)_n{-}OH + (2n-1)\ H_2O$$

(i) What type of reaction is this?

~~Hydrolysis~~ . condensation .

Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

Hydrogen bond.

(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

less active sites are available for enzymes attaches

PEG molecule acts as inhibitor.

(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

~~condensation~~ Hydrolysis

[5]

Examiner comment – grade E

The weaker candidates were able to score fairly well on this question, so those who overall obtained a grade E often scored half marks here.

(a) This candidate demonstrated a common error in part **(i)** comparing **P** and **Q** with each other, rather than with drugs in solution. The answer in part **(ii)** seemed to contradict that given in part **(i)**. Pointing out that the gel casing might slow the drug's absorption gained the mark here. In part **(iii)** the candidate suggested that the gel would react with acid (in the stomach): if this were the case the drug inside would have been broken down *before* reaching the intestine.

(b) This candidate correctly drew attention to the speed of action available through the intravenous route, but did not address the problems of drug hydrolysis/loss via the oral route.

(c) Full marks were gained for the answers to parts **(i)**, **(ii)** and **(iv)**. The candidate's answer to part **(iii)** suggested that the PEG molecule itself would act as an enzyme inhibitor, rather than altering the shape of the drug molecule to hamper its binding to the active site.

Paper 5 – Planning, analysis and evaluation

Question 1

1 When potassium nitrate dissolves in water, the temperature of the solution goes down because the enthalpy of solution is endothermic.

For Examiner's Use

> You are to plan an experiment to investigate how the solubility of potassium nitrate varies with temperature. The units of solubility are grams per one hundred grams of water (g/100g water).

(a) **(i)** Predict how the solubility of potassium nitrate will change if the solution temperature is **increased**.

Explain your prediction using the fact that dissolving potassium nitrate is endothermic.

prediction ....

....

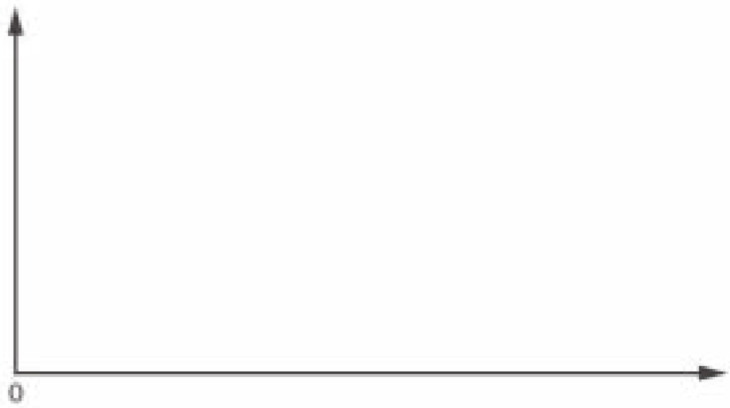
explanation ....

....

....

....

(ii) Display your prediction in the form of a sketch graph, labelling clearly the axes.



[3]

(b) In the experiment you are about to plan, identify the following.

(i) the independent variable ....

(ii) the dependent variable ....

[2]

(c) Design a laboratory experiment to test your prediction in **(a)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials,

a boiling tube,
a looped wire stirrer,
a thermometer covering the temperature range 0 °C to 100 °C.

Describe how you would carry out the experiment. You should

- ensure a wide range of results suitable for analysis by graph,
- decide on the amounts of water and potassium nitrate to use,
- measure the amounts of the two reagents,
- heat the apparatus,
- decide at what point the temperature of the solution is to be taken.

....

For Examiner's Use

(d) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

....

....[1]

(e) Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in **(a)**. The headings **must** include the appropriate units.

[2]

[Total: 15]

For Examiner's Use

Mark scheme

Question	Sections	Indicative material	Mark
1 (a)	PLAN Problem	Predicts that the solubility increases (with temperature). If gave "decreasing" then ecf into sketch and do not mark explanation.	[1]
		KNO_3 needs energy to dissolve OR supplying heat or energy or increasing temperature will promote the endothermic change/ reaction.	[1]
		Any graph showing an increasing solubility with temperature (curve or straight line) that reflects the prediction. Do not accept a concave curve that becomes vertical. Accept a convex curve (accept with a max or an end decline). There can be a plateau in solubility. Have solubility on the *y* axis and temperature on the *x* axis. Ignore units unless the unit is the label. If gave "decreasing" above then ecf into sketch. If the prediction is irrelevant e.g. rate then can mark sketch as stand alone	[1]
(b)	PLAN Problem	**(i)** Temperature as the independent variable.	[1]
		(ii) Solubility as the dependent variable. Has to be a double quantity, not just mass or amount of solute.	[1]
		Ecf "concentration" if given as *y*-axis in sketch.	

(c)	PLAN Methods	There are four different approaches, all of which share the first five marking points. Use 7 number labelled ticks and crosses for these points. (i) At least 5 experiments. (ii) Uses a range of at least 40°C. (iii) Pilot run to choose relative amounts of materials. (iv) Mass by balance. Water by measuring cylinder/pipette/ burette or mass of water by balance. (v) stirs Alternate 1 (vi) Heat mixture to dissolve all the solute. (vii) Cool and measure the temperature at which first crystals appear. OR Alternate 2 (vi) Heats mixture to a particular temperature. (vii) Filters the solution (not cooled or decanted) and weighs the residue. OR Alternate 3 (vi) Heats mixture to a particular temperature. (vii) filters the solution (not cooled or decanted) and evaporates the filtrate and weighs solid. OR Alternate 4 (vi) Heats mixture to dissolve the solute. (vii) Records temperature at which the solute dissolves.	 [1] [1] [1] [1] [1] [1] [1]
(d)	PLAN Methods	Reference to 'hot' apparatus, not Bunsen or water with Handle with tongs/heat resistant gloves/cool before handling	 [1]

(e)	PLAN Methods	**1(c)(i)** & **(ii)** could award here. Mass of solid dissolved; volume/mass of water; solubility; temperature (solution) and units. Only accept a final temperature if it relates to the temperature of solution. All five correct 2 marks; Three or four correct (one/two errors) 1 mark; Two or less correct (more than two errors) zero.	[2]
	Total		**[15]**

General comment

Typically most candidates answered well in parts **(a)** and **(b)**. In part **(c)** answers were often started without a clear path to solubility or an appreciation of the bullet points in the stem.

Example candidate response – grade A

1 When potassium nitrate dissolves in water, the temperature of the solution goes down because the enthalpy of solution is endothermic.

> You are to plan an experiment to investigate how the solubility of potassium nitrate varies with temperature. The units of solubility are grams per one hundred grams of water (g/100g water).

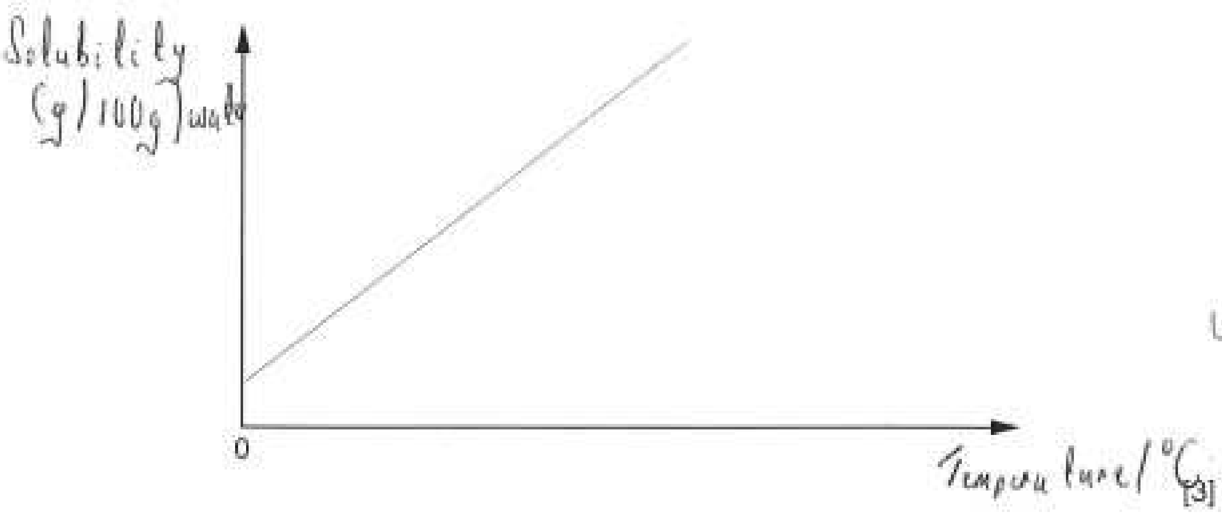
(a) (i) Predict how the solubility of potassium nitrate will change if the solution temperature is **increased**.

Explain your prediction using the fact that dissolving potassium nitrate is endothermic.

prediction: Solubility of potassium nitrate increases with increase in temperature

explanation: $KNO_{3(s)} \rightleftharpoons K^+_{(aq)} + NO_3^-{}_{(aq)}$ $\Delta H^\circ > 0$
since the enthalpy change of solution is greater than zero according to Le Chatelier changes will occur when temperature is increased so as to maintain equilibrium thus when temperature is increase equilibrium shifts to the right increasing solubility

(ii) Display your prediction in the form of a sketch graph, labelling clearly the axes.



[3]

(b) In the experiment you are about to plan, identify the following.

(i) the independent variable: Temperature

(ii) the dependent variable: Solubility of KNO_3

[2]

(c) Design a laboratory experiment to test your prediction in **(a)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials,

- a boiling tube,
- a looped wire stirrer,
- a thermometer covering the temperature range 0 °C to 100 °C.

Describe how you would carry out the experiment. You should

- ensure a wide range of results suitable for analysis by graph, ✓1
- decide on the amounts of water and potassium nitrate to use, ✓2
- measure the amounts of the two reagents, ✗3
- heat the apparatus,
- decide at what point the temperature of the solution is to be taken.

1 – ~~Place an empty boiling tube of about 300 cm³ – 500 cm³ on a balance and measure its mass~~

2 – ~~in an~~ to the empty boiling tube of about ~~300 cm³~~ place

3 – 100 g of distilled water using a wash bottle making sure it is not in excess of 100 g using the tear function.

4 – To the 100 g of distilled water in the boiling tube place a known mass of KNO_3 in excess and shake carefully until it no longer dissolves

5 – Place the solution in the water bath as shown in the diagram and lit the burner measuring the temperature until it reaches 90 °C at the same time stirring carefully with the looped wire stirrer ✓6 ✓5

6 – remove the boiling tube with the solution from the water bath and filter the solution using a funnel, filter paper and receiving container making sure all ~~dissolve~~ the solution is collected. ✓7

7 – heat the filtrate to boiling point until all the liquid has evaporated leaving a white residue of $KNO_{3(s)}$

8 – measure and record the mass of $KNO_{3(s)}$ left after evaporation using the top pan balance ✓4

9 – Repeat steps 1 to 4 and 6 to 9 but using a different temperature in step 5 ~~from~~ and obtain six ~~different~~ more reading with temperature 40 °C; 50 °C, 60 °C; 70 °C, 80 °C, 90 °C **[7]**

(d) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

A hazard is catching fire from the burner.

precaution is wearing fire proof clothing ..... [1]

(e) Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in **(a)**. The headings **must** include the appropriate units.

mass of distilled water used / g	Temperature reached in step 5 / °C	mass of KNO_3 in step 8 / g	solubility of KNO_3 / (g/100g)
100	30	a	a/100
100	40	b	b/100
100	50	c	c/100
100	60	d	d/100
100	70	e	e/100
100	80	f	f/100
100	90	g	g/100

[2]

[Total: 15]

where a, b, c, d, e & f are the masses of KNO_3 obtained at the given temperatures.
To support my prediction would be
The prediction ~~is correct~~ of solubility against Temperature.

Examiner comment – grade A

(a) (i) The prediction made was good and temperature increase was linked to increasing solubility for an endothermic process.

(ii) A good sketch graph was drawn with correctly labelled axes.

(b) Both variables were correctly identified in **(i)** and **(ii)**.

(c) A well reasoned and presented plan was given using numbered points which aids clarity. Whilst not explicit in **(c)**, the number of experiments and range were both clearly stated in the table in **(e)**. In steps 1–3 and 8 the masses of water and dissolved solute measured using the balance were credited. Steps 5–8 describe a solubility experiment as in Alternate 3 in the mark scheme and gained the marks and also the mark for stirring. The only omission was that no trial run to determine reasonable quantities was attempted.

(d) The requirement here was for a hazard specifically related to the experiment rather than a general laboratory hazard.

(e) All the necessary columns were present along with appropriate units.

Example candidate response – grade C

1 When potassium nitrate dissolves in water, the temperature of the solution goes down because the enthalpy of solution is endothermic.

> You are to plan an experiment to investigate how the solubility of potassium nitrate varies with temperature. The units of solubility are grams per one hundred grams of water (g/100g water).

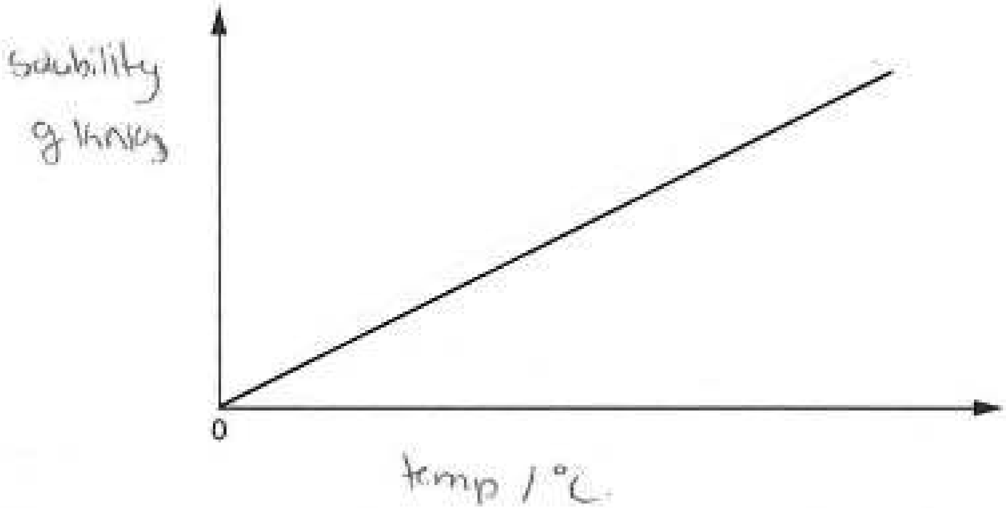
(a) **(i)** Predict how the solubility of potassium nitrate will change if the solution temperature is **increased.**

Explain your prediction using the fact that dissolving potassium nitrate is endothermic.

prediction ...Solubility will increases (Solubility g KNO_3 increases) if temperature increase.

explanation ...As reaction is endothermic the higher the amount of heat available for KNO_3 in solution more molecules have sufficient activation energy for the KNO_3 to dissolve. (Forward reaction favoured)

(ii) Display your prediction in the form of a sketch graph, labelling clearly the axes.



[3]

(b) In the experiment you are about to plan, identify the following.

(i) the independent variable ...Temperature /°C.

(ii) the dependent variable ...KNO_3 dissolved

[2]

(c) Design a laboratory experiment to test your prediction in **(a)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials,

a boiling tube,
a looped wire stirrer,
a thermometer covering the temperature range 0 °C to 100 °C.

Describe how you would carry out the experiment. You should

- ensure a wide range of results suitable for analysis by graph,
- decide on the amounts of water and potassium nitrate to use,
- measure the amounts of the two reagents,
- heat the apparatus,
- decide at what point the temperature of the solution is to be taken.

(i) Set up ~~a~~ thermostatically controlled water bath at 20 °C

(ii) Place 50 cm^3 of distilled water in a boiling tube
NB Using wire stirrer stir water in boiling tube frequently.

(iii) Place this boiling tube in the water bath and leave for a minimum of 5 mins

(iv) While boiling tube is in water measure 5 masses of KNO_3 using a ~~bal~~ balance which are between 15.05 – 14.95 g
masses have to be equal

(v) Place this mass of nitrate in water in the boiling tube after checking ~~water~~ temperature in the boiling tube is 20 °C.

(vi) Leave experiment for 2 – 5 mins (5 10 mins to 7 mins) ~~(...)~~
stirring with a ~~thermometer~~ stirrer gently constantly while this is taking place using a stopwatch to time (keep time constant in all experiments)

(vii) Filter out ~~water~~ water from the boiling tube after allowing to cool dry remaining solid mass of KNO_3 and measure it.

(vi) Record all readings in a table and repeat experiment with temperatures 30 °C ; 40 °C ; 50 °C
60 °C ; 70 °C ; 80 °C. **[7]**

(viii) Draw graph and compare results

For Examiner's Use

(d) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

Boiling tube can get hot hence use gloves to handle any hot apparatus ......[1]

(e) Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in **(a)**. The headings **must** include the appropriate units.

Temperature /°C	Mass of KNO_3 put in boiling tube /g	Mass of KNO_3 crystals filtered /g	Mass of KNO_3 dissolved /g	Volume of H_2O in boiling tube /cm³	Solubility = g x 2
20					
30					
40					
↓					
	100 cm³				

[2]

Examiner comment – grade C

(a) **(i)** The candidate's prediction was good. The explanation of being endothermic, higher heat, forward reaction favoured was just acceptable for credit to be awarded.

(ii) The sketch graph was good.

(b) The independent variable was correct but not the dependent which was in effect a mass of solute. This conflicted with the *y*-axis in the sketch.

(c) The response was reasonably organised using numbered points. There was a good approach to solubility determination that missed marks on points of detail so gained four marks out of seven. The fifth mark (stirring) was gained in step (ii) and the first mark (5 experiments) in step (iv). The approach of the candidate was Alternate 2 in the mark scheme gaining mark six (heating mixture to a particular temperature) in steps (v) and (vi). The idea of filtering in step (vii) was correct, but cooling would cause more solid to be collected so giving an incorrect solubility. The next step gained the mark for a suitable range.

(d) To gain credit, the gloves needed to be described as heatproof.

(e) The table was well done containing all the necessary columns but the solubility column lacked a correct unit.

Example candidate response – grade E

1 When potassium nitrate dissolves in water, the temperature of the solution goes down because the enthalpy of solution is endothermic.

> You are to plan an experiment to investigate how the solubility of potassium nitrate varies with temperature. The units of solubility are grams per one hundred grams of water (g/100g water).

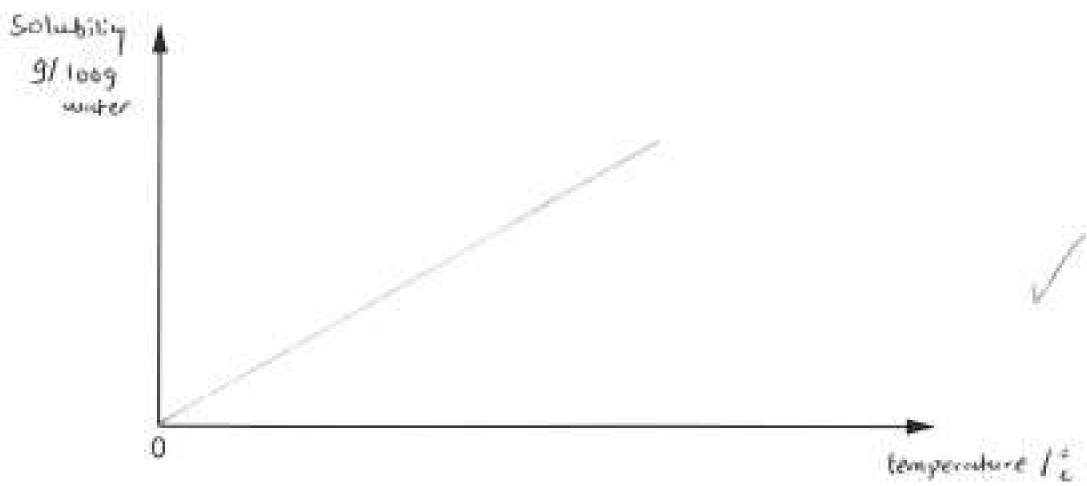
(a) (i) Predict how the solubility of potassium nitrate will change if the solution temperature is **increased**.

Explain your prediction using the fact that dissolving potassium nitrate is endothermic.

prediction The Solubility of potassium nitrate will increase on increasing temperature as it will absorb temperature

explanation Solubility increases because molecules will gain kinetic energy hence will increase the solubility of potassium nitrate

(ii) Display your prediction in the form of a sketch graph, labelling clearly the axes.



[3]

(b) In the experiment you are about to plan, identify the following.

(i) the independent variable temperature of solution

(ii) the dependent variable Solubility of potassium nitrate

[2]

(c) Design a laboratory experiment to test your prediction in **(a)**.

In addition to the standard apparatus present in a laboratory you are provided with the following materials,

a boiling tube,
a looped wire stirrer,
a thermometer covering the temperature range 0 °C to 100 °C.

Describe how you would carry out the experiment. You should

- ensure a wide range of results suitable for analysis by graph,
- decide on the amounts of water and potassium nitrate to use,
- measure the amounts of the two reagents,
- heat the apparatus,
- decide at what point the temperature of the solution is to be taken.

Step 1: A known volume of water will be measured using a graduated 50 cm^3 measuring cylinder (volume of 30 cm^3 of water used)

Step 2: The mass of potassium nitrate will be measured using a blanced (from a range of 5 to 10 g.)

Step 3: The volume of water is transfered in a ~~plastic cup~~ boiling tube and the initial temperature recorded.

~~Step 4: The mass of potassium nitrate will be added to the plastic cup, and placed in a hot water bath~~

Step 4: The mass of potassium is then added to the boiling tube and ~~a source of heat~~ the content of the tube is allow to warm.

Step 5: The mixture is stirred using the looped wire to allow a uniform temperature throughout. 5

Step 6: The temperature of the solution will be recorded at equal interval of time.

Step 7: The experiment is repeated for sevral values whereby the temperature is varied and solubility of potassium nitrate is obtained.

(d) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

As the experiment involves heating gloves must be worn to protect the hand to heating element. [1]

(e) Draw a table with appropriate headings to show the data you would record when carrying out your experiments and the values you would calculate in order to construct a graph to support or reject your prediction in **(a)**. The headings **must** include the appropriate units.

Experiment number	Mass of potassium nitrate used / g	Volume of water used / cm^3	Initial temperature / °C	Final temperature / °C	Change in temperature / °C

x1
x2
x3

[2]

Examiner comment – grade E

(a) (i) The candidate's prediction was correct although the final phrase 'will absorb temperature' has no real meaning. The explanation, whilst not incorrect, does not explain the prediction in terms of promoting the endothermic change.

(ii) The sketch graph here was good and complete in every detail.

(b) Both the independent and dependent variables were correctly identified in **(i)** and **(ii)**.

(c) Answering by way of numbered points was an aid to clarity. However, the bullet points in the stem were not properly addressed leading to a low score. Up to step 5 the candidate was progressing reasonably and gained some credit for measuring and stirring. However step 6 misses how solution was achieved and the measurement of time was irrelevant. Step 7 does not indicate the number of experiments proposed nor their range.

(d) A more detailed description of gloves (i.e. heatproof) was required to gain credit.

(e) The table contains irrelevant temperature columns (final temperature was accepted as temperature of solution). There was no column for solubility. The units were correctly presented.

Question 2

For Examiner's Use

2 Chemical reactions occur more rapidly as the temperature of the reaction mixture increases. The mathematical relationship that summarises this is

$$\log_{10}(\text{rate of reaction}) = \frac{-E_A}{19T}$$

where E_A is the **activation energy** of the reaction and **T** is the **absolute temperature** in Kelvin and the **rate of reaction** can be taken as the reciprocal of the time taken in seconds **(1/time)**.

An experiment was carried out to investigate this relationship using dilute hydrochloric acid and aqueous sodium thiosulfate.

- $20\,cm^3$ of dilute hydrochloric acid was placed in a boiling tube contained in a water bath.
- $20\,cm^3$ of aqueous sodium thiosulfate was added to the dilute hydrochloric acid, while stirring and a stopwatch started.
- The temperature of the water bath was recorded.
- After a period of time the liquid became cloudy (opaque) due to the formation of a precipitate of sulfur.
- As soon as this cloudiness (opacity) appeared the time was recorded.
- The temperature of the water bath was raised and the whole experiment repeated.

(a) The results of several such experiments are recorded below.

Process the results in the table to calculate **$\log_{10}$ (rate of reaction)**, the reciprocal of the absolute temperature (**1/T**) and the 'rate of reaction' (**1/time**). You should expect the values of **$\log_{10}$ (rate of reaction)** to be negative.

Record these values to **three significant figures** in the additional columns of the table.

Label the columns you use. For each column you use include units where appropriate and an expression to show how your values are calculated.

You may use the column headings A to F for these expressions (e.g. A–B). [3]

A	B	C	D	E	F
temperature / °C	absolute temperature / K	time / s			
20.0	293	60.3			
30.0	303	46.8			
40.0	313	41.6			
45.0	318	31.6			
50.0	323	28.8			
55.0	328	25.1			
60.0	333	21.0			
65.0	338	20.4			
70.0	343	18.1			
80.0	353	15.1			

(b) Plot a graph to show the relationship between **$\log_{10}$ (rate of reaction)** and the reciprocal of the absolute temperature. You are reminded that the values for **$\log_{10}$ (rate of reaction)** are negative.
Draw the line of best fit.

(c) Circle and label on the graph any point(s) you consider to be anomalous. For each anomalous point give a different reason why it is anomalous, clearly stating which point you are describing.

For Examiner's Use

....

....

....

....

....

....

....

.... [3]

(d) Comment on whether the results obtained can be considered as reliable.

....

.... [1]

(e) Determine the slope of the graph. Mark clearly on the graph any construction lines and show clearly in your calculation how the values from the intercepts were used in the calculation of the slope.

[2]

(f) Using the value of the slope of your graph calculated in **(f)** calculate a value for the **activation energy, E_A**. Correct use of the equation will produce an answer in $kJ\,mol^{-1}$.

[1]

(g) By considering the movement of particles in the reaction explain why the rate of reaction increases with increasing temperature.

For Examiner's Use

[2]

[Total: 15]

Mark scheme

Question	Sections	Indicative material	Mark
2 (a)	ACE Data	Log_{10}(rate) or Log_{10}(1/time) or Log_{10}(1/t). One of these labels also serves as expression, full column no units. Accept log with no base.	[1]
		Reciprocal absolute temperature or reciprocal Kelvin temperature or 1/T (not temp etc.). One of these labels also serves as expression, full column with unit, K^{-1}. Don't accept $1/T \times 10^{-3}/K^{-1}$ but $/10^{-3}K^{-1}$ OK	[1]
		Data in both columns above to 3 sig figs and correct, allow 2 errors.	[1]
		Allow salvage mark for rate column if ALL correct. A heading of 1/time or 1/t or 1/C also serves as expression.	
(b)	ACE Data	Unambiguously labelled axes. 1/T on the *x*-axis and log_{10}(rate) on the *y* axis AND appropriate scaling. Ignore units unless it is the label.	[1]
		Correctly plotted points. Ecf incorrectly calculated data. All 10 points need to be plotted. Check points 3 & 7 and 1 & 10 and any others off the line.	[1]
		Line of best fit.	[1]
		Allow plot and line marks if other axes used.	

(c)	ACE Evaluation	Allow the candidate to select up to five anomalies which must include that furthest from the line. This mark is available if other axes used. The data has two anomalies, Points 3 & 7. Point 3, Timed to past opacity (not late stopping the clock alone), or solutions not equilibrated with water bath temperature or clock started early. Point 7, Timed to prior to opacity (not early stopping the clock alone), or clock started late. Give a rescue mark if both correct anomalies present but not linked to their points. These last two marks not available if other axes used.	[1] [1] [1]
(d)	ACE Evaluation	Either no repeats OR five or more points not on line hence unreliable OR most points on line OR points produce straight line hence reliable. This mark not available if other axes used.	[1]
(e)	ACE Data	Has construction lines on the plot. States intercept readings from them. (Could be to data points if the line and construction is to that point. Powers of 10 (e.g. × 10^{-3}) must be included if necessary) then calculates the slope (around –1050). Slope is $(y_1 - y_2)/(x_1 - x_2)$. The sign of the gradient must be correct from the sign produced from the intercept calculations. Allow these marks if other axes used.	[1] [1]
(f)	ACE Conclusions	Correct calculation. Any calculation that has slope above multiplied by 19 i.e. $-E_A$ = slope × 19. Or slope = $-E_A/19$. Ignore units. Also accept that calculation subsequently divided by 1000 i.e. about 19950 or 19.95. T is not in this calculation. Allow this mark for other plots.	[1]
(g)	ACE Conclusions	Increased K.E/energy/speed. More collisions/unit time or more frequent collisions or more chance of collisions or more energetic collisions or more collisions exceeding activation energy or more successful collisions or more effective collisions. NOT just more collisions.	[1] [1]
	Total		**[15]**

General comment

This was a complex data set using negative log data that was handled reasonably by most candidates. Most mark loss was in the detail e.g. not quoting data to three significant figures. The reasons given for anomalies were often inadequate. For example, stating the 'time was wrong' or even 'time was too long' are not explanations. Such a reason would need to be related to an experimental action such as 'the clock was stopped after opacity was reached'.

Example candidate response – grade A

2 Chemical reactions occur more rapidly as the temperature of the reaction mixture increases. The mathematical relationship that summarises this is

$$\log_{10}\,(\text{rate of reaction}) = \frac{-E_A}{19T}$$

where E_A is the **activation energy** of the reaction and **T** is the **absolute temperature** in Kelvin and the **rate of reaction** can be taken as the reciprocal of the time taken in seconds **(1/time)**.

An experiment was carried out to investigate this relationship using dilute hydrochloric acid and aqueous sodium thiosulfate.

- $20\,cm^3$ of dilute hydrochloric acid was placed in a boiling tube contained in a water bath.
- $20\,cm^3$ of aqueous sodium thiosulfate was added to the dilute hydrochloric acid, while stirring and a stopwatch started.
- The temperature of the water bath was recorded.
- After a period of time the liquid became cloudy (opaque) due to the formation of a precipitate of sulfur.
- As soon as this cloudiness (opacity) appeared the time was recorded.
- The temperature of the water bath was raised and the whole experiment repeated.

(a) The results of several such experiments are recorded below.

Process the results in the table to calculate **$\log_{10}$ (rate of reaction)**, the reciprocal of the absolute temperature (**1/T**) and the 'rate of reaction' (**1/time**). You should expect the values of **$\log_{10}$ (rate of reaction)** to be negative.

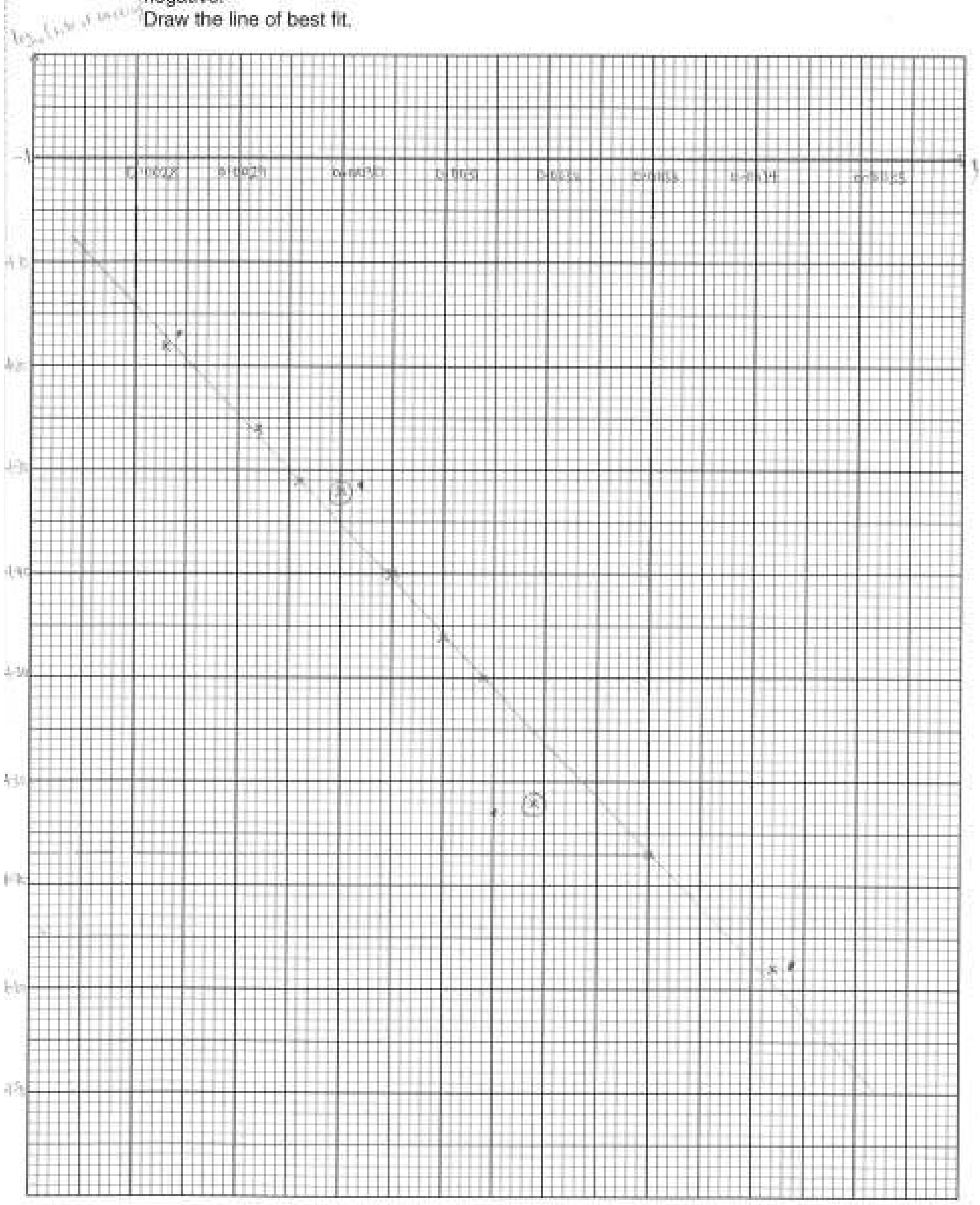
Record these values to **three significant figures** in the additional columns of the table.

Label the columns you use. For each column you use include units where appropriate and an expression to show how your values are calculated.

You may use the column headings A to F for these expressions (e.g. A–B). [3]

A	B	C	D	E	F
temperature / °C	absolute temperature / K	time / s	rate of reaction / s^{-1} $\left(\frac{1}{C}\right)$	$\log_{10}$ (rate of reaction) ($\log_{10}$ D)	reciprocal of absolute temperature (1/B) / K^{-1}
20.0	293	60.3	0.0166	−1.78	0.00342
30.0	303	46.8	0.0214	−1.67	0.00330
40.0	313	41.6	0.0240	−1.62	0.00319
45.0	318	31.6	0.0316	−1.50	0.00314
50.0	323	28.8	0.0347	−1.46	0.00310
55.0	328	25.1	0.0398	−1.40	0.00305
60.0	333	21.0	0.0476	−1.32	0.00300
65.0	338	20.4	0.0490	−1.31	0.00296
70.0	343	18.1	0.0552	−1.26	0.00292
80.0	353	15.1	0.0662	−1.18	0.00283

(b) Plot a graph to show the relationship between $\log_{10}$ **(rate of reaction)** and the reciprocal of the absolute temperature. You are reminded that the values for $\log_{10}$ **(rate of reaction)** are negative.
Draw the line of best fit.



[3]

(c) Circle and label on the graph any point(s) you consider to be anomalous. For each anomalous point give a different reason why it is anomalous, clearly stating which point you are describing.

~~For~~ The anomalous point at (0.00300, −1.32) is due to the experimenter ~~slow reaction time as the experimenter~~ stopping the stopwatch before the cloudiness appeared. ~~Some~~ ✓

The anomalous point at (0.00319, −1.62) is due to the experimenter stopping the stop watch after the cloudiness had appeared (slow reaction time). ✓

[3]

(d) Comment on whether the results obtained can be considered as reliable.

The results obtained ~~cannot~~ be considered as being reliable because there are ~~many~~ more points off the line of best fit. ✗ [1]

(e) Determine the slope of the graph. Mark clearly on the graph any construction lines and show clearly in your calculation how the values from the intercepts were used in the calculation of the slope.

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta \log_{10}(\text{rate of reaction})}{\Delta (K^{-1})} = \frac{-1.14 - (-1.67)}{0.0033 - 0.0028}$$ ✓

$$\text{Slope} = \frac{0.53}{5 \times 10^{-4}} = 1060\,\text{K}$$ ✗

[2]

(f) Using the value of the slope of your graph calculated in (e) calculate a value for the **activation energy, E_A**. Correct use of the equation will produce an answer in kJ mol^{-1}.

~~$\log_{10}(\text{reaction})$~~ ~~$\log_{10}(\text{rate of reaction}) = \frac{-E_A}{19T}$~~

~~$-E_A = \log_{10}(\text{rate of reaction}) \times 19T$~~

~~$\frac{-E_A}{19} = \frac{\log_{10}(\text{rate of reaction})}{T^2} \times T$~~

~~$\frac{1}{T^2} \times \frac{-E_A}{19} = 1060$~~

$-E_A = 1060 \times 19 \times 3.3^2$

$0.53 = \frac{-E_A}{19} \times 5 \times 10^{-4}$ ✓

$E_A = -20140\,\text{kJ mol}^{-1}$

[1]

~~$E_A = -1.8 \times 10^{9}\,\text{kJ mol}^{-1}$~~

~~$0.53 = \frac{-E_A}{19} \times 5 \times 10^{-4}$~~

(g) By considering the movement of particles in the reaction explain why the rate of reaction increases with increasing temperature.

This is because as temperature increases, the kinetic energy of the molecules increase ~~causing them to cause more effective collision~~ above the activation energy, causing them to cause more effective collision. Therefore, rate of reaction also increases.

[2]

Examiner comment – grade A

(a) The table headings were all correct, but the data had one error (0.00342 should have been 0.00341). Candidates were allowed two data errors without penalty.

(b) The plot was very well presented.

(c) Both the anomalies were correctly identified and the reason for each was correct as would be expected from a grade A candidate.

(d) The candidate's plot showed eight points exactly on the line, or only slightly off, so the candidate's response should have recognised that within acceptable experimental errors these results were reliable.

(e) The candidate had reasonable construction lines (including one to a point on the line) and read the intercepts correctly. However the data was crossed over in the calculation.

$$\frac{-1.14-(-1.67)}{0.0033-0.0028} \text{ should have been } \frac{-1.14-(-1.67)}{0.0028-0.0033}$$

This would have given a slope of -1060, the negative sign reflecting the direction of the plot.

(f) The candidate calculated a value for E_A which (although incorrect) was allowed in terms of error carried forward.

(g) The candidate made a good response to the question based on kinetic energy and effective collisions.

Example candidate response – grade C

2 Chemical reactions occur more rapidly as the temperature of the reaction mixture increases. The mathematical relationship that summarises this is

$$\log_{10}(\text{rate of reaction}) = \frac{-E_A}{19T}$$

where $\mathbf{E_A}$ is the **activation energy** of the reaction and **T** is the **absolute temperature** in Kelvin and the **rate of reaction** can be taken as the reciprocal of the time taken in seconds **(1/time)**.

An experiment was carried out to investigate this relationship using dilute hydrochloric acid and aqueous sodium thiosulfate.

- 20 cm^3 of dilute hydrochloric acid was placed in a boiling tube contained in a water bath.
- 20 cm^3 of aqueous sodium thiosulfate was added to the dilute hydrochloric acid, while stirring and a stopwatch started.
- The temperature of the water bath was recorded.
- After a period of time the liquid became cloudy (opaque) due to the formation of a precipitate of sulfur.
- As soon as this cloudiness (opacity) appeared the time was recorded.
- The temperature of the water bath was raised and the whole experiment repeated.

(a) The results of several such experiments are recorded below.

Process the results in the table to calculate $\mathbf{log_{10}}$ **(rate of reaction)**, the reciprocal of the absolute temperature **(1/T)** and the 'rate of reaction' (**1/time**). You should expect the values of $\mathbf{log_{10}}$ **(rate of reaction)** to be negative.

Record these values to **three significant figures** in the additional columns of the table.

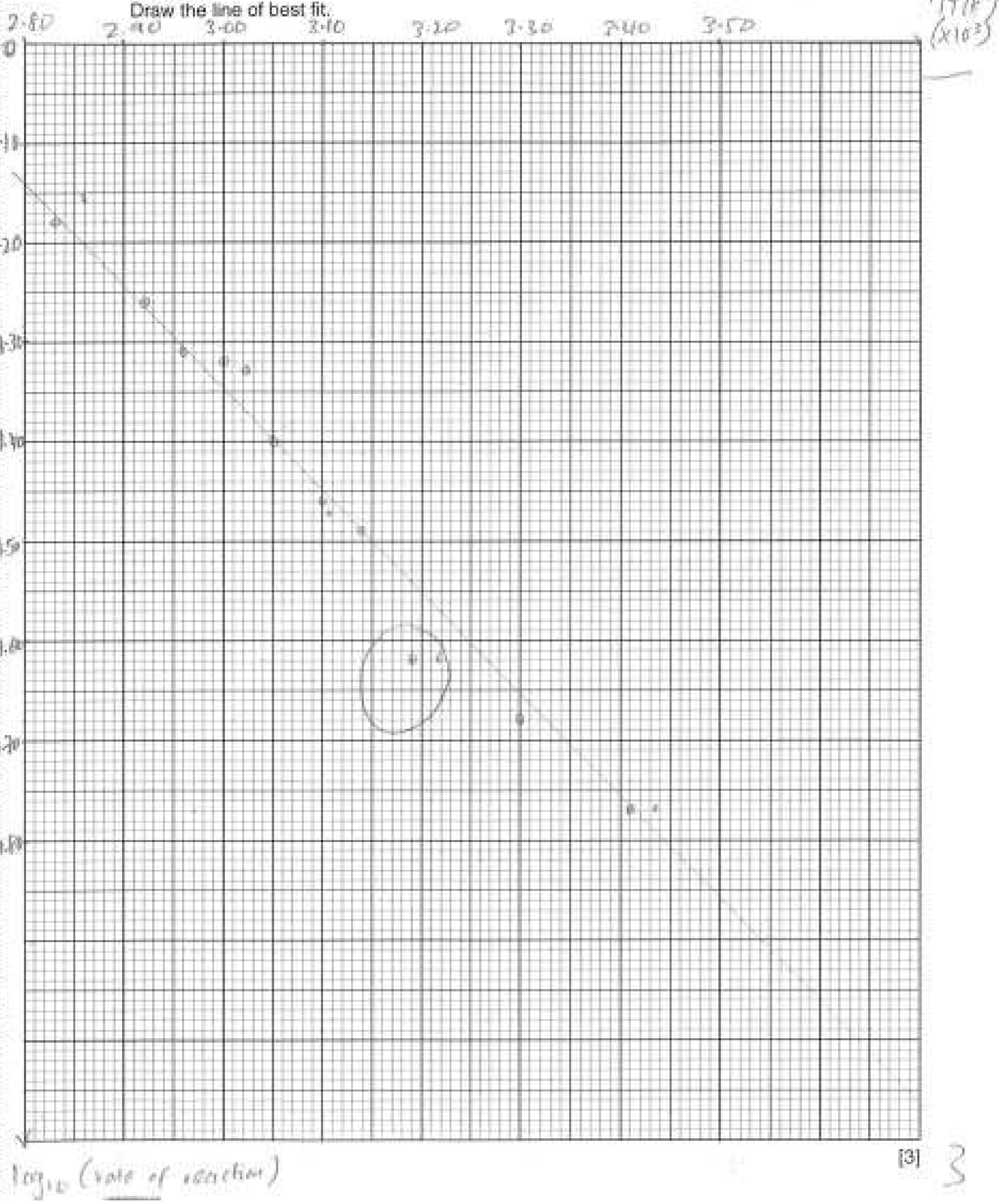
Label the columns you use. For each column you use include units where appropriate and an expression to show how your values are calculated.

You may use the column headings A to F for these expressions (e.g. A–B). [3]

A	B	C	D	E	F
temperature / °C	absolute temperature / K	time / s	1/T / K^{-1} (1/B)	1/time / s^{-1} (1/C)	$\log_{10}$(rate of reaction) (log E)
20.0	293	60.3	3.41×10^{-3}	0.017	−1.77
30.0	303	46.8	3.30×10^{-3}	0.021	−1.68
40.0	313	41.6	3.19×10^{-3}	0.024	−1.62
45.0	318	31.6	3.14×10^{-3}	0.032	−1.49
50.0	323	28.8	3.10×10^{-3}	0.035	−1.46
55.0	328	25.1	3.05×10^{-3}	0.040	−1.40
60.0	333	21.0	3.00×10^{-3}	0.048	−1.32
65.0	338	20.4	2.96×10^{-3}	0.049	−1.31
70.0	343	18.1	2.92×10^{-3}	0.055	−1.26
80.0	353	15.1	2.83×10^{-3}	0.066	−1.18

(b) Plot a graph to show the relationship between **log$_{10}$ (rate of reaction)** and the reciprocal of the absolute temperature. You are reminded that the values for **log$_{10}$ (rate of reaction)** are negative.

Draw the line of best fit.



[3]

(c) Circle and label on the graph any point(s) you consider to be anomalous. For each anomalous point give a different reason why it is anomalous, clearly stating which point you are describing.

$(3.19 \times 10^{-3}, -1.62)$, there might have been heat loss to the surroundings

[3]

1

(d) Comment on whether the results obtained can be considered as reliable.

Yes, since nearly all the points are said to be on the line of best fit [1]

1

(e) Determine the slope of the graph. Mark clearly on the graph any construction lines and show clearly in your calculation how the values from the intercepts were used in the calculation of the slope.

$(2.83 \times 10^{-3}, -1.18)$ $(3.41 \times 10^{-3}, -1.77)$

$$m = \frac{-1.77 - (-1.18)}{3.41 \times 10^{-3} - (2.83 \times 10^{-3})}$$

$$= \frac{-0.59}{5.8 \times 10^{-4}} = 10172.4$$

$y = mx + c$

$-1.18 = (10172.4)(2.83 \times 10^{-3}) + c$

$c = -29.97$

[2]

0

(f) Using the value of the slope of your graph calculated in (e) calculate a value for the **activation energy, E_A**. Correct use of the equation will produce an answer in $kJ\,mol^{-1}$.

$$(-1.62) = -\frac{EA}{19(313)}$$

[1]

$EA = 9634.14\ kJ\,mol^{-1}$

0

(g) By considering the movement of particles in the reaction explain why the rate of reaction increases with increasing temperature.

Particles gain energy greater than Activation Energy. There are more frequent ~~successful~~ successful collisions ✓

[2]

Examiner comment – grade C

(a) The candidate scored both marks for the table headings but not for the data. The 1/T data was good but the 1/time data was recorded to 2 significant figures rather than 3. This led to errors in the third significant figure in three values in $\log_{10}$(rate) leading to the loss of the third mark.

(b) Full marks were awarded for a well plotted graph.

(c) Whilst data may contain more than one anomaly, it was acceptable for only one to be identified provided that it was the most anomalous point as was the case here. However, the reason given was unrelated to the experiment.

(d) This was a very good comment on reliability which required a statement about the points being on the line.

(e) There were no construction lines so intercepts could not be read from the graph. The candidate picked out values from the table. Points on the line could be used provided they had construction lines to them. In this case the subsequent calculation was incorrect; it gives a value of the gradient as -1017.24.

(f) The candidate attempted to calculate E_A by substitution not by using the slope previously calculated in **(e)** as required by the question.

(g) The candidate made a good response to the question based on kinetic energy and frequency of collision.

Example candidate response – grade E

2 Chemical reactions occur more rapidly as the temperature of the reaction mixture increases. The mathematical relationship that summarises this is

$$\log_{10} \text{(rate of reaction)} = \frac{-E_A}{19T}$$

where $\mathbf{E_A}$ is the **activation energy** of the reaction and **T** is the **absolute temperature** in Kelvin and the **rate of reaction** can be taken as the reciprocal of the time taken in seconds **(1/time)**.

An experiment was carried out to investigate this relationship using dilute hydrochloric acid and aqueous sodium thiosulfate.

- 20 cm^3 of dilute hydrochloric acid was placed in a boiling tube contained in a water bath.
- 20 cm^3 of aqueous sodium thiosulfate was added to the dilute hydrochloric acid, while stirring and a stopwatch started.
- The temperature of the water bath was recorded.
- After a period of time the liquid became cloudy (opaque) due to the formation of a precipitate of sulfur.
- As soon as this cloudiness (opacity) appeared the time was recorded.
- The temperature of the water bath was raised and the whole experiment repeated.

(a) The results of several such experiments are recorded below.

Process the results in the table to calculate $\boxed{\textbf{log}_{10}\textbf{ (rate of reaction)}}$, the reciprocal of the absolute temperature **(1/T)** and the 'rate of reaction' **(1/time)**. You should expect the values of **log$_{10}$ (rate of reaction)** to be negative.

1/T / 1/time

Record these values to **three significant figures** in the additional columns of the table.

Label the columns you use. For each column you use include units where appropriate and an expression to show how your values are calculated.

You may use the column headings A to F for these expressions (e.g. A–B). [3]

log$_{10}$ (rate of reaction)

A	B	C	D	E	F
temperature /°C	absolute temperature /K	time /s	~~log$_{10}$ (rate of reaction)~~ $\frac{1}{B}$ $\left(\frac{1}{T}\right)$	rate of reaction $\frac{1}{\text{time}}$ log$\left(\frac{1}{C}\right)$	
20.0	293	60.3	0.00341	−1.78	
30.0	303	46.8	0.00330	−1.67	
40.0	313	41.6	0.00319	−1.62	
45.0	318	31.6	0.00314	−1.50	
50.0	323	28.8	0.00310	−1.46	
55.0	328	25.1	0.00305	−1.40	
60.0	333	21.0	0.00300	−1.32	
65.0	338	20.4	0.00296	−1.31	
70.0	343	18.1	0.00292	−1.26	
80.0	353	15.1	0.00283	−1.18	

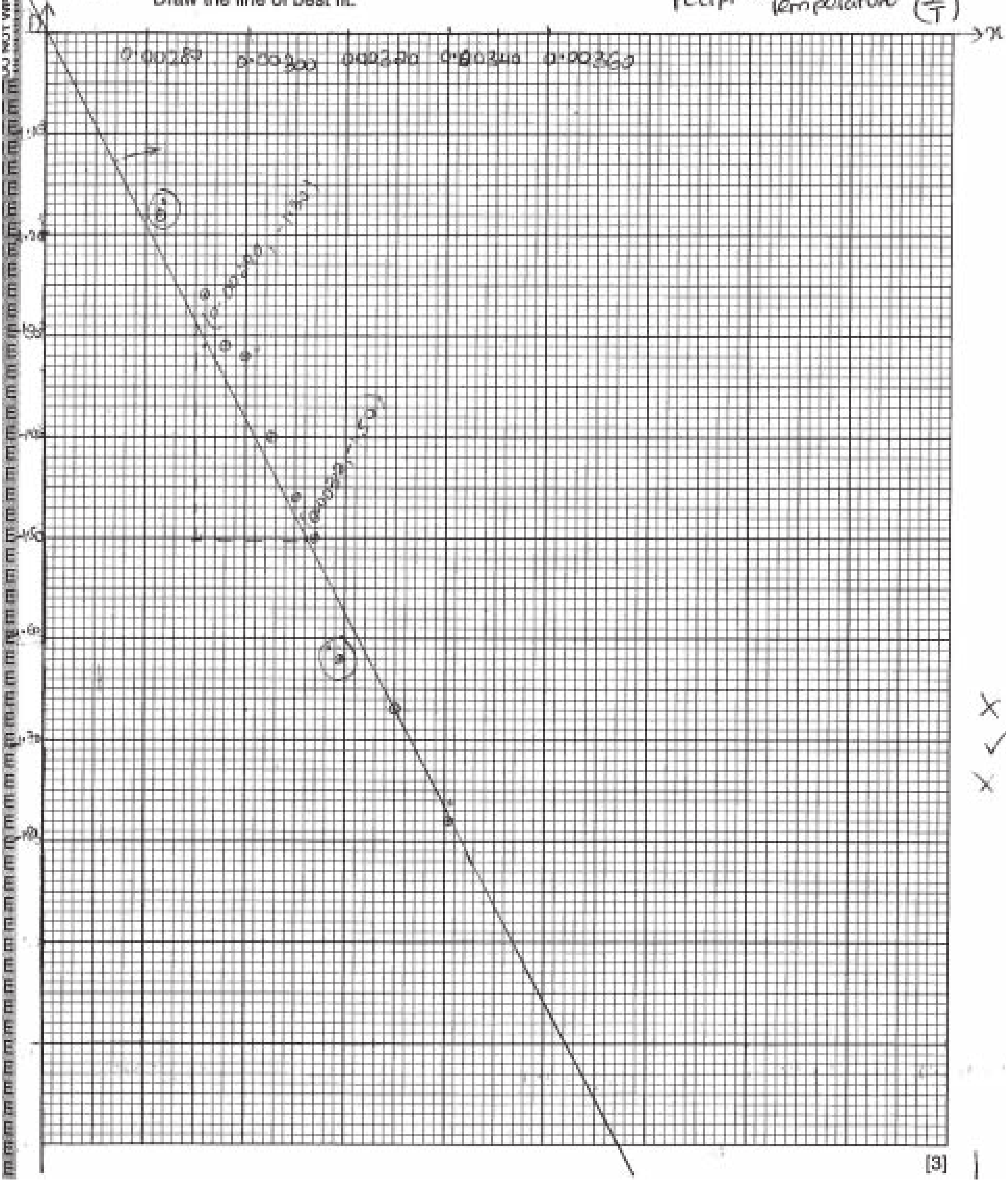
x n800

(b) Plot a graph to show the relationship between $\log_{10}$ **(rate of reaction)** and the reciprocal of the absolute temperature. You are reminded that the values for $\log_{10}$ **(rate of reaction)** are negative.

Draw the line of best fit.

log₁₀ (rate of reaction)

reciprocal of absolute temperature $(\frac{1}{T})$



[3]

(c) Circle and label on the graph any point(s) you consider to be anomalous. For each anomalous point give a different reason why it is anomalous, clearly stating which point you are describing.

(0.00319, −1.62). The ~~mass~~ reciprocal absolute temperature was low as the ~~stopwatch was started~~ it was read before the acid was added. ✓

The reciprocal absolute temperature was high as the ~~stopwatch~~ temperature was read after the acid was added ✗

(0.00283, −1.18) ~~The temperature was high~~ rep abs
~~The reciprocal of absolute temperature was high as the temperature was not maintained~~ [3]

(d) Comment on whether the results obtained can be considered as reliable.

~~No as the values are not con~~ No, as the values are not consistent only one point fit the line through the origin. ✓ [1]

(e) Determine the slope of the graph. Mark clearly on the graph any construction lines and show clearly in your calculation how the values from the intercepts were used in the calculation of the slope.

(0.00290, −1.30) (0.00312, −1.50) ✓

$m = \frac{-1.50 - (-1.30)}{0.00312 - 0.00290} = \frac{-2.8}{0.00031}$

-909.09 ✗

$= -\cancel{4032.25}$ 9

$= -909$ [2]

(f) Using the value of the slope of your graph calculated in (e) calculate a value for the **activation energy, E_A**. Correct use of the equation will produce an answer in $kJ\,mol^{-1}$.

$\log_{10}(\text{rate of reaction}) = \frac{-EA}{19T}$

$-1.50 = \frac{-EA}{19x}$ ✗ [1]

(g) By considering the movement of particles in the reaction explain why the rate of reaction increases with increasing temperature.

As temperature increases, the frequency of effective collison also increases with increasing kinetic energy as the energy is higher than the activation energy.

[2]

Examiner comment – grade E

(a) The column headings did not receive credit. Column D was missing its unit ($/K^{-1}$). Column E had a conflict with two different headings. The two columns of data were correctly calculated and reported for the third mark.

(b) The mark for axes was not awarded since the plot did not cover at least half of the available grid in the *x*-axis direction. The plotting was correct so gained the middle mark. Given the points as plotted, the line should have been twisted to the right to encompass the majority of points so did not gain the final mark.

(c) Two anomalies were correctly identified but the reasons were inadequate. The reasons offered were those of the plotted data and not on the experimental reasons behind them.

(d) Since most of the points on the candidate's plot were not on the line as drawn, this answer was accepted.

(e) The candidate drew construction lines (if over a small scale), so gained the first mark. However, there was an error in reading the intercept; 1.30 should have been 1.29 so the gradient calculation was wrong.

(f) To calculate E_A, the gradient needed to be equated to its expression ($-E_A/19$) extracted from the equation which was not attempted.

(g) The candidate made a good response to the question based on kinetic energy and frequency of collision.

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