Example Candidate Responses

Cambridge International Level 3
Pre-U Certificate in
CHEMISTRY (9791)

UNIVERSITY of CAMBRIDGE
International Examinations

Cambridge Pre-U

Example Candidate Responses

Chemistry (9791)

Cambridge International Level 3
Pre-U Certificate in Chemistry (Principal)

Cambridge International Level 3 Pre-U Certificate

Chemistry

9791

Contents

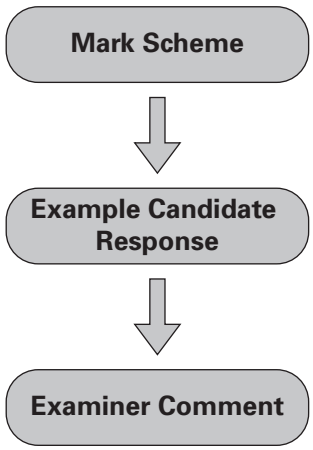
Introduction

The main aim of this booklet is to exemplify standards for those teaching Cambridge Pre-U, and to show how different levels of candidates' performance relate to the subject's curriculum and assessment objectives.

Cambridge Pre-U is reported in three bands (Distinction, Merit and Pass) each divided into three grades (D1, D2, D3; M1, M2, M3; P1, P2, P3).

In this booklet a range of candidate responses has been chosen to illustrate as far as possible each band (Distinction, Merit and Pass). 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 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 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.

Teachers are reminded that a full syllabus and other teacher support materials are available on www.cie.org.uk. For past papers and Examiner Reports please contact CIE on international@cie.org.uk.

Components at a Glance

Component	Component Title	Duration	Weighting (%)	Type of Assessment
Paper 1	Part A Multiple Choice	1 hour	15	Written paper, externally set and marked
Paper 2	Part A Written	2 hours 15 minutes	35	Written paper, externally set and marked
Paper 3	Part B Written	2 hours 15 minutes	35	Written paper, externally set and marked
Paper 4	Practical	2 hours	15	Practical exam, externally set and marked

This booklet contains a selection of example candidate responses and examiner comments for Papers 2, 3 and 4.

Paper 2 Part A Written

Question 1 Mark Scheme

(a) ethanol: 46 g mol^{-1}
octane: 114 g mol^{-1}
1 mark if both numbers correct
no penalty for incorrect sig. figs. [1]

(b) density in g cm^{-3} = 2 g mol^{-1} / 24000 cm^3 mol^{-1} = 8.3×10^{-5} g cm^{-3}
no penalty for incorrect sig. figs. [1]

(c) zero (by definition)
award this mark if the zero is just entered in the table [1]

(d) –285.8 kJ mol^{-1}
the mark is given for indicating that it is the same as the enthalpy of formation given in the question [1]

(e) $C_8H_{18}(l) + 25/2O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$ (1)
equation must be per mole of octane and correctly balanced for the first mark
correct state symbols for octane, oxygen, carbon dioxide and water (1) [2]

(f) Δ_cH^e (octane) = $8\Delta_fH^e$ (CO_2) + $9\Delta_fH^e$ (H_2O) – Δ_fH^e (octane)
= {(8 × –393.5) + (9 × –285.8) – (–250)} kJ mol^{-1}
= {–3148.0 – 2572.2 + 250.0} kJ mol^{-1}
= –5470.2 kJ mol^{-1} (3)
$\Delta_fH^e(CO_2)$ and $\Delta_fH^e(H_2O)$ multiplied by 8 and 9, respectively (1)
correct signs (1)
2 marks given if all correct apart from an arithmetical slip
2 marks given for 5470.2 kJ mol^{-1} [max 3]

(g) **(i)** methanol: –726.0 kJ mol^{-1} / 32 g mol^{-1} = –22.69 kJ g^{-1} [1]

(ii) hydrogen: –285.8 kJ mol^{-1} / 2 g mol^{-1} = –142.9 kJ g^{-1}
accept from 2 to 5 sig. figs.
no penalties for missing units or forgetting minus sign
–1 for each wrong answer
–1 if sig. figs. outside the allowed range (only penalise once) [1]

(h) **(i)** ethanol: $-1367.3\ kJ\ mol^{-1} \times 0.789\ g\ cm^{-3} / 46\ g\ mol^{-1}$
$= -23.5\ kJ\ cm^{-3}$ [1]

(ii) octane: $-5470.2\ kJ\ mol^{-1} \times 0.703\ g\ cm^{-3} / 114\ g\ mol^{-1}$
$= -33.7\ kJ\ cm^{-3}$
accept only 2 or 3 sig. figs.
no penalties for missing units or forgetting minus sign
–1 for each error
–1 if sig. figs. outside the allowed range (only penalise once)
where working is correct but final answer is inexplicably wrong, allow the mark [1]

(i) the enthalpy change of combustion value for hydrogen is for standard conditions, and so relates to gaseous hydrogen, not to liquid hydrogen
OR no account taken of different temperatures / latent heat of vaporisation of hydrogen
allow comment about how the value of the density of liquid hydrogen is unsuitable for the calculation of energy per unit volume for gaseous hydrogen
allow just a reference to the different state of hydrogen [1]

[Total: 14]

Example Candidate Response – Distinction (D1)

1 Table 1.1 gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

Table 1.1

name	formula	molar mass /g mol^{-1}	density /g cm^{-3}	$\Delta_c H^{\ominus}$ (298 K) /kJ mol^{-1}	$\Delta_f H^{\ominus}$ (298 K) /kJ mol^{-1}
methanol	CH_3OH	32	0.793[a]	–726.0	–239.1
ethanol	C_2H_5OH	46	0.789[a]	–1367.3	–277.1
liquid hydrogen	H_2	2	0.0711[b]	✓	
octane	C_8H_{18}	114	0.703[a]	✓	–250.0

[a] At 298 K and 1 bar pressure.
[b] At 20 K and 1 bar pressure.

(a) Insert the missing molar mass values in the table. [1]

(b) Calculate the density of **gaseous** hydrogen at 298 K and 1 bar pressure.
Assume 1 mol of any gas occupies 24 dm^3 at 298 K and 1 bar pressure. Give your answer in g cm^{-3}.

$46\ g\ mol^{-1}$

$\frac{\frac{24}{1000}}{46} = 5.22 \times 10^{-4}$

$24\ mol\ dm^{-3} = \frac{24 \times 1000}{1000^3}\ mol\ cm^{-3}$

..... 5.22×10^{-4} ✗ g cm^{-3} [1]

(c) What is the value of the standard enthalpy of formation of hydrogen **gas**, H_2?

..... $0.000\ kJ\ mol^{-1}$ ✓ [1]

(d) Use the information in Table 1.2 to give the value of the standard enthalpy of combustion of hydrogen.

Table 1.2

name	$\Delta_f H^{\ominus}$ (298 K) /kJ mol^{-1}
water	–285.8
carbon dioxide	–393.5

..... $-285.8\ kJ\ mol^{-1}$ ✓ [1]

(e) Write down the chemical equation that represents the standard enthalpy of combustion of octane. Include state symbols.

$2C_8H_{18(l)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(l)}$ [2]

$C_8H_{18(l)} + 12.5O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(l)}$ ✓✓ 2

(f) Use the enthalpy of formation data in Table 1.1 and Table 1.2 to calculate the standard enthalpy of combustion of octane.

$2C_8H_{18(l)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(l)}$

-230×2

-393.5×16

-285.8×18

$8C_{(s)} + 25O_{2(g)} + 9H_{2(g)}$

$(-393.5 \times 16 - 285.8 \times 18) + 500 = -10940.4 \text{ kJ mol}^{-1}$ ✓

$= 5470.2$ ✓

$-10940 \text{ kJ mol}^{-1}$

$-5470 \text{ kJ mol}^{-1}$ [3] 3

(g) An important property of a fuel, especially when the fuel has to be lifted (such as in aviation), is the energy released on combustion *per gram* of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298 K for methanol and hydrogen gas.

(i) methanol

-726 kJ mol^{-1}

$= -726 \text{ kJ mol}^{-1}$

$\times 32 \text{ g mol}^{-1}$

$= -22.69 \text{ kJ g}^{-1}$

-22.7 kJ g^{-1} ✓

(ii) hydrogen gas

$\frac{-285.8 \text{ kJ mol}^{-1}}{2 \text{ g mol}^{-1}} = -142.9 \text{ kJ g}^{-1}$ ✓

-143 kJ g^{-1} [2] 2

(h) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion *per cm*^{3} of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for ethanol and octane.

(i) ethanol

$\frac{0.789\ g\ cm^{-3}}{46\ g\ mol^{-1}} = 0.017\ mol\ cm^{-3}$

$-1367.3\ kJ\ mol^{-1} \times 0.017\ mol\ cm^{-3}$

$= -23.45\ kJ\ cm^{-3}$

$-23.5\ kJ\ cm^{-3}$ ✓

2

(ii) octane

$\frac{0.703\ g\ cm^{-3}}{114\ g\ mol^{-1}} = 0.00617\ mol\ cm^{-3} \times -5470\ kJ\ mol^{-1} = -33.733\ kJ\ cm^{-3}$ ✓

$-33.7\ kJ\ cm^{-3}$ [2]

(i) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with the other fuels.

The density of hydrogen given is at 20K rather than 298K, so the comparison would not be considerable ✓ [1]

1

13 [Total: 14]

Examiner Comment

The candidate was able to complete almost all of the calculations correctly but failed to read **(b)** with sufficient care.

Example Candidate Response – Distinction

1 Table 1.1 gives some data on four fuel sources: methanol, ethanol, hydrogen and octane. Octane can serve as a rough approximation of petrol.

Table 1.1

name	formula	molar mass /g mol^{-1}	density /g cm^{-3}	$\Delta_c H^\ominus$ (298 K) /kJ mol^{-1}	$\Delta_f H^\ominus$ (298 K) /kJ mol^{-1}
methanol	CH_3OH	32	0.793[a]	−726.0	−239.1
ethanol	C_2H_5OH	46	0.789[a]	−1367.3	−277.1
liquid hydrogen	H_2	2	0.0711[b]		
octane	C_8H_{18}	114	0.703[a]		−250.0

[a] At 298 K and 1 bar pressure.
[b] At 20 K and 1 bar pressure.

(a) Insert the missing molar mass values in the table. [1]

(b) Calculate the density of **gaseous** hydrogen at 298 K and 1 bar pressure. Assume 1 mol of any gas occupies 24 dm^3 at 298 K and 1 bar pressure. Give your answer in g cm^{-3}.

Density = Mass / Volume

Mass of H_2 (g) at 298K = 1 × 2 = 2

$= \frac{2}{24\,dm^3}$

$= 83.3\ g\,cm^{-3}$

83.3 g cm^{-3} [1]

(c) What is the value of the standard enthalpy of formation of hydrogen **gas**, H_2?

0 kJ mol^{-1} [1]

(d) Use the information in Table 1.2 to give the value of the standard enthalpy of combustion of hydrogen.

$H_2 + O_2 \rightarrow H_2O$

0 0 −393.5 −285.8

Table 1.2

name	$\Delta_f H^\ominus$ (298 K) /kJ mol^{-1}
water	−285.8
carbon dioxide	−393.5

−285.8 kJ mol^{-1} [1]

(e) Write down the chemical equation that represents the standard enthalpy of combustion of octane. Include state symbols.

$C_8H_{18(l)} + {}^{25}/_2 O_{2(g)} \longrightarrow 8CO_{2(g)} + 9H_2O_{(l)}$ ✓✓ [2]

2

(f) Use the enthalpy of formation data in Table 1.1 and Table 1.2 to calculate the standard enthalpy of combustion of octane.

$C_8H_{18(l)} + {}^{25}/_2 O_{2(g)} \xrightarrow{\Delta H_c} 8CO_{2(g)} + 9H_2O_{(l)}$

$-250.0 \quad 0 \quad -393.5\times8 \quad -285.8\times9$

$8C_{(s)} + {}^{25}/_2 O_{2(g)} + 9H_{2(g)}$ ✓✓✓

$\Delta H_c = -(-250.0) + (-393.5\times8) + (-285.8\times9)$

$= -5470.2\ kJmol^{-1}$

$-5470.2\ kJmol^{-1}$ [3]

3

(g) An important property of a fuel, especially when the fuel has to be lifted (such as in aviation), is the energy released on combustion *per gram* of fuel.

Calculate the enthalpy change of combustion per gram of fuel at 1 bar pressure and 298 K for methanol and hydrogen gas.

$\frac{Mr}{mass} \times \frac{1}{Mr}$

(i) methanol

$-726.0\ kJmol^{-1}$

$= -726 \times 32$

$= -23232\ kJg^{-1}$

✗ $-23232\ kJg^{-1}$

(ii) hydrogen gas

$-285.8\ kJmol^{-1}$

$= -285.8 \times 2$

$= -571.6\ kJg^{-1}$

✓ecf

✗ $-571.6\ kJg^{-1}$ [2]

1

(h) Another important characteristic of a fuel, especially when there is a fuel tank of limited size, is the energy released on combustion *per* cm^3 of fuel.

Calculate the enthalpy change of combustion per cm^3 of fuel for ethanol and octane.

$\frac{Mc}{mass} \times \frac{1}{cm^3}$.

(i) ethanol

$-1367.3\ kJ\,mol^{-1}$

$= -1367.3 \times 0.789 \times 46$

$= -49624.8\ kJ\,cm^{-3}$ (to 1 dp)

√ref 1 way s.f.

$-49624.8\ kJ\,cm^{-3}$

(ii) octane

$-5470.2\ kJ\,mol^{-1}$

$= -5470.2 \times 0.703 \times 114$

$= -438392.8\ kJ\,cm^{-3}$ (to 1 dp)

√ref

$-438392.8\ kJ\,cm^{-3}$ [2]

(i) Explain why, given the data in the question, it is not strictly possible to make a fair comparison of the energy released per cm^3 of liquid hydrogen with the other fuels.

Liquid hydrogen's density is measured at 20 K whereas other fuels at 298 K, so density not comparable, i.e. energy is not comparable [1]

[Total: 14]

11

Examiner Comment

The candidate showed a good understanding of the principles involved in most of the calculations but in **(b)** failed to convert dm^3 into cm^3 and made a careless error in **(g)**. Also a lack of appreciation of significant figures was shown in **(h)**.

Question 2 Mark Scheme

(a) 178/(178 + 32) × 100% = 84.8% [1]

(b) correct plotting of point in van Arkel triangle (1)
the point has coordinates (2.39, 2.45) half a gradation of leeway either side, i.e. 0.05 on the scale, is acceptable
it is an insulator (1) [2]

(c) it is ionic [1]

(d) reaction 1: $HfO_2 + 4HCl \rightarrow HfCl_4 + 2H_2O$ (1)
reaction 2: $HfCl_4 + 2Mg \rightarrow Hf + 2MgCl_2$ (1)
ecf incorrect hafnium chloride formula in step 2 from step 1 [2]

[Total: 6]

Example Candidate Response – Distinction

2 The Intel® super-fast 45 nm Core 2 processors are based on Penryn technology. This involves the use, for the first time in computer chips, of an oxide of hafnium.

(a) This oxide of hafnium has the formula HfO_2. Calculate the percentage of hafnium by mass in this oxide.

M_ Hf = 178

$\frac{178}{178+32} = 0.848 \times 100 = 84.76\%$

84.8 % [1]

(b) Table 2.1 provides the electronegativity data for O and Hf.

Table 2.1

element	electronegativity
O	3.61
Hf	1.16

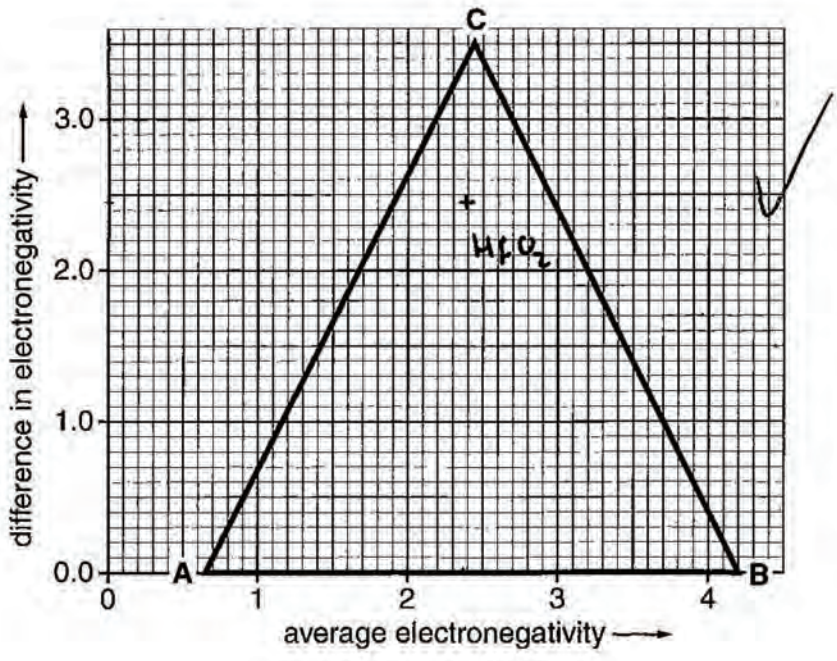
3.61−1.16 = 2.45

$\frac{3.61+1.16}{2} = 2.385$

Computer chips contain electrical conductors, semiconductors and insulators. On the van Arkel triangle mark the point corresponding to the oxide of hafnium and use this point to deduce its electrical properties. Ring the correct option.

The oxide of hafnium is

conductor **semiconductor** **insulator**



[2]

(c) Use your van Arkel plot to decide whether the oxide of hafnium is best described as ionic, covalent or metallic. Ring the correct option below.

The oxide of hafnium is best described as

ionic **covalent** **metallic** [1]

(d) Elemental hafnium has neutron-absorbing properties that are useful in nuclear reactors. It can be extracted from the oxide, HfO_2, by the following reactions.

reaction 1 reaction with hydrochloric acid
reaction 2 reduction of a product of **reaction 1** with magnesium

Write balanced equations for these reactions.

equation for **reaction 1**

$HfO_2 + 4HCl \rightarrow HfCl_4 + 2H_2O$

equation for **reaction 2**

$HfCl_4 + 2Mg \rightarrow 2MgCl_2 + Hf$ [2]

[Total: 6]

Examiner Comment

A Distinction level candidate would be expected to achieve full marks on this question.

Question 3 Mark Scheme

(a) CsF [1]

(b) clear that a Cs electron is in the F outer shell (1)
charges shown on the ions (1)
allow a Cs ion with 8 electrons shown in the outer shell
no marks awarded if there is sharing of electrons [2]

(c) largest possible difference in electronegativity between its two constituent elements owtte [1]

(d) high boiling point / low vapour pressure / does not evaporate easily [1]

(e) wide separation of charges / large ions AND low charges both needed for mark [1]

(f) high surface tension (1)
(relatively) high melting and/or boiling points or liquid at rtp (compared to analogous compounds) or high specific thermal capacity (1)
less dense as a solid than as a liquid (owtte) or greatest density at 4° C (1) [max 2]

(g) H bond drawn between hydrogen on one molecule and oxygen on another (1)
oxygen lone pair drawn at the start of one of the H bonds and both ends of a dipole shown on each molecule (1)
bond angle of 180° around an H-bonding hydrogen – shown explicitly or looks like 180° intended (1) [3]

(h) two H bonds shown between two amine groups on melamine and the carbonyl oxygens on PTCDI, and an H bond shown between the NH group on the PTCDI and the –N= atom on melamine that is between the two H-bonding amine groups. (2)
for both marks the H-bonds from the amine groups must be from one of the two hydrogens of each amine in particular, rather than just from $–NH_2$ otherwise just 1 mark is given
ecf from **(g)** if the notation for an H-bond is incorrect
no marks if all three H bonds aren't correctly identified
small errors in copying down the structures should not be penalised as long as they don't affect the H-bonding interaction [2]

[Total: 13]

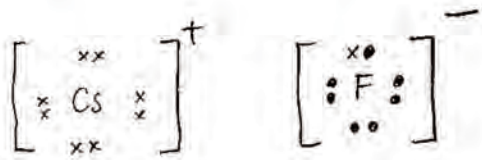
Example Candidate Response – Distinction (D1)

3 The compound whose bonding most resembles pure ionic bonding is caesium fluoride.

(a) Write down the formula of caesium fluoride.

CsF ✓ [1]

(b) Draw a dot-cross diagram to show the bonding in caesium fluoride. Show outer electrons only.



✓✓ [2]

(c) Explain why caesium fluoride is the compound whose bonding most closely resembles pure ionic.

The difference in electronegativity between caesium and fluorine is the ✓greatest out of all binary compounds. [1]

(d) Virtually all ionic compounds are solids at room temperature and pressure. However, researchers have designed ionic compounds whose ionic bonding is so weak that they are liquids under these conditions. Ionic liquids are often easy to handle as solvents as they are non-volatile; they have also recently found use in solar cells for this reason.

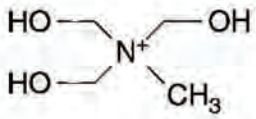
Explain what is meant by *non-volatile*.

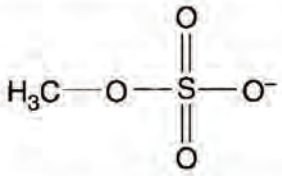
They do not evaporate easily ✓ [1]

1

(e) In the pure ionic bonding model, the ionic bond energy is proportional to the charge on each ion and inversely proportional to the distance between the charges, which are considered to be located at the centre of ions.

The structure of an ionic substance which is a liquid at room temperature and has been used in thermometers (reported in *Green Chemistry*, 2008) is shown below.





Suggest two features of these ions that account for the compound having such a low melting point.

1. There is a large amount of steric hindrance between the charges resulting in low ionic bond strength ✓ (bod)

2. The charges on each ion are only 1+ and 1− respectively, making the ionic bond weak [1]

(f) Hydrogen-bonding is weaker than ionic or covalent bonding, but accounts for many important intermolecular attractions.

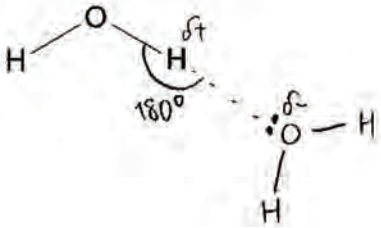
State two anomalous properties of water that are the result of hydrogen-bonding.

1. Solid water (ice) is less dense than the liquid form ✓

2. Higher boiling point than all other Group 16 hydrogen compounds ✓ [2]

2

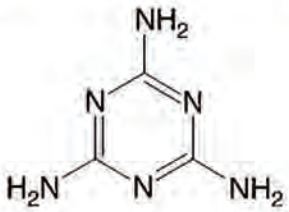
(g) Draw a second molecule of water and a hydrogen-bond between the two molecules. Indicate the bond angle around the hydrogen atom involved in the hydrogen-bond. Include all relevant lone pairs and dipoles.



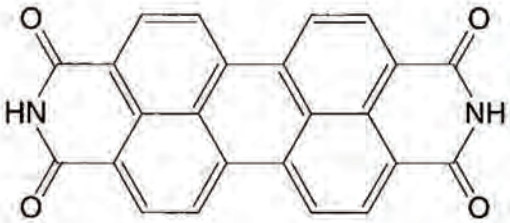
✓✓✓ [3]

3

(h) Hydrogen-bonding is directional (i.e. a specific link between two atoms can be drawn) and has many applications in linking together molecules in an organised way. This linking has been put to use recently by researchers designing self-assembling surface networks for applications in nanotechnology (reported in *Nature*, 2008).



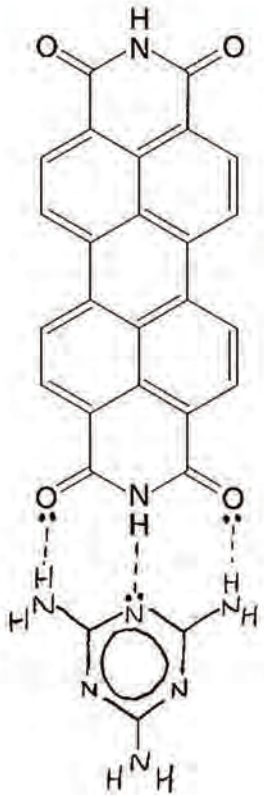
1,3,5-triazine-2,4,6-triamine (melamine)



perylene-3,4,9,10-tetracarboxylic diimide (PTCDI)

Fig. 3.1

The two molecules in Fig. 3.1 were chosen for the self-assembling network. A molecule of melamine and a molecule of PTCDI attach together strongly via three hydrogen bonds. Suggest where these **three** hydrogen-bonds form by drawing the melamine below in the correct orientation, with the hydrogen-bonds connecting the relevant atoms.



✓✓ 2

[2]

[Total: 13]

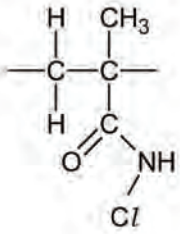
13

Examiner Comment

A Distinction candidate would have probably scored 10/11 marks, with marks for **(h)** being the most difficult to score.

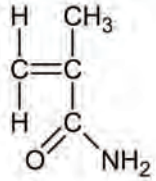
Question 4 Mark Scheme

(a) allow either the repeat fragment or the notation with it in brackets
brackets must be used if a skeletal formula is used to represent the repeat unit
only two carbons in the backbone should be shown in the fragment or between the brackets
allow any unambiguous structural formula



[1]

(b) the monomer should show a C=C double bond between the two backbone carbons from the repeat unit, and an amide in place of the N-chloroamide
the C=C double bond must be explicit rather than implied



[1]

(c) **(i)** (+)1 [1]

(ii) (+)1
ecf from **(c)(i)**, i.e. answer to **(c)(ii)** should be the same as **(c)(i)** [1]

(iii) oxidation: $2I^- \rightarrow I_2 + 2e^-$ (1)
reduction: $ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$
or $HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O$ (1) [2]

(iv) starch [1]

(v) 12.50 cm^3 × 0.100 mol dm^{-3} = 0.00125 mol
no sig. figs. or unit penalties [1]

(vi) 0.00125 mol / 2 = 0.000625 mol
no sig. figs. or unit penalties
ecf from **(v)**, i.e. answer from **(v)** should be divided by 2 [1]

(vii) 0.000625 mol × 35.5 g mol^{-1} × 100 cm^3 / 10 cm^3 = 0.222 g (2)
1 mark for multiplying answer to **(vi)** by 35.5 g mol^{-1}
1 mark for scaling up by 10, even if this isn't explicitly explained.
no sig. figs. or unit penalties
ecf from **(i)** [2]

[Total: 11]

Example Candidate Response – Distinction

4 Chemists have recently found a way of making the strong, light-weight and thermally stable polymer, Kevlar®, to be antibacterial (reported in *Industrial & Engineering Chemistry Research*, 2008). This was achieved by coating it with another polymer, a fragment of which is shown in Fig. 4.1.

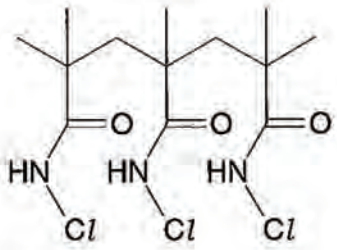
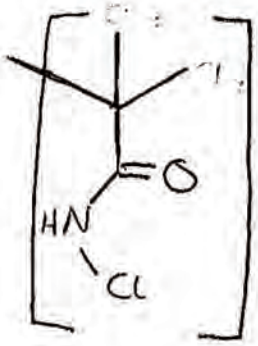


Fig. 4.1

(a) Draw the repeat unit of the polymer structure shown in Fig. 4.1.



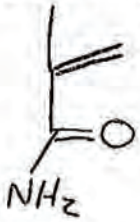
X 0

[1]

(b) The polymer shown in Fig. 4.1 is made by the following reactions:

reaction 1 an addition polymerisation reaction of a monomer known as MAA
reaction 2 the substitution of a hydrogen atom in the polymer with a chlorine atom using bleach

Draw the structure of the monomer MAA.



✓ 1

[1]

(c) Not all the nitrogen atoms in the polymer end up bonded to a chlorine atom. The quantity of chlorine actually present in the polymer can be determined using **reactions 3, 4 and 5.**

A known mass of polymer (written as XCONH–C*l*) is hydrolysed to convert the chlorine content of the polymer to chloric(I) acid, HOC*l*:

reaction 3 $XCONH\text{–}Cl + H_2O \rightarrow XCONH_2 + HOCl$
(where X = remainder of polymer)

The chlorine content is then 'converted' to iodine:

reaction 4 $HOCl + 2KI + H^+ \rightarrow I_2 + KCl + H_2O + K^+$

The quantity of iodine is determined using a titration with sodium thiosulfate:

reaction 5 $I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$

(i) State the oxidation number of the chlorine in $HOCl$.

+1 ✓ [1]

(ii) Given that **reaction 3** is a hydrolysis reaction, state the oxidation number of chlorine in the polymer.

+1 ✓ [1]

(iii) Write ionic half equations for the oxidation and reduction processes in **reaction 4**.

oxidation $2I^- \rightarrow I_2 + 2e^-$ ✓

reduction $Cl^+ + 2e^- \rightarrow Cl^-$ ✗ [2]

In the analysis of a sample of polymer, 1.00 g of the polymer was hydrolysed (**reaction 3**).

The resulting mixture was reacted with excess acidified potassium iodide (**reaction 4**) and then made up to 100 cm^3 with distilled water.

10.0 cm^3 of this solution reacted with exactly 12.50 cm^3 of sodium thiosulfate solution of concentration 0.100 mol dm^{-3} (**reaction 5**).

(iv) Name a suitable indicator for this titration.

Starch ✓

..... [1]

(v) Determine the amount (in moles) of sodium thiosulfate used in the titration.

$mol = \frac{12.50}{1000} \times 0.100$

1.25×10^{-3} ✓

..... mol [1]

(vi) Determine the amount (in moles) of iodine, I_2, in the titration.

$1.25 \times 10^{-3} \div 2 =$

6.25×10^{-4} ✓

..... mol [1]

(vii) Determine the mass of chlorine present in the sample of polymer.

$mass = 6.25 \times 10^{-4} \times 35.5$ ✓

Stoichiometry I_2 : Cl is 1:1

so 6.25×10^{-4} mol Cl

0.0222g (3SF)

..... [2]

[Total: 11]

8

Examiner Comment

In **(a)** the candidate was unable to draw the repeat unit of the polymer. The reduction reaction in **(c) (iii)** was targeted at the most able candidates. A scaling factor of 10 was missed in **(c) (vii)**.

Example Candidate Response – Merit

4 Chemists have recently found a way of making the strong, light-weight and thermally stable polymer, Kevlar®, to be antibacterial (reported in *Industrial & Engineering Chemistry Research*, 2008). This was achieved by coating it with another polymer, a fragment of which is shown in Fig. 4.1.

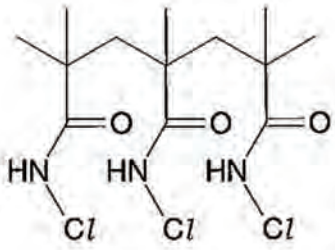


Fig. 4.1

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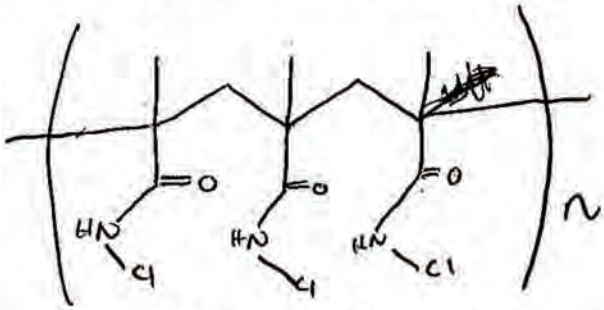


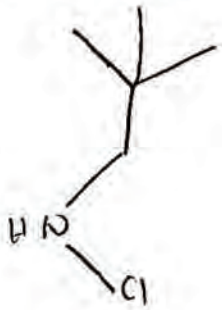
X O

[1]

(b) The polymer shown in Fig. 4.1 is made by the following reactions:

reaction 1 an addition polymerisation reaction of a monomer known as MAA
reaction 2 the substitution of a hydrogen atom in the polymer with a chlorine atom using bleach

Draw the structure of the monomer MAA.



X O

[1]

(c) Not all the nitrogen atoms in the polymer end up bonded to a chlorine atom. The quantity of chlorine actually present in the polymer can be determined using **reactions 3, 4** and **5**.

A known mass of polymer (written as XCONH–C*l*) is hydrolysed to convert the chlorine content of the polymer to chloric(I) acid, HOC*l*:

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(i) State the oxidation number of the chlorine in $HOCl$.

+1 ✓ [1]

(ii) Given that **reaction 3** is a hydrolysis reaction, state the oxidation number of chlorine in the polymer.

+1 ✓ [1]

(iii) Write ionic half equations for the oxidation and reduction processes in **reaction 4**.

oxidation $2I^- \rightarrow I_2 + 2e^-$ ✓

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The resulting mixture was reacted with excess acidified potassium iodide (**reaction 4**) and then made up to 100 cm^3 with distilled water.

10.0 cm^3 of this solution reacted with exactly 12.50 cm^3 of sodium thiosulfate solution of concentration 0.100 mol dm^{-3} (**reaction 5**).

(iv) Name a suitable indicator for this titration.

..... [1]

(v) Determine the amount (in moles) of sodium thiosulfate used in the titration.

mol = vol x conc

1.25×10^{-3} ..... mol [1]

(vi) Determine the amount (in moles) of iodine, I_2, in the titration.

$1.25 \times 10^{-3} / 2$

6.25×10^{-4} ..... mol [1]

(vii) Determine the mass of chlorine present in the sample of polymer.

10 x

..... [2]

[Total: 11]

5

Examiner Comment

The candidate scored on most of the lower level questions although they failed to attempt **(c) (iv)** which tested basic knowledge. The overall standard of the answer was improved by scoring in **(c) (ii)** and for the oxidation half-equation in **(c) (iii)**.

Question 5 Mark Scheme

(a) 292 – 122 = 170 [1]

(b) 9 [1]

(c) 18
ecf from part **(b)**, i.e. the number of elements wide = twice the number of orbitals [1]

(d) 4p 5s 4d 5p 6s 4f 5d [1]

(e) 6d, 7p, 8s and 5g should be added to the diagram as below [1]

1s	2s	3s	4s	5s	6s	7s	**8s**
	2p	3p	4p	5p	6p	**7p**	
		3d	4d	5d	**6d**		
			4f	5f			
				5g			

(f) two *g* electrons [1]

[Total: 6]

Example Candidate Response – Pass

5 The scientific community was shocked at the recent claim of the discovery of an isotope of a new element with a mass number of 292 (published in *arXiv*, 2008): this is over 50 mass units higher than uranium, the heaviest known naturally-occurring element. There is a possibility that there is an 'island of stability' beyond the known Periodic Table at some very high atomic numbers.

(a) The authors of this claim suggested that the atomic number of the element is 122. How many neutrons are there in this isotope?

170 ✓ [1] 1

(b) If this element really exists then it will require a new block of the periodic table, corresponding to the occupancy of another type of subshell, beyond the *s*, *p*, *d* and *f*. This would be a *g* subshell, which is predicted to be found in the 5th shell of an atom, i.e. the 5g subshell.

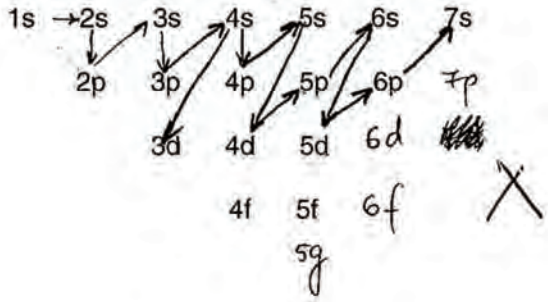
Based upon the sequence of subshells in the Periodic Table, *s*, *p*, *d*, *f*, predict how many orbitals there are in a *g* subshell.

9 (nine) subshells ✓ [1] 1

(c) Predict how many elements there would be in the first row of the *g*-block.

18 ✓ [1] 1

Below is a scheme of the 17 lowest energy subshells, which can be used to show the order in which the subshells are filled by electrons (the Aufbau principle).



(d) List the order of filling subshells from 4p to 5d.

4p → 5p → 6s → 5d ✗ [1] 0

(e) The subshells in the scheme above are those that are occupied by the elements up to uranium. Add to the above diagram the next four subshells that would be expected to be filled. [1] 0

(f) Following the Aufbau principle, how many electrons in the 5g subshell would element 122 be expected to have?

✗ [1] 0

[Total: 6] 3

Examiner Comment

The candidate was able to use their knowledge of atomic structure and *s, p, d, f* orbitals and extend it to a new element containing a *g* subshell scoring the marks for **(a)**, **(b)** and **(e)**. However, the candidate was unable to apply the Aufbau principle to this new element which would have raised their level of achievement.

Question 6 Mark Scheme

(a) 5 signals [1]

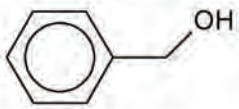
(b) 3 isomers [1]

(c) any oxidising agent, e.g. manganate, dichromate, chlorate
ignore omission of acidification where necessary
oxidising agents that lack an oxygen atom need to be indicated as (aq)
if a formula is given it must be correct to earn the mark
if an oxidation number is quoted it must be correct to earn the mark [1]

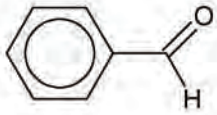
(d) Grignard (reagent) [1]

(e) 1: (nucleophilic) substitution allow hydrolysis (1)
5: hydrolysis (1)
6: dehydration / elimination allow reduction as FGL of functional group carbon has decreased by 1 (1) [3]

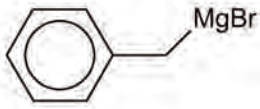
(f) A: benzyl alcohol (phenylmethanol) (1)



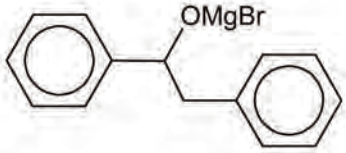
B: benzaldehyde (1)



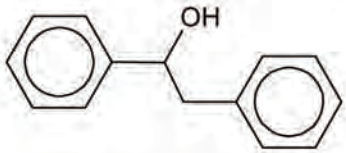
C: benzylmagnesium bromide (1)



D: $PhCH(OMgBr)CH_2Ph$ (1)



E: $PhCH(OH)CH_2Ph$ (1)

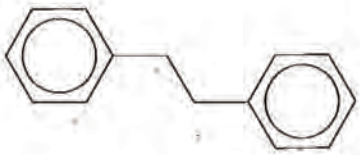


allow all structural and displayed formulae as long as structure is unambiguous
penalise repeated systematic or trivial errors only once [5]

[Total: 12]

Example Candidate Response – Pass

6 A survey in 2008 of the 24 million known organic compounds identified the most common structural motifs. The 3rd most popular shape (after the hexagon and pentagon) was based on the 1,2-diphenylethane molecule.



C_6H_6

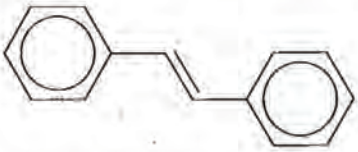
(a) How many signals would there be in the carbon-13 NMR spectrum of the 1,2-diphenylethane molecule?

3 X [1] 0

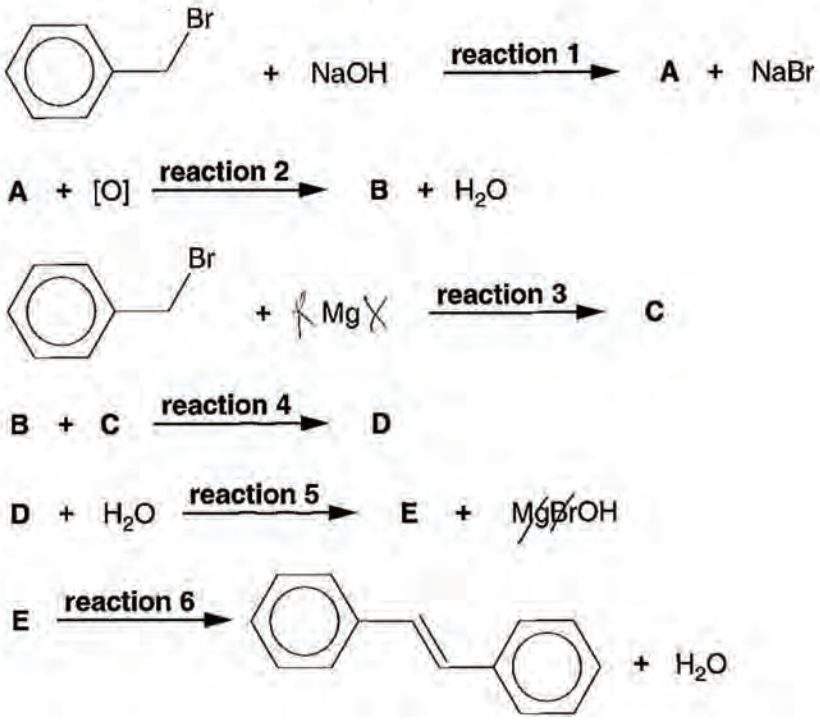
(b) If one of the hydrogen atoms on one of the phenyl groups of 1,2-diphenylethane is substituted with a chlorine atom, how many possible isomers would there be?

5 X [1] 0

A closely related compound to 1,2-diphenylethane is 1,2-diphenylethene, commonly known as stilbene.



Stilbene can be synthesised from (bromomethyl)benzene according to the scheme below. The reactions are labelled **1** to **6** above the reaction arrows. The benzene ring does not take part in any of these reactions.



(c) **Reaction 2** is a partial oxidation. In the equation [O] represents the oxygen atom provided from some suitable reagents. Suggest such a reagent.

acidified Potassium Permanganate $H^+/KMnO_4$ ✓ [1]

(d) What is the name of the **type** of compound produced in **reaction 3**?

Metal hydride ✗ [1]

(e) Classify the **type** of reaction in **1, 5** and **6**.

reaction 1 Substitution ✓ [1]

reaction 5 hydrolysis ✓ [1]

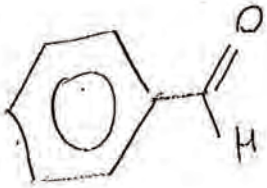
reaction 6 Condensation ✗ [1]

(f) Draw the structures of unknowns **A** to **E**.

A

✓ [1]

B

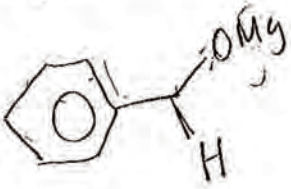


✓ [1]

C

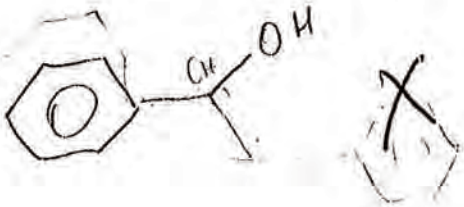
✗ [1]

D



✗ [1]

E



✗ [1]

5 [Total: 12]

Examiner Comment

The candidate showed some knowledge and understanding of the chemistry of halogenoalknes and alcohols in recognising the types of reactions 1 and 5, identifying the products of reactions 1 and 2, and recalling a reagent to oxidise product A.

Question 7 Mark Scheme

(a) δ+ on the I and δ– on the N
OR correct use of arrow nomenclature [1]

(b) (i) $NH_3 + 3F_2 \rightarrow NF_3 + 3HF$ [1]

(ii) $2NF_3 \rightarrow N_2 + 3F_2$ or with stoichiometry 1:1/2:3/2 [1]

(iii) correct dot-cross diagram, including lone pairs on the fluorines (1)
shape = pyramidal (or trigonal pyramidal) (1)
bond angle indicated as anything from 102 to 107° (1)
(actual bond angle is 102.3 degrees: there is weak bonding pair-bonding pair repulsion due to the electron density in the N–F bonds being shifted towards the electronegative fluorine atoms) [3]

(iv) stronger N–F bonds / higher activation energy
allow: since the F–F bond is weaker than the C*l*–C*l* bond the thermal decomposition of NF_3 will be less exothermic than for NCl_3 [1]

(c) (i) $N_2O_5 + H_2O \rightarrow 2HNO_3$ [1]

(ii) $12HNO_3 + P_4O_{10} \rightarrow 6N_2O_5 + 4H_3PO_4$ (2)
accept $6HNO_3 + P_2O_5 \rightarrow 3N_2O_5 + 2H_3PO_4$
1 mark for correct formulae but incorrect balancing [2]

(iii) $NO_2^+ NO_3^-$ or NO_2NO_3 [1]

[Total: 11]

Example Candidate Response – Distinction (D1)

7 Nitrogen forms a variety of oxides and halides.

(a) Nitrogen triiodide, NI_3, is an explosive that detonates with a snap even when only touched lightly. Given that the electronegativity value for nitrogen is 3.07 and for iodine is 2.36, indicate below the dipole in an N–I bond.

$\delta-$ $\delta+$
N–I ✓

[1] 1

(b) (i) Nitrogen trifluoride, NF_3, can be prepared by reacting ammonia with fluorine. In this reaction the fluorine oxidises the nitrogen in ammonia while the oxidation number of hydrogen is unchanged.

Give the equation for this reaction.

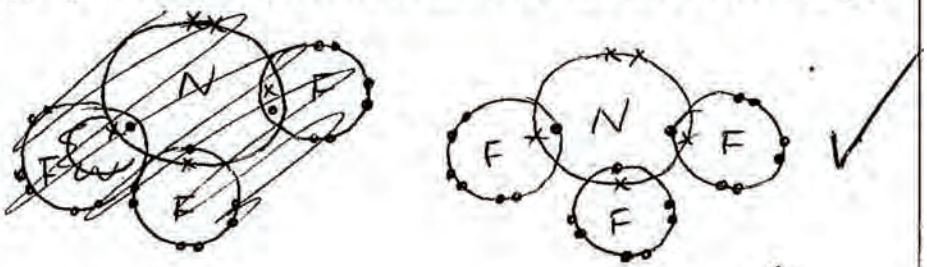
$NH_3 + 6F \longrightarrow NF_3 + 3HF$ X [1] 0

(ii) Nitrogen trifluoride is used to etch silicon in microelectronics. It is decomposed to its elements and the fluorine is used to attack the silicon.

Give the equation for the decomposition of nitrogen trifluoride.

$2NF_3 \longrightarrow N_2 + 3F_2$ ✓ [1] 1

(iii) Nitrogen trifluoride is a molecule that has attracted controversy recently for its possible potent contribution to the greenhouse effect. Draw the dot-cross diagram of this molecule; only include outer electrons. State the shape and the bond angle.



✓

shape trigonal bipyramidal ✓

bond angle 107° ✓ [3]

(iv) Whereas nitrogen trifluoride is reasonably easy to handle, nitrogen trichloride is an extremely dangerous explosive. Suggest why nitrogen trifluoride is more stable than the other nitrogen trihalides.

Because of the short N - F bond which it makes it have a stronger bond enthalpy. ✓ [1]

(c) N_2O_5 is a less well-known oxide of nitrogen.

(i) N_2O_5 is the anhydride of nitric acid, which means that it reacts with water to produce the acid. Write an equation for N_2O_5 reacting with water.

$N_2O_5 + H_2O \rightarrow 2HNO_3$ [1]

(ii) N_2O_5 can be made by reacting nitric acid with a dehydrating agent such as phosphorus(V) oxide. Bearing in mind that phosphorus(V) oxide is the anhydride of phosphoric acid, H_3PO_4, write an equation for the reaction between nitric acid and phosphorus(V) oxide.

$6HNO_3 + P_2O_5 \rightarrow 2H_3PO_4 + 3N_2O_5$ [2]

(iii) In the solid state N_2O_5 is an ionic compound. Given that N_2O_5 is sometimes known as 'nitronium nitrate' write the ionic formula representation of N_2O_5.

$NO_2 NO_3$ [1]

[Total: 11]

10

Examiner Comment

Although the overall performance on this question was excellent the candidate made a serious error in the basic chemical knowledge required for **(b) (i)**.

Example Candidate Response – Merit

7 Nitrogen forms a variety of oxides and halides.

For Examiner's Use

(a) Nitrogen triiodide, NI_3, is an explosive that detonates with a snap even when only touched lightly. Given that the electronegativity value for nitrogen is 3.07 and for iodine is 2.36, indicate below the dipole in an N–I bond.

$\delta^- \quad \delta^+$
N–I ✓ [1]

1 ✓

(b) (i) Nitrogen trifluoride, NF_3, can be prepared by reacting ammonia with fluorine. In this reaction the fluorine oxidises the nitrogen in ammonia while the oxidation number of hydrogen is unchanged.

Give the equation for this reaction.

$NH_3 + 3F_2 \longrightarrow NF_3 + 3HF$ ✓ [1]

1 ✓

(ii) Nitrogen trifluoride is used to etch silicon in microelectronics. It is decomposed to its elements and the fluorine is used to attack the silicon.

Give the equation for the decomposition of nitrogen trifluoride.

$2NF_3 \longrightarrow N_2 + 3F_2$ ✓ [1]

1 ✓

(iii) Nitrogen trifluoride is a molecule that has attracted controversy recently for its possible potent contribution to the greenhouse effect. Draw the dot-cross diagram of this molecule; only include outer electrons. State the shape and the bond angle.

✓

$109.5 - 2.5 = 107°$

tetrahedral shape

shape tetrahedral ✗

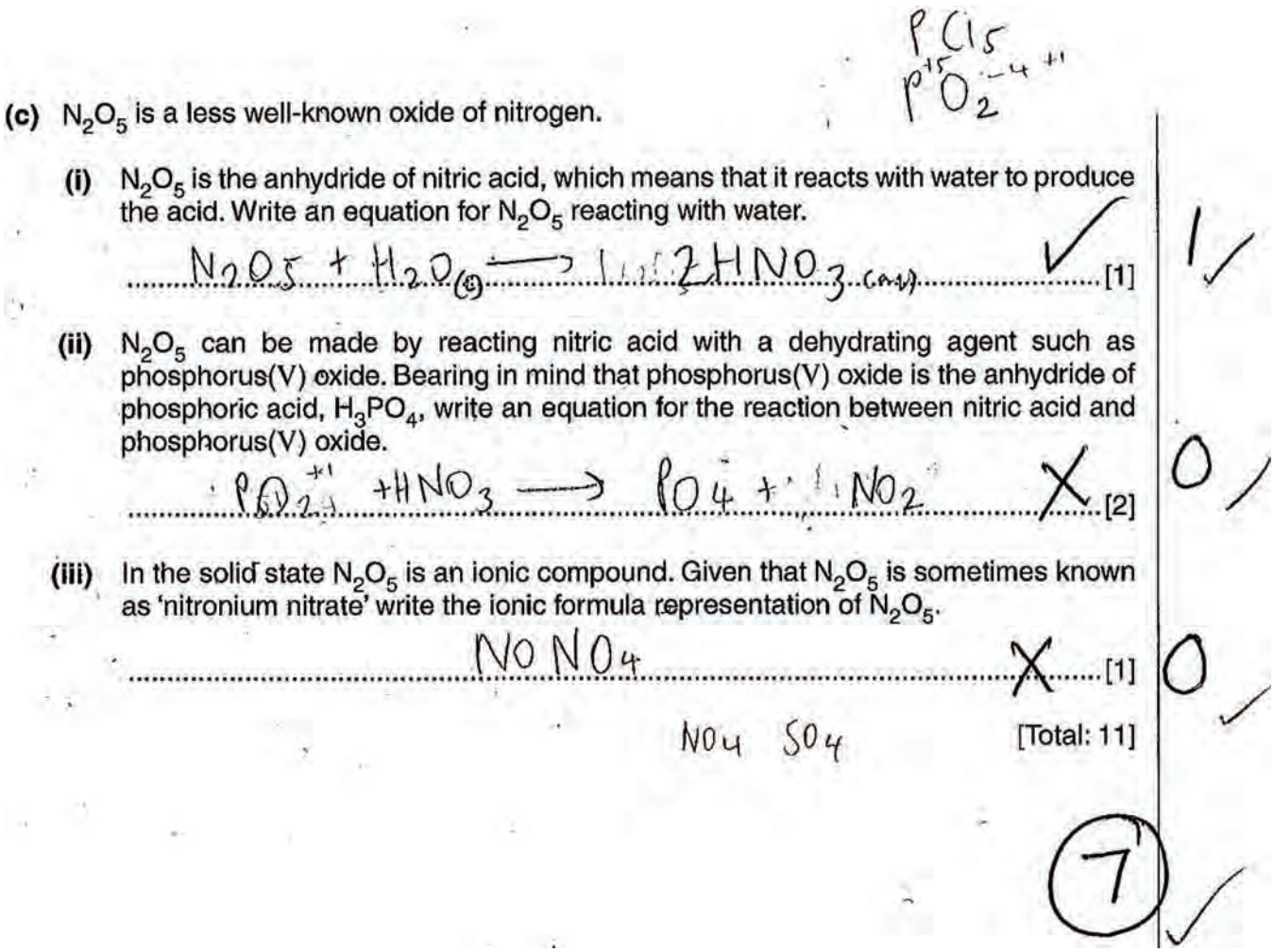
bond angle 107° ✓ [3]

2 ✓

(iv) Whereas nitrogen trifluoride is reasonably easy to handle, nitrogen trichloride is an extremely dangerous explosive. Suggest why nitrogen trifluoride is more stable than the other nitrogen trihalides.

The F–N bond will be very short and strong ✓ meaning more energy required to break it making it more stable [1]

1 ✓



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(i) N_2O_5 is the anhydride of nitric acid, which means that it reacts with water to produce the acid. Write an equation for N_2O_5 reacting with water.

$N_2O_5 + H_2O_{(g)} \longrightarrow 1:2HNO_3$ (aq) ✓ [1]

(ii) N_2O_5 can be made by reacting nitric acid with a dehydrating agent such as phosphorus(V) oxide. Bearing in mind that phosphorus(V) oxide is the anhydride of phosphoric acid, H_3PO_4, write an equation for the reaction between nitric acid and phosphorus(V) oxide.

$PO_2 + HNO_3 \longrightarrow PO_4 + NO_2$ ✗ [2]

(iii) In the solid state N_2O_5 is an ionic compound. Given that N_2O_5 is sometimes known as 'nitronium nitrate' write the ionic formula representation of N_2O_5.

$NONO_4$ ✗ [1]

NO_4 SO_4

[Total: 11]

Examiner Comment

The candidate showed an understanding of electronegativity values and correctly predicted the dipole in an N–I bond. In **(b) (i)**, **(b) (ii)** and **(c)** the candidate was able to write the balanced equations using the information given but was not able to write the more difficult equation in **(c) (ii)**. Part **(b) (iii)** was targeted at the lower grades but the candidate only scored 2/3 marks. The candidate showed an understanding of bond lengths/strengths in a covalent compound but was unable to use the information in **(c) (iii)** to write an ionic formula, the more accessible and widely scored mark.

Question 8 Mark Scheme

(a) cis (or Z) [1]

(b) ictadeca-6,9,12,15-tetraenoic acid
accept tetrenoic instead of tetraenoic
accept without the hyphens or with hyphens instead of commas. [1]

(c) $2^5 = 32$ geometric isomers [1]

(d) instantaneous dipole – induced dipole forces [1]

(e) the 3rd from last carbon atom from the COOH functional group is the final one in a C=C double bond (owtte) [1]

(f) $BrCH_2CHBrCH_3$ (1)
accept any unambiguous structure that is correct.
1,2-dibromopropane (1)
don't penalise errors with commas, spaces or hyphens [2]

(g) (i) amount of C=C bonds in 100 g = 6 × 100 g / 328 g mol^{-1} = 1.83 mol (1)
mass of iodine required = 1.83 mol × 254 g mol^{-1} = 465 g (1)
ecf for second mark if correct calculation with wrong number of C=C bonds.
1 mark lost for not quoting final answer to 3 or 4 sig. figs.
no penalties for missing units [2]

(ii) oleic acid $C_{18}H_{34}O_2$ [1]

(h) (i) the I–Cl bond has a (permanent) dipole [1]

(ii) use of cervonic acid in calculation (as it reacts with the most ICl) (1)
vol of 25% excess ICl
= 1.25 × (6 × 0.100 g / 328 g mol^{-1}) / 0.100 mol dm^{-3} = 22.9 cm^3 (1)
give this mark if a correct calculation has been performed with another fatty acid.
excess ICl to be used = 25.0 cm^3 (1)
ecf for rounding up the volume of ICl to a pipette size (10 cm^3, 20 cm^3 or 50 cm^3)
transferred using a pipette (1) [4]

(iii) transfer sample directly to stoppered flask (1)
250 cm^3 flask (1)
transfer using 1,1,1-trichloroethane washings (1)
leave for 30 minutes after adding Wijs' reagent (1)
measuring cylinder used for adding KI (1)
measuring cylinder used for adding water (1)
$Na_2S_2O_3$ dispensed from a burette or use of the word "titrate" or "titration" (1)
starch indicator (1)
blue-black to colourless (1)
white tile (1)
shaking of (stoppered) flask after $Na_2S_2O_3$ additions ("swirling" not enough) (1)
working with 1,1,1-trichloroethane in a fume cupboard (1) [max 8]

(iv) vol $Na_2S_2O_3(aq)$ × 0.100 mol dm^{-3} = amount $Na_2S_2O_3(aq)$ (1)
amount $Na_2S_2O_3(aq)$ = 2 × amount IC*l* (excess) (1)
amount IC*l* (reacted) = amount IC*l* (initial) – amount IC*l* (excess) (1)
compare this amount IC*l* (reacted) with n(C=C bonds) × 0.100 g / molar mass for each fatty acid (in order to identify the fatty acid, which will be the one that most closely resembles the experimental value.) (1)
loss of 1 mark for confusing I_2 with IC*l*. [4]

[Total: 27]

Example Candidate Response – Distinction (D1)

8 Evidence is accumulating that omega-3 oils help to protect us from schizophrenia and depression, and even improve learning and memory. Omega-3 oils are glyceryl esters of omega-3 fatty acids.

One omega-3 fatty acid is cervonic acid.

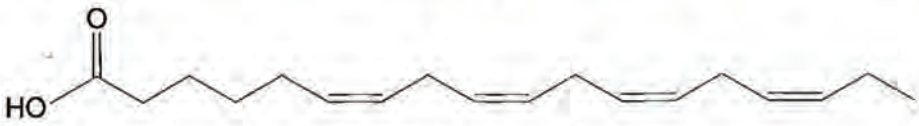
cervonic acid

(a) Which configuration of the C=C double bonds is present in this molecule?

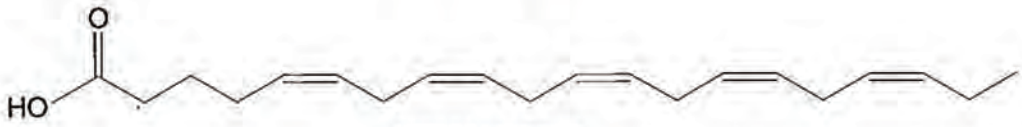
cis ✓ [1]

1

The systematic name of cervonic acid (ignoring geometric isomerism) is docosa-4,7,10,13,16,19-hexaenoic acid. "Docosa" indicates that there is a 22-carbon chain. The numbers indicate the carbon atom where the C=C double bonds start, counting from the carboxylic acid (–COOH) functional group. "Hexaen" indicates that there are six double bonds in the chain. Two other omega-3 fatty acids are stearidonic acid and timnodonic acid.



stearidonic acid



timnodonic acid

(b) "Octadeca" indicates that there is an 18-carbon chain. Write down the systematic name for stearidonic acid. Ignore the geometric isomerism.

Octadeca- 6, 9, 12, 15 butaenoic pentaenoic acid ✗ [1]

0

(c) How many geometric isomers are there of timnodonic acid, including the molecule shown?

32 ✓ [1]

1

(d) What is the name of the intermolecular force that will operate between the hydrocarbon chains? Ring the correct option. [1]

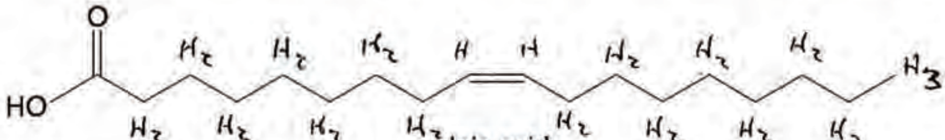
permanent dipole-permanent dipole

hydrogen bonding

instantaneous dipole-induced dipole ✓

1

(e) Another fatty acid that is believed to have beneficial health effects is oleic acid.



oleic acid

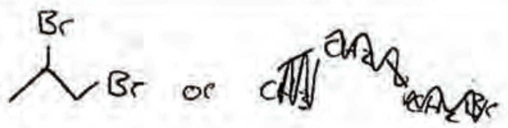
"Omega" is the **last** letter of the Greek alphabet. By comparing oleic acid, which is **not** an omega-3 acid, with the omega-3 fatty acids in part **(a)**, suggest what "omega-3" relates to in the structure of these oils and fatty acids.

That there is a double bond 3 carbons away from the end of the hydrocarbon chain ✓ [1]

1

(f) It is possible to differentiate between different types of fatty acids and oils in the laboratory by measuring the degree of unsaturation in the hydrocarbon chains. Halogens react with alkenes in an addition reaction.

Draw the structure of the product when propene reacts with Br_2 and name it systematically.

structure	 ✓
name	1,2 di-bromopropane ✓

[2]

2

(g) Table 8.1 shows information about various fatty acids.

Table 8.1

fatty acid	molecular formula	molar mass / g mol^{-1}	number of C=C double bonds
cervonic acid	$C_{22}H_{32}O_2$	328	6
stearidonic acid	$C_{18}H_{28}O_2$	276	4
timnodonic acid	$C_{20}H_{30}O_2$	302	5
oleic acid	$C_{18}H_{34}O_2$ ✓	282	1

$C_{18}H_{34}O_2$ (is not legible)

(i) The degree of unsaturation in a fatty acid is commonly expressed by the mass of iodine that reacts with 100.0 g of the acid. Use the information in Table 8.1 to calculate the mass of iodine that would react with 100.0 g of cervonic acid. Use an appropriate number of significant figures in your answer.

Reacts with 6 I_2 $6 \times 0.3049 = x \div (127 \times 2)$ ✓✓

Mol acid = $\frac{100}{328}$ = 0.3059 mol

464.6 g (4SF) [2]

2

(ii) Write the molecular formula of oleic acid in Table 8.1. [1]

(h) The interhalogen compound IC*l* also reacts with alkenes in an addition reaction. It is commonly used as *Wijs' reagent*, a 0.100 mol dm^{-3} solution of IC*l* in glacial ethanoic acid. IC*l* reacts faster with alkenes than the pure halogens and so can be used to determine volumetrically the unsaturation in fatty acids and oils.

(i) Suggest why IC*l* reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

ICl has a dipole. The δ+ of the I in ICl will also help encourage electrophilic addition across the C=C bond. Pure halogens have no dipole, so will not undergo electrophilic addition easily. [1]

For the volumetric determination, 30 minutes is required for the reaction between the fatty acid and Wijs' reagent to go to completion. A common solvent for Wijs' reagent and the fatty acids is 1,1,1-trichloroethane.

You are to design an experiment using Wijs' reagent to identify an unknown fatty acid that is one of cervonic acid, stearidonic acid or timnodonic acid. You have 0.100 g of the unknown acid dissolved in 20 cm^3 of 1,1,1-trichloroethane.

You should aim to produce data that is as accurate as possible using conventional laboratory methods.

You should use the information in Table 8.1.

(ii) The first part of the experiment involves adding an accurately known excess of Wijs' reagent to the fatty acid solution. The amount of Wijs' reagent should be at least 25% greater than the maximum amount that could be required to react with the fatty acid.

Work out a suitable volume of Wijs' reagent to add to the fatty acid solution and explain how you would add this quantity in the laboratory.

Cervonic acid has most double bonds, and an only slightly higher ~~lowest molar mass is stearidonic acid (276) so there~~ would be molar mass - it would need most Wijs' reagent.

Mol acid = $\frac{0.1}{328} = 3.05 \times 10^{-4}$ mol

will need $6 \times 3.05 \times 10^{-4}$ mol Wijs' = 1.83×10^{-3} mol

conc. Wijs' is 0.1 mol/dm^3

mol = conc × volume volume = $(1.83 \times 10^{-3}) \div 0.1$

$= 0.0183$ dm^3

$= 18.3$ cm^3

25% XS = at least $18.3 \times 1.25 = 22.9$ cm^3

So add 25 cm^3 Wijs' with a 25 cm^3 pipette - as this is most accurate way to measure [4]

After this reaction is complete, 10 cm^3 of a 2.0 mol dm^{-3} aqueous solution of KI is added to the non-aqueous fatty acid solution to convert the excess IC*l* to iodine, I_2.

$$ICl + KI \rightarrow I_2 + KCl$$

This quantity of KI(aq) should be a large excess. Next, 100 cm^3 of deionised water is added to the mixture. The iodine is distributed between the aqueous and non-aqueous phases.

(iii) The second part of the experiment involves determining the amount of iodine generated by the excess IC*l*. This is done using a 0.100 mol dm^{-3} solution of sodium thiosulfate, $Na_2S_2O_3$.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The whole mixture is reacted with sodium thiosulfate in one batch since the iodine is distributed between the phases. In this reaction considerable shaking is needed to ensure adequate mixing of the phases.

Write out a method for both parts of the experiment that a fellow student could follow. The original fatty acid solution comes in a small sample bottle that is nearly full. Include safety considerations.

Using a 25 cm^3 pipette, transfer 25 cm^3 of the Wijs' reagent to the fatty acid solution.* Stir the mixture with a glass rod, then leave for 30 minutes. After this time, add 10 cm^3 of KI solution (1.0 mol/dm^3) measured with a measuring cylinder to the conical flask. Using a measuring cylinder, add 100 cm^3 water to the flask. Shake the mixture well, with a bung in the top of the flask. Add 5 drops of starch to the flask & swirl the contents. There will appear a blue-black colour. Fill a burette (50 cm^3) with sodium thiosulphate and begin a titration. Add the thiosulphate in 1 cm^3 batches. Between each addition, place a bung into the top of the flask & shake well for 5 seconds. Continue this process until there is a colour change from blue-black to colourless. Make a note of the volume of thiosulphate added.

SAFETY precautions: When shaking the conical flask,

* 250 in a 1000 cm^3 volumetric conical flask.

there is a slight chance that some of the reactants may escape - make sure that the bung is securely in place when shaking, & wear goggles to protect eyes if some reactants do escape. - they may be irritants or otherwise harmful If acid is splashed on skin, wash the area with a large & excess of tap water. Also, some of the solvents eg ethanoic acid & trichloroethane will be highly flammable - do not have any naked flames in the laboratory. [8]

8 max.

(iv) Explain how you would work out the identity of the fatty acid given the volume of thiosulfate obtained from the experiment.

volume thiosulphate (cm^3) ÷ 1000 = mol ÷ concentration
find mol thiosulphate used using above eq^ ✓
Because of stoichiometry - we know that ½ this number of mol I_2 has been used, and there is the same mol ICl as I_2
From the moles used of 'Wijs' solution* (calculated in part ii) subtract the mol ICl left over at the end (the same as the I_2 used up by thiosulphate) ✓. This gives the amount in moles of ICl which reacted with the acid. Using the data in table 8.1, calculate the theoretical amount of acid in 1.00 g of each acid used^. Now compare the ratios of the mol acid used : mol ICl left - one of these ratios will correspond to the number of double bonds in the acid - and this will be the acid used. Eg a 1:6 ratio of mol acid : mol ICl shows 6 double bonds are present - if the acid has 6 double bonds*, then this is the one which was tested. [4]
[Total: 27]

3

25

* initially

* refer to table 8.1

Examiner Comment

This good Distinction candidate has only dropped 2 marks. Writing 'butaenoic' in part **(b)** was a common error even at Distinction level. Part **(h) (iv)** was targeted at the most able candidates and gaining 3 out of the 4 marks here was a good achievement.

Example Candidate Response – Distinction

8 Evidence is accumulating that omega-3 oils help to protect us from schizophrenia and depression, and even improve learning and memory. Omega-3 oils are glyceryl esters of omega-3 fatty acids.

One omega-3 fatty acid is cervonic acid.

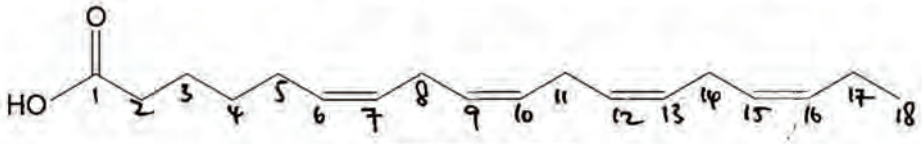
cervonic acid

(a) Which configuration of the C=C double bonds is present in this molecule?

CIS – configuration ✓ [1]

1

The systematic name of cervonic acid (ignoring geometric isomerism) is docosa-4,7,10,13,16,19-hexaenoic acid. "Docosa" indicates that there is a 22-carbon chain. The numbers indicate the carbon atom where the C=C double bonds start, counting from the carboxylic acid (–COOH) functional group. "Hexaen" indicates that there are six double bonds in the chain. Two other omega-3 fatty acids are stearidonic acid and timnodonic acid.



stearidonic acid

timnodonic acid

(b) "Octadeca" indicates that there is an 18-carbon chain. Write down the systematic name for stearidonic acid. Ignore the geometric isomerism.

Octadeca-6,9,12,15-butenoic acid ✗ [1]

0

(c) How many geometric isomers are there of timnodonic acid, including the molecule shown?

25 ✗ [1]

0

(d) What is the name of the intermolecular force that will operate between the hydrocarbon chains? Ring the correct option. [1]

permanent dipole-permanent dipole

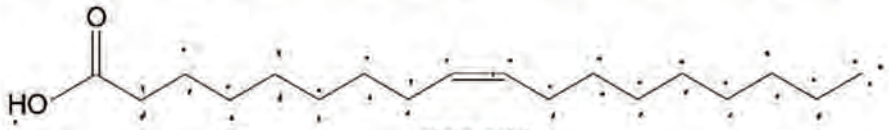
hydrogen bonding

instantaneous dipole-induced dipole

hydrogen bonds

0

(e) Another fatty acid that is believed to have beneficial health effects is oleic acid.



oleic acid

"Omega" is the **last** letter of the Greek alphabet. By comparing oleic acid, which is **not** an omega-3 acid, with the omega-3 fatty acids in part **(a)**, suggest what "omega-3" relates to in the structure of these oils and fatty acids.

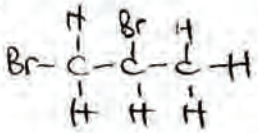
There must be at least 3 double bonds (C=C) in the chain, with C=C bonds [1]

0

(f) It is possible to differentiate between different types of fatty acids and oils in the laboratory by measuring the degree of unsaturation in the hydrocarbon chains. Halogens react with alkenes in an addition reaction.

Draw the structure of the product when propene reacts with Br_2 and name it systematically.

structure



name 1,2-dibromopropane

[2]

2

(g) Table 8.1 shows information about various fatty acids.

Table 8.1

fatty acid	molecular formula	molar mass /g mol^{-1}	number of C=C double bonds
cervonic acid	$C_{22}H_{32}O_2$	328	6
stearidonic acid	$C_{18}H_{28}O_2$	276	4
timnodonic acid	$C_{20}H_{30}O_2$	302	5
oleic acid	$C_{18}H_{34}O_2$	282	1

(i) The degree of unsaturation in a fatty acid is commonly expressed by the mass of iodine that reacts with 100.0 g of the acid. Use the information in Table 8.1 to calculate the mass of iodine that would react with 100.0 g of cervonic acid. Use an appropriate number of significant figures in your answer.

Cervonic acid + 6 I_2 → ....

$n = \frac{100}{328}$

$= 0.305$

$n = 0.305 \times 6$

$= 1.829$

mass $= 1.829 \times 127 \times 2$

$= 464.6$

464.6 g (to 1 dp) [2]

2

[Turn over

(ii) Write the molecular formula of oleic acid in Table 8.1. [1]

(h) The interhalogen compound IC*l* also reacts with alkenes in an addition reaction. It is commonly used as *Wijs' reagent*, a 0.100 mol dm^{-3} solution of IC*l* in glacial ethanoic acid. IC*l* reacts faster with alkenes than the pure halogens and so can be used to determine volumetrically the unsaturation in fatty acids and oils.

(i) Suggest why IC*l* reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

ICl is polar, with $\delta\oplus$ Cl^- ions. pure halogen has no dipole moments and are non-polar. $\delta\oplus$ I in ICl can attract alkene π-bond (high e⁻ density) easier to break it, acting as an electrophile, so react faster. Pure halogen do not have dipoles. [1]

For the volumetric determination, 30 minutes is required for the reaction between the fatty acid and Wijs' reagent to go to completion. A common solvent for Wijs' reagent and the fatty acids is 1,1,1-trichloroethane.

You are to design an experiment using Wijs' reagent to identify an unknown fatty acid that is one of cervonic acid, stearidonic acid or timnodonic acid. You have 0.100 g of the unknown acid dissolved in 20 cm^3 of 1,1,1-trichloroethane.

You should aim to produce data that is as accurate as possible using conventional laboratory methods.

You should use the information in Table 8.1.

(ii) The first part of the experiment involves adding an accurately known excess of Wijs' reagent to the fatty acid solution. The amount of Wijs' reagent should be at least 25% greater than the maximum amount that could be required to react with the fatty acid.

Work out a suitable volume of Wijs' reagent to add to the fatty acid solution and explain how you would add this quantity in the laboratory.

Cervonic acid has the most number of C=C, = 6

∴ 12 I^- will be substituted to the acid, ~~12 moles of~~

Cervonic acid + (12) ICl → ~~After Halogenation~~ saturated.

$n(\text{Cervonic acid}) = \frac{0.1}{328} = 3.04 \times 10^{-4}$

$n(ICl) = 12 \times 3.04 \times 10^{-4} = 3.65 \times 10^{-3}$ mol

Least vol of ICl for cervonic acid $= \frac{3.66 \times 10^{-3}\ \text{mol}}{0.1\ \text{mol dm}^{-3}}$

$= 0.0365\ \text{dm}^3$

$= 36.585\ \text{cm}^3$

Suitable volume $= 36.585\ \text{cm}^3 \times (1 + 25\%)$

$= 45.7\ \text{cm}^3$ (to 3 s.f.) [4]

After this reaction is complete, 10 cm^3 of a 2.0 mol dm^{-3} aqueous solution of KI is added to the non-aqueous fatty acid solution to convert the excess IC*l* to iodine, I_2.

$$ICl + KI \rightarrow I_2 + KCl$$

This quantity of KI(aq) should be a large excess. Next, 100 cm^3 of deionised water is added to the mixture. The iodine is distributed between the aqueous and non-aqueous phases.

(iii) The second part of the experiment involves determining the amount of iodine generated by the excess IC*l*. This is done using a 0.100 mol dm^{-3} solution of sodium thiosulfate, $Na_2S_2O_3$.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The whole mixture is reacted with sodium thiosulfate in one batch since the iodine is distributed between the phases. In this reaction considerable shaking is needed to ensure adequate mixing of the phases.

Write out a method for both parts of the experiment that a fellow student could follow. The original fatty acid solution comes in a small sample bottle that is nearly full. Include safety considerations.

1st Part :

(1) Using a pipette with measuring 20 cm^3, transfer 20 cm^3 of fatty acid from sample bottle to a 300 cm^3 conical flask.

(2) Using a 100 cm^3 burette with graduate measuring of 1 cm^3, add 50 cm^3 of Wijs' reagent into flask. Take safety precaution, wear goggles and lab coat to ensure no chemicals are spilled on body. Before use burette, rinse with water then reagent, empty jet space, remove funnell before start adding reagent.

(3) Leave mixture standing in room temperature for 30 minutes, shake constantly. Seal flasks with a bung to ensure nothing contaminate mixture.

(4) Using a 10 cm^3 measuring cylinder, measure 10 cm^3 KI (2M) and add to mixture. Shake well to ensure reaction.

(5) Using a 100 cm^3 measuring cylinder, measure 100 cm^3 deionised water to mixture. Leave to allow iodine goes into equilibrium portion.

2nd part:

(1) Using a new 100 cm^3 burette, rinse with water, then with $Na_2S_2O_3$, empty jet space, fill up burette, take out funnell

(read carefully from menisc)

ad record the inital volum of $Na_2S_2O_3$ on burette readg.

(2) Adding 1 drop of $Na_2S_2O_3$ at a time into mixture, stop when the mixture colour is pale yellow

(3) Using a dropper (graduate readg $1\,cm^3$) add 2 cm^3 of starch solution into mixture, it should turn purple

(4) continue titrating until mixture turn colorless.

(5) record final volum on burette and calculate titre.

(6) Repeat experiment until a constant readg of titre within $\pm 0.1\,cm^3$ [8]

6

(iv) Explain how you would work out the identity of the fatty acid given the volume of thiosulfate obtained from the experiment.

Know's volume of thiosulfate = x cm^3

mole = $0.1\,mol\,dm^{-3} \cdot \frac{x}{1000} = 1 \times 10^{-4}x$ mole

$n(I_2) = 5 \times 10^{-5}x$ mole ✓÷2

n (excess ICl) = $5 \times 10^{-5}x$ mole

n (ICl used to react with fatty acid) = $3.66 \times 10^{-3} - 5 \times 10^{-5}x$ ✓

let fatty acid Mr be y

mole of fatty acid = $\frac{0.1}{y}$

If cervonic acid, ICl used is 12x mole of fatty acid ✓

Stearidonic acid 8x

timnodonic acid. 10x

Plug in y with the 3 acid and see which is the correct ratio. That will be the acid ✓

[4]

[Total: 27]

18

Examiner Comment

The candidate performed well in part **(h) (iv)** suggesting how a relevant but unfamiliar calculation could be carried out but was unable to do the more accessible calculation in part **(h) (ii)**. An incorrect answer was given to part **(d)** which would not have been expected at this level.

Paper 3 Part B Written

Question 1 Mark Scheme

Question Number	Expected Answer	Max Marks	Rationale
1 (a) (i)	(A and B) $H^+ + CO_3^{2-} \rightarrow HCO_3^-$	1	1/2 for overall equation
(ii)	(C and D) $HCO_3^- + H^+ \rightarrow H_2O + CO_2$	1	1/2 for both non-ionic
(b) (i)	methyl yellow	1	
(ii)	pK_a of indicator matches pH change at equivalence	1	allow pK_a on vertical section of graph owtte
(iii)	from Yellow to Red	1	
(c)	$18.8 \times 0.200 / 1000 = 3.76 \times 10^{-3}$ mol of HNO_3 so amount $Na_2CO_3 = 3.76 \times 10^{-3} / 2 = 1.88 \times 10^{-3}$ mol so conc $= 1.88 \times 10^{-3} \times 1000 / 20 = 0.094$ mol dm^{-3} $= 0.094 \times 106 = 9.964$ g dm^{-3}	 1 1 1	allow 9.96 do not allow 10/10.0 ecf ecf
(d) (i)	$H_2O \rightleftharpoons H^+ + OH^-$ / $2H_2O \rightleftharpoons H_3O^+ + OH^-$	1	
(ii)	$K_c = [H^+][OH^-]/[H_2O]$ $[H_2O]$ const negligible dissociation / equilibrium left	1 1 1	 allow water is in large excess
(iii)	$[H^+] = \sqrt{51.3 \times 10^{-14}} = 7.16 \times 10^{-7}$ (mol dm^{-3}) pH = –log $7.16 \times 10^{-7} = 6.15$	1 1 + 1	allow 6.14
(iv)	(endothermic) $[H^+]$ higher at higher temperature so equilibrium moves right with increased temperature / increased temperature favours endothermic change	1 1	 allow ecf from **(d)(iii)**
(e)	$5 \times 1 / 1000 = 5 \times 10^{-3}$ mol of H^+ $0.1 \times 1.00 \times 10^{-4} = 1 \times 10^{-5}$ mol of HCl in soln $1 \times 10^{-5} + 5 \times 10^{-3}$ in 105 cm^3 $= 5.01 \times 10^{-3} / 0.105 = 0.0477$ mol dm^{-3} pH = -log 0.0477 = 1.32 calculation of initial pH = 4.77 after addition of HCl; $0.01 + 5 \times 10^{-3} = 0.015$ mol $= 0.015 \times 1000 / 105 = 0.143$ mol dm^{-3} CH_3COOH and $0.01 - 5 \times 10^{-3} = 0.005$ mol $= 0.005 \times 1000 / 105 = 0.0476$ mol dm^{-3} CH_3COO^- pH = pK_a – log [acid] / [salt] $= 4.77 - \log 0.143 / 0.0476 = 4.17$	1 1 1 1 1 1 1 1	 1.32 = 4 marks 4.17 = 4 marks
		[25]	

Example Candidate Response – Distinction

1 Fig. 1.1 shows the pH changes during the addition of 0.200 mol dm^{-3} HNO_3 to 20.0 cm^3 of a solution of sodium carbonate, Na_2CO_3.

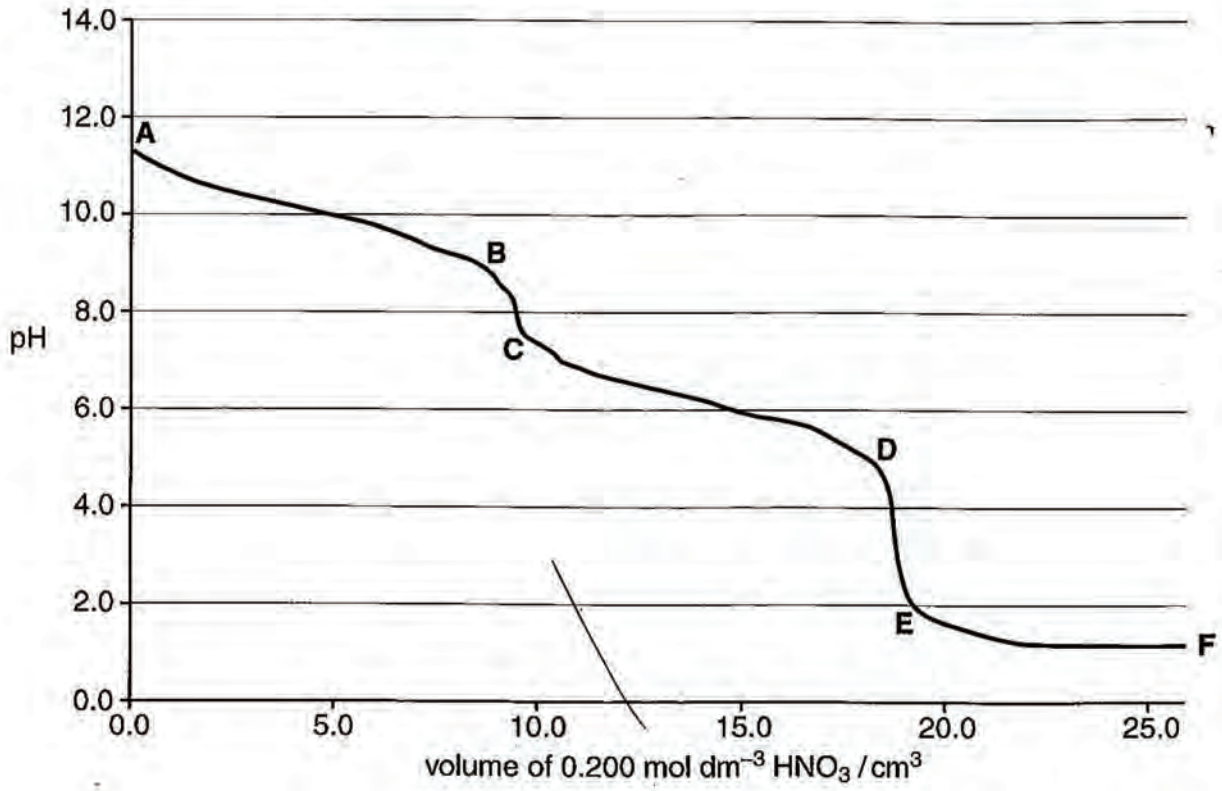


Fig. 1.1

(a) Write **ionic** equations for the reactions which occur in the solution between point **A** and point **B** on the graph and between point **C** and point **D** on the graph.

(i) ionic equation for the reaction occurring between **A** and **B**

$HNO_3 \rightleftharpoons NO_3^- + H^+$ ..... [1]

(ii) ionic equation for the reaction occurring between **C** and **D**

$OH^- + H^+ \rightarrow H_2O$ ..... [1]

$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$

(b) Table 1.1 gives some information about seven different indicators.

Table 1.1

indicator	pK_a	acid form	base form
thymol blue	1.6	yellow	blue
methyl yellow	3.3	red	yellow
chlorophenol red	6.0	yellow	red
bromothymol blue	7.1	yellow	blue
cresol purple	8.3	yellow	purple
thymolphthalein	9.9	colourless	blue
alizarin yellow	11.0	yellow	red

(i) From the information given in Table 1.1 choose the indicator that would be most suitable for determining the end-point occurring between points **D** and **E** on the graph.

methyl yellow [1] 1

(ii) Explain your choice.

the pKa value within the steepest part of the curve (neutralisation point) [1] 1

(iii) What colour change will be seen with this indicator at the end-point?

yellow → red [1] 1

(c) Calculate the concentration, in $g\,dm^{-3}$, of sodium carbonate present in the original solution, given that the end-point between **D** and **E** occurs after $18.80\,cm^3$ of HNO_3 have been added.

$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O$

18.8 cm³

moles of $HNO_3 = \frac{18.8}{1000} \times 0.2$

$= 1.76 \times 10^{-3}$ mol

1.88×10^{-3} mol → Na_2CO_3

$(23 \times 2) + (12) + (16 \times 3) = 106$

$106 \times 1.88 \times 10^{-3} =$ mass

$= 0.19928$

$\frac{0.19928}{\frac{20}{1000}}$

9.96 g dm⁻³ [3] 3

(d) (i) Write an equation for the dissociation of water.

$H_2O \rightleftharpoons H^+ + OH^-$ ✓ [1] 1

(ii) Use the equation in **(d)(i)** to write an expression for the equilibrium constant, K_c, for this reaction. Use this expression to show that $K_w = [H^+][OH^-]$. Justify and explain your reasoning.

$K_c = \frac{[products]}{[reactants]}$ ✗ $\frac{[H^+][OH^-]}{[H_2O]}$

$K_w = [H^+][OH^-]$

As water is a much larger quantity compared to H^+ & OH^- its concentration is considered constant and hence omitted. [3] 2

(iii) At 373K the ionic product of water, K_w, has a value of 51.3×10^{-14} mol^2 dm^{-6}. Use this information to calculate the pH of water at 373K. Give your answer to 3 significant figures.

$51.3 \times 10^{-14} = [H^+]^2$

$[H^+] = 7.162... \times 10^{-7}$

$pH = -\log_{10}[H^+]$

$= 6.14494...$

6.14 ✓✓ [3] 3

(iv) At 298K the pH of water is 7.00. Use this information to state whether the dissociation of water is endothermic or exothermic and explain your answer.

From (iii) we can tell that raising temperature decreased the pH. Equilibriums tries to oppose the change, so if less $[H^+]$ is needed, the forwards reaction is slowed ✗ and so it must be exothermic ✗ [2] 0

(e) Calculate the final pH, at 298 K, after a 5.00 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added separately to

(i) 100 cm^3 of a solution of 1.00×10^{-4} mol dm^{-3} hydrochloric acid.

$HCl \rightarrow H^+ + Cl^-$

$1 \times \frac{5}{1000} + M10^{-4} \times \frac{100}{1000} = 5.01 \times 10^{-3}$ mol (total mole of H^+)

$\frac{5.01 \times 10^{-3}}{\frac{105}{1000}} = 0.047714...$

$pH = -\log_{10}$ ↓

pH = 1.32 //// 4 [4]

(ii) 100 cm^3 of a solution that contains 0.100 mol dm^{-3} ethanoic acid and 0.100 mol dm^{-3} sodium ethanoate.
(K_a for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K)

$CH_3COOH \rightarrow CH_3COO^- + H^+$

$\frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = K_a$

$pH = pKa + \log \frac{base}{acid}$

$pH = pKa$ (without addition of HCl)

↓ 4.77 ✓

$1.7 \times 10^{-5} = \frac{[H^+] \times 0.1}{0.1}$

$[H^+] = 1.7 \times 10^{-5}$ mol/dm^3

moles of $H^+ = 1.7 \times 10^{-5} \times \frac{100}{1000}$

$= 1.7 \times 10^{-6}$ moles

pH = 1.48 [4] 1

[Total: 25]

$\frac{5}{1000}$ moles of H^+ in HCl $= \frac{5}{1000} \times 1 = 0.005$

total mole of $H^+ = 5.0017 \times 10^{-3}$ 18

$\frac{5.0017 \times 10^{-3}}{\frac{5}{1000} + \frac{100}{1000}} = 0.03334...$

↑ total conc of H^+

$pH = -\log(0.0333...)$

Examiner Comment

The salvage mark for an overall ionic equation was earned in **(a)** with full marks in **(b)** and **(c)**. Part **(d)** was generally answered well but confusion between rate and equilibrium lost marks in part **(iv)**.

As with many candidates, part **(e) (i)** earned full marks but the buffer calculation in **(e) (ii)** proved more challenging, although 1 mark was earned here for the initial pH calculation.

Example Candidate Response – Distinction

1 Fig. 1.1 shows the pH changes during the addition of 0.200 mol dm^{-3} HNO_3 to 20.0 cm^3 of a solution of sodium carbonate, Na_2CO_3.

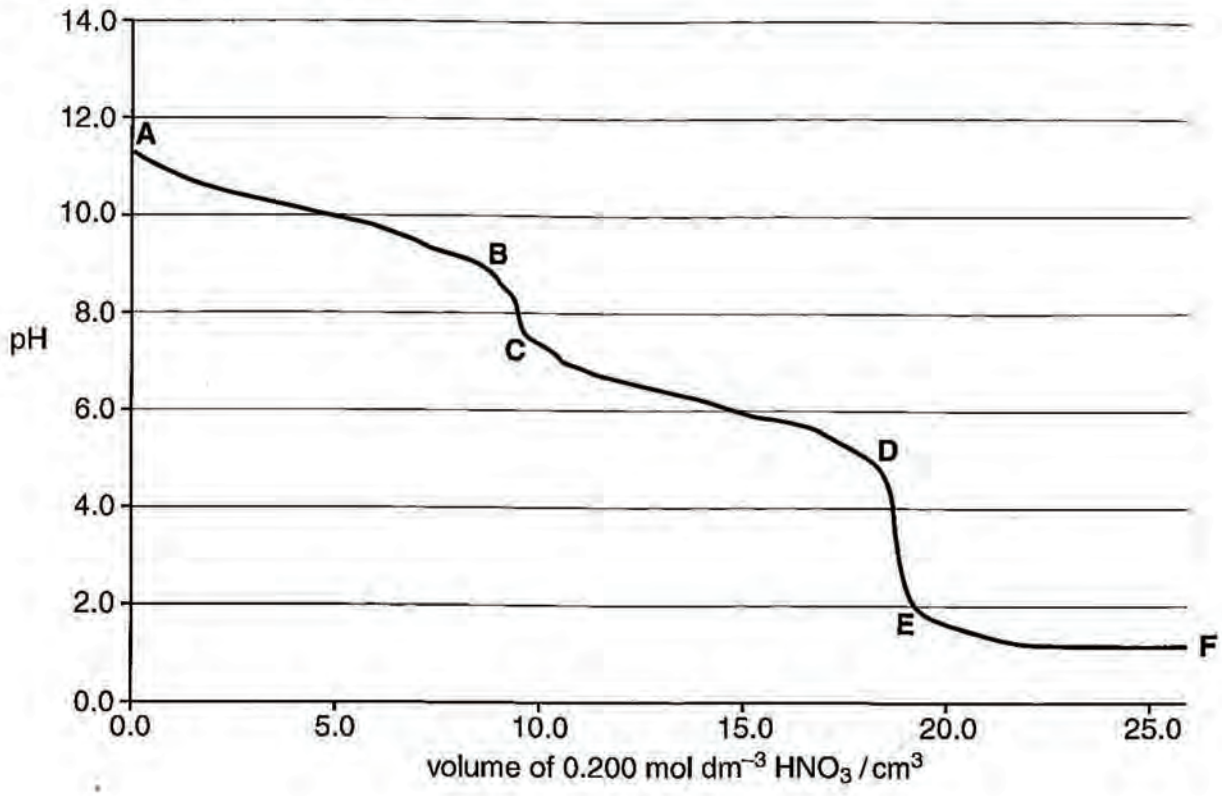


Fig. 1.1

(a) Write **ionic** equations for the reactions which occur in the solution between point **A** and point **B** on the graph and between point **C** and point **D** on the graph.

(i) ionic equation for the reaction occurring between **A** and **B**

$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$ ✓ [1] 1

(ii) ionic equation for the reaction occurring between **C** and **D**

$NO_3^- + Na^+ \rightarrow NaNO_3$ ✗ [1] 0

(b) Table 1.1 gives some information about seven different indicators.

Table 1.1

indicator	pK_a	acid form	base form
thymol blue	1.6	yellow	blue
methyl yellow	3.3	red	yellow
chlorophenol red	6.0	yellow	red
bromothymol blue	7.1	yellow	blue
cresol purple	8.3	yellow	purple
thymolphthalein	9.9	colourless	blue
alizarin yellow	11.0	yellow	red

(i) From the information given in Table 1.1 choose the indicator that would be most suitable for determining the end-point occurring between points **D** and **E** on the graph.

methyl yellow ..... [1]

(ii) Explain your choice.

The pKa is 3.3, and the relevant steep section of the curve is between pHs 2 and 4. ..... [1]

(iii) What colour change will be seen with this indicator at the end-point?

yellow to red ..... [1]

(c) Calculate the concentration, in $g\,dm^{-3}$, of sodium carbonate present in the original solution, given that the end-point between **D** and **E** occurs after $18.80\,cm^3$ of HNO_3 have been added.

1:1 ratio of HNO_3 to Na_2CO_3

$18.8\,cm^3$ of HNO_3 at $0.2\,mol\,dm^{-3}$

$\therefore 0.2 \times 0.0188 = 3.76 \times 10^{-3}$ mol HNO_3

$\therefore 3.76 \times 10^{-3}$ mol Na_2CO_3

1 mol = $23 \times 2 + 12 + 3 \times 16 = 106\,g$

0.3986 mol present (4SF)

in $20\,cm^3$ of solution

$20\,cm^3 = \frac{1}{50}\,dm^3$

$\therefore$ 19.9 (3sf) $g\,dm^{-3}$

19.9 (3sf) $g\,dm^{-3}$ [3]

Yes

(d) (i) Write an equation for the dissociation of water.

$H_2O \rightleftharpoons H^+ + OH^-$ ✓ [1]

(ii) Use the equation in **(d)(i)** to write an expression for the equilibrium constant, K_c, for this reaction. Use this expression to show that $K_w = [H^+][OH^-]$. Justify and explain your reasoning.

$$K_c = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}}$$ ✓

$[H_2O]_{eq}$ is effectively 1 since water barely dissociates at all, leaving $K_w = [H^+][OH^-]$ [3]

(iii) At 373 K the ionic product of water, K_w, has a value of $51.3 \times 10^{-14}\,mol^2\,dm^{-6}$. Use this information to calculate the pH of water at 373 K. Give your answer to 3 significant figures.

$K_w = [H^+][OH^-]$

$\approx [H^+]^2$

$\therefore [H^+] = \sqrt{51.3 \times 10^{-14}\,mol^2\,dm^{-6}}$

$= 7.162 \times 10^{-7}$ (4sf)

$pH = -\log_{10}[H^+]$

$= 6.14$ (3sf) 6.14 [3]

(iv) At 298 K the pH of water is 7.00. Use this information to state whether the dissociation of water is endothermic or exothermic and explain your answer.

pH lowered at higher temp., therefore forwards reaction favoured. $H_2O \rightleftharpoons H^+ + OH^-$ as there are more H^+ ions present. This means forwards reaction is endothermic. [2]

(e) Calculate the final pH, at 298 K, after a 5.00 cm^3 portion of 1.00 mol dm^{-3} hydrochloric acid is added separately to

(i) 100 cm^3 of a solution of 1.00×10^{-4} mol dm^{-3} hydrochloric acid.

1×10^{-5} mol present

0.005 mol HCl added

$\therefore$ 5.01×10^{-3} mol HCl present in 0.105 dm^3

$\therefore$ 0.04771 mol dm^{-3} of HCl (4 s.f.)

HCl fully dissociates

$\therefore$ 0.04771 (4 s.f.) mol dm^{-3} of hydrogen

$pH = -\log_{10}[H^+]$

$= 1.32$ (3 s.f.)

pH = 1.32 [4]

4

(ii) 100 cm^3 of a solution that contains 0.100 mol dm^{-3} ethanoic acid and 0.100 mol dm^{-3} sodium ethanoate.
(K_a for ethanoic acid is 1.70×10^{-5} mol dm^{-3} at 298 K)

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$\approx \frac{[H^+]^2}{[CH_3COOH]} = \frac{[H^+]^2}{0.1}$$

$$1.7 \times 10^{-5} = \frac{[H^+]^2}{0.1}$$

$$1.7 \times 10^{-6} = [H^+]^2$$

$[H^+] = 1.304$ (4 s.f.) $\times 10^{-3}$ mol dm^{-3}

pH = 1.31 (3 s.f.) [4]

0

0.005 mol HCl added

$\therefore$ 0.005 mol H^+ added

[Total: 25]

tot H^+ = 1.304 $\times 10^{-4}$ mol + 0.005

$= 5.130$ (4 s.f.) $\times 10^{-3}$ mol

$[H^+]$ conc $= \frac{5.130 \times 10^{-4}}{0.105} = 0.04886$ (4 s.f.) mol dm^{-3}

$-\log_{10}[H^+] = 1.311$ (4 s.f.)

17

Examiner Comment

This question is from a script earning a solid Distinction overall.

As with many candidates part **(a)** proved tougher than expected and this became a high level discriminator. A mark was allowed here for the overall equation but two separate steps were needed.

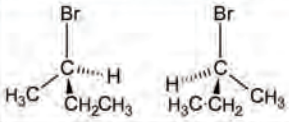
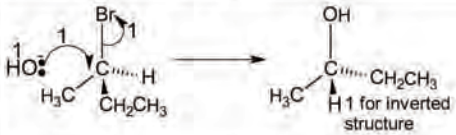
Part **(b)** was correct and the only mark lost in part **(c)** was for the incorrect ratio. This was careless given the equation in **(a)** and ecf was allowed from there on.

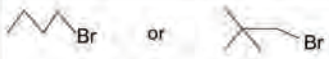
In part **(d)** surprisingly few candidates recognised the reason for leaving [H_2O] out of the K_w expression and the suggestion here (that its concentration is 1) was often seen. Correct calculations in parts **(iii)** and **(iv)** gained full marks.

Most candidates were correctly able to calculate the pH in part **(e) (i)** but part **(e) (ii)** was another high level discriminator with many candidates failing to recognise the context of a buffer calculation.

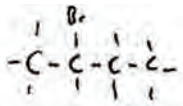
The clarity of exposition in part **(d) (iv)** gives evidence of solving chemical problems and rationalising unfamiliar material while the clear calculation in part **(e) (i)** also gives evidence of good problem solving.

Question 2 Mark Scheme

2 (a)	(i)	high temperature and ethanol as solvent	2	one mark for each solvent and third mark for any appropriate mention of temperature
	(ii)	(lower temperature) and water as solvent	1	
(b)	(i)	molecule with non-superimposable mirror-image form / molecule with 4 different groups attached to the same (C) atom / no plane of symmetry	1	do not allow molecules allow atoms in place of groups
	(ii)	equimolar mixture of two enantiomers / optical isomers	1	
	(iii)	stereoisomers that are not enantiomers / non-superimposable mirror images	1	
	(iv)		2	
(c)	(i)		4	
	(ii)	S-(+)-butan-2-ol	2	R-(+)- butan-2-ol/S-(-)-butan-2-ol/S-(+)-propan-2-ol all = 1/2

(d)	(i)	RX = 1st order: Expt 1 to 2 [RX] ×3 = rate ×3 so directly	1	
	(ii)	proportional	1	
	(iii)	OH^- = 1st order: Expt 1 to 3 doubling [RX] would double rate to 8.0×10^{-4} so doubling again due to doubling $[OH^-]$ so also directly proportional (2) rate = k[RX][OH^-] (ecf) (1) $4.0 \times 10^{-4} = k \times 0.050 \times 0.10$ (1) $k = 4.0 \times 10^{-4}/0.005 = 0.08$ (1) $dm^3\ mol^{-1}\ s^{-1}$ (1)	6	
	(iv)		1	
			[23]	

Example Candidate Response – Merit



2 2-bromobutane reacts with potassium hydroxide by either elimination or nucleophilic substitution depending on a combination of factors.

(a) State the conditions needed to bring about each of these reactions.

(i) elimination

1 atm, 298 K, c. HBr

(ii) nucleophilic substitution

~~H_2SO_4~~ Heat under reflux, conc. H_2SO_4 [3]

6

(b) 2-bromobutane is a *chiral* molecule and, when it is prepared by the reaction between but-1-ene and hydrogen bromide, a *racemate* is formed. The enantiomers in the *racemate* can be converted to *diastereoisomers* by covalent derivatisation with suitable *chiral* reagents. Pure samples of each of the enantiomers can then be obtained by simple separation techniques as the *diastereoisomers* have different physical and chemical properties.

Give definitions of each of the words in italics.

(i) *chiral* – A central carbon atom is bonded to four different groups or ions. [1]

1

(ii) *racemate* – A racemic mixture, where there are equal amounts of both optical isomers present in the solution, making the solution optically inactive. [1]

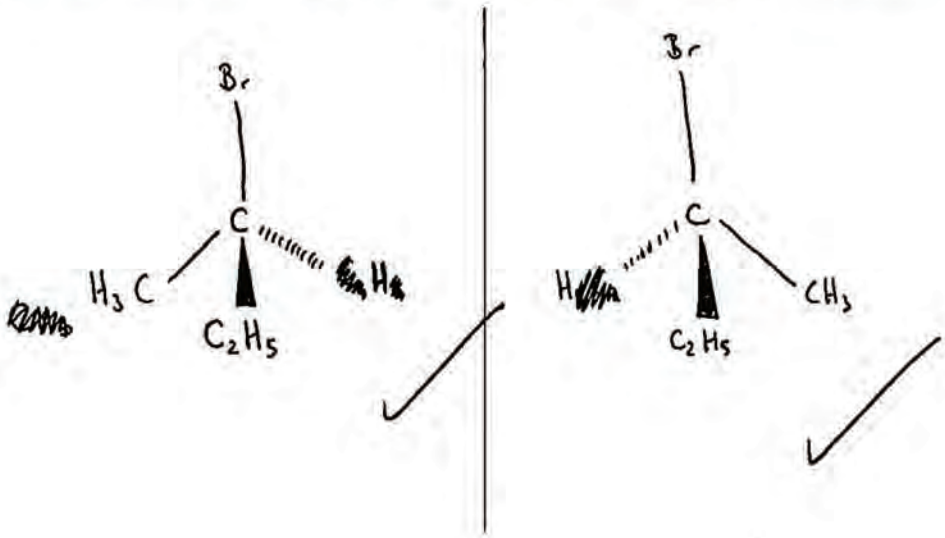
1

(iii) *diastereoisomers* – 2 Molecules containing the same atom but with a different spatial arrangement, causing them to rotate the plane-polarised light in opposite directions. [1]

0

X

(iv) Draw suitable diagrams of the two different enantiomers of 2-bromobutane.

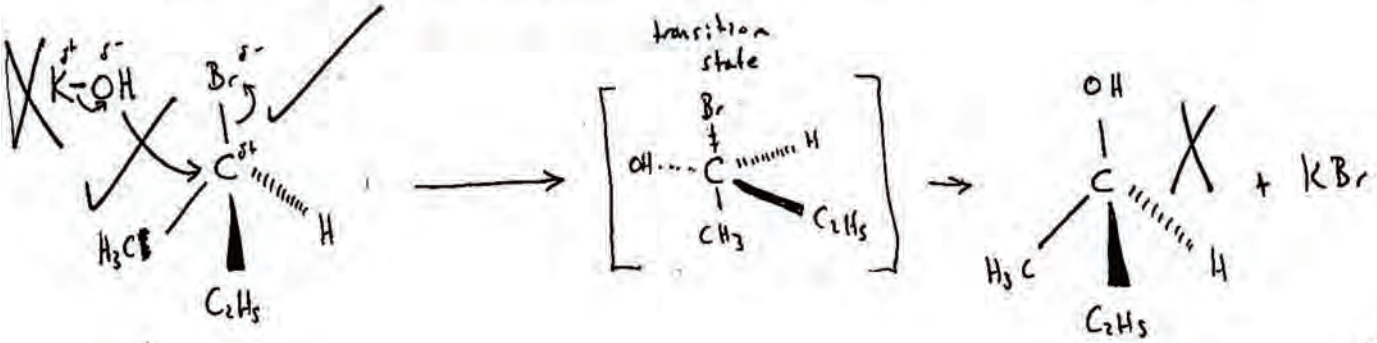


[2]

2

(c) When R-(–)-2-bromobutane undergoes nucleophilic substitution with potassium hydroxide under appropriate conditions the reaction proceeds predominantly by the S_N2 mechanism. When the progress of the reaction is followed in a polarimeter the optical activity is seen to change gradually from –23.1° via zero to +13.5°.

(i) Draw a curly-arrow mechanism for the reaction that is taking place. Show the 3-D structures of the reactant and product clearly.



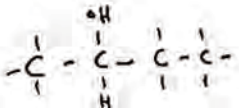
[4]

2

(ii) Give the systematic name of the organic product.

butan-2-ol ..... [2]

0



(d) The kinetics of the reaction of a different bromoalkane (RBr) with aqueous alkali were investigated at 323 K. The results are shown in Table 2.1.

Table 2.1

experiment	[RBr]/mol dm^{-3}	[OH$^-$]/mol dm^{-3}	initial rate/mol dm^{-3} s^{-1}
1	0.05	0.10	4.0×10^{-4}
2	0.15	0.10	1.2×10^{-3}
3	0.10	0.20	1.6×10^{-3}

(i) Deduce the order of reaction with respect to RBr and with respect to the hydroxide ion, OH^-.

Give reasons for each of your answers.

$[RBr]^2$ - When the concentration doubles the rate quadruples (x4)

$2^2 = 4$ ∴ order = 2

$[OH^-]^2$ - When the concentration doubles the rate quadruples (x4)

$2^2 = 4$ ∴ order = 2

0

.....[4]

(ii) Write the rate equation for the reaction.

rate = $k[RBr]^2[OH^-]^2$ ✓eq

.....[1] 1

(iii) Calculate the value of the rate constant, *k*, at 323 K and give its units.

Plug in values from exp. 1:

$4.0 \times 10^{-4} = k[0.05]^2[0.10]^2$

$k = 16$

✓eq

$k = 16$ ∧ .....[3] 2

(iv) Draw the skeletal formula of RBr, which is an isomer of 2-bromobutane.

X

[1] 0

[Total: 23]

9

Examiner Comment

Overall this script fell in the low Merit band.

Many candidates failed to remember the crucial distinction between elimination and nucleophilic substitution of halogenoalkanes being in the choice of solvent and temperature.

The more familiar definitions were remembered in part **(b)** but, again as with many, the less familiar diastereoisomers caused problems and was confused with enantiomers. It was rare to see such clear 3-D diagrams in part **(iv)** but 2 marks were earned in this case.

Clear use of curly arrows and unambiguous representation of inversion were the keys in part **(c) (i)** but there was no inversion shown here and, in part **(ii)** the clue in the stem failed to stimulate the correct response of a full systematic name with appropriate prefixes.

Question 3 Mark Scheme

3 (a)	(i)	for CO change is from 2 moles of gas to 1 mole gas and 1 mole solid whereas for SiO change is from 2 moles of gas to 2 moles of solid owtte decrease in disorder / randomness is greater with SiO	1 1	
	(ii)	2 moles of solid produce 2 moles of solid owtte very little change in disorder	1 1	
(b)	(i)	$\Delta_r S = \Sigma S_{products} - \Sigma S_{reactants} = (31.1 + 55.3) - (2 \times 50)$ $= -13.4$ (J K^{-1} mol^{-1})	2	+36.4 = 1/2 (not x2) -29.5 = 1/2 (reversed 55.3 and 55)
	(ii)	$\Delta_r G^{\ominus} = \Delta H - T\Delta S = -126.8 - (298 \times -3.4 / 1000)$ $= -122.8$ (kJ mol^{-1}) (–22800 J mol^{-1})	2	–118 ecf from 36.4 / –137.6 ecf from –29.5 allow –123 do not allow –122 units not required but must be consistent
(c)	(i)	$\Delta_r G^{\ominus} = -RT\ln K_p$ so $\ln K_p = \Delta_r G^{\ominus} / -RT$ $= -120.1 \times 10^{-3} / (-8.31 \times 298) = 48.50$ so $K_p = 1.15 \times 10^{21}$	2	3.72×10^{21} = 1 / 2 (used 122.8 from **3(b)(ii)**) 1.05 = 1 / 2 (no $\times 10^3$ ignore units
	(ii)	$\Delta_r G^{\ominus} = 0 = \Delta H - T\Delta S$ so $\Delta H = T\Delta S$ and $T = \Delta H/\Delta S$ $= -172500/-175.9 = 980.7$ K	2	allow 981 K
	(iii)	activation energy / kinetic barrier too high	1	
			[13]	

Example Candidate Response – Distinction

3 The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^\ominus$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^\ominus$ (298 K) / kJ mol^{-1}	$\Delta_r G^\ominus$ (298 K) / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

gases have a much higher entropy than solids

SiO has a giant covalent structure, CO has a simple covalent one. So SiO changes from a gas to SiO_2 which is a solid, CO changes to CO_2 ..... [2]

they are both gases, no phase change.

(ii) PbO is so close to zero.

No phase change and the enthalpy change is the driving force so there is no need for a large entropy for the reaction to be feasible ..... [2]

Also no change in the number of moles.

0

1

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^{\ominus}(298\,K)/J\,K^{-1}\,mol^{-1}$
germanium, Ge(s)	31.1
germanium monoxide, GeO(s)	50.0
germanium dioxide, GeO_2(s)	55.3

(i) Calculate the standard entropy change, $\Delta_r S^{\ominus}(298\,K)$, for the disproportionation of germanium monoxide.

$2GeO \rightarrow Ge + GeO_2$

$31.3 + 55.3 - (50.0 \times 2)$

X

✓

-13.4 [2]

1

(ii) Calculate the standard free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the same reaction.

$\Delta G = \Delta H - T\Delta S$

$-126.8 \times 1000 - (298)(-13.4)$

// 40/mol

-123 [2]

2

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO,

$\Delta G = -RT\ln K$

$-120.1 \times 1000 = -8.31 \times 298 \ln K$

//

$1.15 \times 10^{21}\ Pa^{-1}$ [2]

2

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

0 = −172.5 × 1000 − T (−175.9)

981 K .... [2]   2

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

~~Room temperature is 298. Not enough time, it reacts~~
~~with the oxygen in the air to produce CO2~~ ....[1]   1

The reaction has a very high activation energy

You have to break the triple bond C≡O

[Total: 13]

9

Examiner Comment

A Distinction level response; albeit one that started poorly. Clear references to states of matter and molar quantities were needed with the general advice being to be as specific as possible with references to given data.

A slip in part **(b) (i)** was the only other source of lost marks in this response with the calculations clear and a recall of the concept of the activation barrier in part **(d)**.

Example Candidate Response – Distinction

3 The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^\ominus$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^\ominus$ (298 K) / kJ mol^{-1}	$\Delta_r G^\ominus$ (298 K) / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

~~SiO is a solid, whereas~~ SiO produces 2 solids whereas CO makes a solid and a gas. Gases have much higher entropy so in CO there is less of a change X [2] O

(ii) PbO is so close to zero.

Changing from a solid to some more solids both of which would have low entropies so there is not much of a difference between the values as most solids have similarly low entropies [2] /

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^{\ominus}(298\,K)/J\,K^{-1}\,mol^{-1}$
germanium, Ge(s)	31.1
germanium monoxide, GeO(s)	50.0
germanium dioxide, GeO_2(s)	55.3

(i) Calculate the standard entropy change, $\Delta_r S^{\ominus}(298\,K)$, for the disproportionation of germanium monoxide.

$2GeO \longrightarrow GeO_2 + Ge$

$(31.1 + 55.3) - (50.0 \times 2) =$

$-13.6\ J\,K^{-1}\,mol^{-1}$ [2]

(ii) Calculate the standard free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the same reaction.

$\Delta G = \Delta H - T\Delta S$

$= -126\,800 - (298 \times -13.6)$

$= -122747.2$

$-122.7\ kJ\,mol^{-1}$ [2]

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO,

$\Delta G = -RT\ln K$

$-120106 = -8.31 \times 298 \times \ln K$

$48.5 = \ln K$

$K_p = 1.15 \times 10^{21}$

1.15×10^{21} [2]

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

$\Delta G = \Delta H - T\Delta S$

$\Delta G = -172500 - T \times -175$ Solve for $\Delta G = 0$

$172500 = T \times 175$

$985.7 = T$

985.7 K ✓ [2] 1

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

High activation energy, which can't be reached at room temperature ✓ [1] 1

[Total: 13]

9

Examiner Comment

Overall an outstanding Distinction level script, which therefore shows what a high level discriminator question **3 (a)** proved to be. This candidate only earned 1/4 here as, although the end result was mentioned in part **(a) (i)**, for each reaction there was no mention of the change involved.

Again, the key to success here is a specific, detailed description of the state changes that occur.

A slip in transposing data in part **(c) (ii)** was the only other source of a lost mark in this question but does illustrate the need for care at all levels.

Example Candidate Response – Merit

3 The elements of Group 14 can all form monoxides and dioxides. The stabilities of the monoxides, with respect to disproportionation into the element and the dioxide, vary. The equations for the disproportionation reactions are given in Table 3.1 together with some thermodynamic data for the reactions.

Table 3.1

disproportionation equation	$\Delta_r S^\ominus$ (298 K) / J K^{-1} mol^{-1}	$\Delta_r H^\ominus$ (298 K) / kJ mol^{-1}	$\Delta_r G^\ominus$ (298 K) / kJ mol^{-1}
$2CO(g) \rightarrow C(s) + CO_2(g)$	–175.9	–172.5	–120.1
$2SiO(g) \rightarrow Si(s) + SiO_2(s)$	–362.9	–711.5	–603.4
$2GeO(s) \rightarrow Ge(s) + GeO_2(s)$		–126.8	
$2SnO(s) \rightarrow Sn(s) + SnO_2(s)$	–9.200	–9.100	–6.360
$2PbO(s) \rightarrow Pb(s) + PbO_2(s)$	–4.000	+157.2	+158.4

(a) Explain why the entropy change for the disproportionation of

(i) SiO is so much bigger than for CO,

Since SiO has a giant lattice structure, it takes a lot of energy to disproportionate. X

[2]

(ii) PbO is so close to zero.

Since Lead has a low electronegativity compared with the other Group 14 elements, it forms a weak intermolecular bond with the oxygen, thereby making it easier to break. X [2]

(b) Table 3.2 gives the standard molar entropies for germanium and its oxides.

Table 3.2

name	standard molar entropy at 298 K, $S^{\ominus}(298\,K)/J\,K^{-1}\,mol^{-1}$
germanium, Ge(s)	31.1
germanium monoxide, GeO(s)	50.0
germanium dioxide, GeO_2(s)	55.3

(i) Calculate the standard entropy change, $\Delta_r S^{\ominus}(298\,K)$, for the disproportionation of germanium monoxide.

$2GeO_{(s)} \rightarrow Ge_{(s)} + GeO_{2(s)}$

$\Delta S = \Delta S_{products} - \Delta S_{reactants}$

$= (31.1 + 55.3) - 2(50)$

$= -13.6$

$-13.6\,JK^{-1}mol^{-1}$ [2] 2

(ii) Calculate the standard free energy change, $\Delta_r G^{\ominus}(298\,K)$, for the same reaction.

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -126.8\,kJmol^{-1} - (298K \times -13.6\,JK^{-1}mol^{-1})$

$= -126.8\,kJmol^{-1} + 4052.8\,Jmol^{-1}$

$= -122747.2\,Jmol^{-1}$

$= -123\,kJmol^{-1}$

$-123\,kJmol^{-1}$ [2] 2

(c) Use data from Table 3.1 to calculate

(i) the value of the equilibrium constant, K_p, for the disproportionation of carbon monoxide, CO,

$2CO_{(g)} \rightarrow C_{(s)} + CO_{2(g)}$

$\Delta G^{\ominus} = -RT\ln K$

$\frac{\Delta G^{\ominus}}{-RT} = \ln K \quad \therefore K = e^{\frac{\Delta G^{\ominus}}{-RT}} = e^{\frac{-120.4}{-8.31 \times 298}} = e^{0.048} = 1.0497$

1.05 [2] 1

(ii) the temperature above which the disproportionation of carbon monoxide ceases to be favourable.

900K [2]

(d) Explain why carbon monoxide does not spontaneously disproportionate at room temperature.

This is because the value of $\Delta_r G^\ominus$ is less than zero. [1]

[Total: 13]

5

Examiner Comment

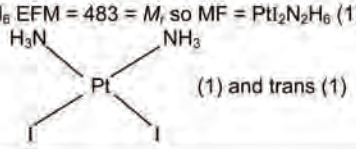
In part **(a)** there was no evidence of any recall of the key principles governing the sign and magnitude of entropy and the candidate seemed to be confused between entropy and enthalpy.

The calculations in part **(b)** were done well but, in part **(c) (i)** the candidate failed to convert $\Delta_r G$ to Joules and, in **(c) (ii)** defining $\Delta_r G$ as zero and proceeding from there was not seen.

The candidate also failed to recognise the concept of the activation energy barrier in part **(d)**.

Consistent use of appropriate significant figures throughout part **(b)** provide evidence of a concern for accuracy and precision.

Question 4 Mark Scheme

4	(a)	Pt I N H 40.37 52.59 5.80 1.24 (1) 195 127 14 1 0.207 0.414 0.414 1.24 (1) 0.207 0.207 0.207 0.207 1.00 2.00 2.00 5.99 so EF = $PtI_2N_2H_6$ EFM = 483 = M_r so MF = $PtI_2N_2H_6$ (1)  (1) and trans (1)	5	must see link of EFM to RFM
		bond Angle = 90°	1	ecf
	(b)	(octahedral) e.g. $Co(H_2O)_6^{2+}$ angle = 90° (tetrahedral) e.g. $CoCl_4^{2-}$ angle = 109–110°	3	both angles needed for third mark NB $CoCl_4^-$ doesn't exist
	(c)	lobes of two orbitals directed along cartesian axes lobes of three orbitals directed between cartesian axes results in split of energy levels of d orbitals promotion of electrons between orbitals absorbs in visible region	1 1 1 1	
			[13]	

Example Candidate Response – Distinction

4 The complex compound diamminedichloroplatinum(II) has two isomeric forms, one of which can be prepared from potassium tetrachloroplatinate(II) as shown in the reaction sequence in Fig. 4.1.

$K_2[PtCl_4] \rightarrow K_2[PtI_4] \rightarrow \mathbf{X} \rightarrow [Pt(H_2O)_2(NH_3)_2](NO_3)_2 \rightarrow$ diamminedichloroplatinum(II)

Fig. 4.1

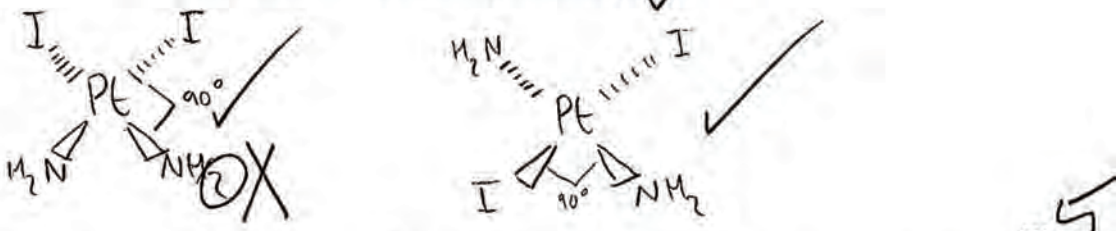
Compound **X** has the composition by mass Pt 40.37%, I 52.59%, N 5.80% and H 1.24% and a relative molecular mass of 483.

(a) Calculate the molecular formula of **X**, draw its two possible structures and indicate the ligand-platinum-ligand bond angle.

	Pt	I	N	H
%	40.37	52.54	5.80	1.24
% / A_r	0.207	0.414	~~0.414~~ 0.414	1.24
~~smallest~~	~~1.62~~ 1	~~2.75~~ 2	2	5.99

Empirical formula = $PtI_2N_2H_6$

$\frac{483}{195+2\times127+2\times14+6\times1} = 1$ ✓



[6] 5

(b) Cobalt forms both octahedral and tetrahedral complexes. Give the identities of one complex ion of cobalt with each shape and, in each case, state the ligand-cobalt-ligand bond angle.

octahedral $[Co(OH)_6]^{2-}$ X

bond angle 90° ✓

tetrahedral $[CoCl_4]^{-}$ ^

bond angle 109.5°

[3] 1

(c) With reference to the **3-D orientation** of d orbitals in an octahedral transition metal complex explain why such complexes are usually coloured.

The ligands in octahedral complexes lie at 90° to each other. They are on the same lines as the ~~d orbitals~~ d_{z^2}, $d_{x^2-y^2}$ subshells. The d_{xy}, d_{xz}, and d_{yz} subshells lie between the ligands. Therefore they are slightly lower energy than the other two. the energy gap is such that coloured light will be absorbed or emitted when the electrons move between the shells. [4] 3

[Total: 13]

9

Examiner Comment

This was a good Distinction level script with this response exemplifying the overall standard.

In part **(a)** the development of the empirical formula to the molecular formula using the relative molecular mass was clearly shown and the only mark lost was for a slip in the structures – possibly the 'squashed up' molecular formula hindered back checking.

Part **(b)** again highlighted the need for specific recall of some example ions whilst part **(c)** was again only marred by an explanation couched in terms of emission.

The quality of responses to part **(a)** and part **(c)** suggest an understanding of chemical reactions, structure and the use of a model for describing colour of complexes.

Example Candidate Response – Merit

4 The complex compound diamminedichloroplatinum(II) has two isomeric forms, one of which can be prepared from potassium tetrachloroplatinate(II) as shown in the reaction sequence in Fig. 4.1.

$K_2[PtCl_4] \rightarrow K_2[PtI_4] \rightarrow \mathbf{X} \rightarrow [Pt(H_2O)_2(NH_3)_2](NO_3)_2 \rightarrow$ diamminedichloroplatinum(II)

Fig. 4.1

Compound **X** has the composition by mass Pt 40.37%, I 52.59%, N 5.80% and H 1.24% and a relative molecular mass of 483.

(a) Calculate the molecular formula of **X**, draw its two possible structures and indicate the ligand-platinum-ligand bond angle.

$\frac{40.37}{100} \times 483 = 194.99 = 1\,Pt$

$\frac{52.59}{100} \times 483 = 254.01 = 2\,I$ ✓

$\frac{5.80}{100} \times 483 = 28.014 = 2\,N$ ✓

$\frac{1.24}{100} \times 483 = 5.9892 = 6\,H$

∴ molecular formula = $[Pt(NH_3)_2]I_2$ [6] 2

(b) Cobalt forms both octahedral and tetrahedral complexes. Give the identities of one complex ion of cobalt with each shape and, in each case, state the ligand-cobalt-ligand bond angle.

octahedral $[Co(H_2O)_6]^{3+}$ ✓ tetrahedral $[CoCl_4]^{-}$ ✗

bond angle 90° ✓ bond angle 109.5°

[3] 2

(c) With reference to the **3-D orientation** of d orbitals in an octahedral transition metal complex explain why such complexes are usually coloured.

In an octahedral transition metal complex 3 of the orbitals have a 3-D orientation that favours ligand bonding, where the orbitals are not on the same axes as the ligand bonds. However the x^2-y^2 and z^2 orbitals point along the bond axes, inducing electron repulsion between the orbital and the transition metal meaning those orbitals are higher energy. This means an electron can be promoted to those orbitals and then drop again, releasing coloured light. This is why the transition metal complexes are coloured. [4] 3

[Total: 13]

7

Examiner Comment

Overall this script was at the level of a high Merit and this question in itself was around the Distinction boundary.

The empirical formula was calculated correctly but the candidate failed to justify a molecular formula or to draw the isomers, which may have been due to not reading the question carefully.

An incorrect charge for $CoCl_4^{2-}$ cost a mark in part **(b)** whilst a generally good account of colour in part **(c)** was only marred by a reference to emission of coloured light as the promoted electron 'dropped', when what is required is a reference to absorption leaving the complementary colour.

Example Candidate Response – Merit

4 The complex compound diamminedichloroplatinum(II) has two isomeric forms, one of which can be prepared from potassium tetrachloroplatinate(II) as shown in the reaction sequence in Fig. 4.1.

$$K_2[PtCl_4] \longrightarrow K_2[PtI_4] \longrightarrow \mathbf{X} \longrightarrow [Pt(H_2O)_2(NH_3)_2](NO_3)_2 \longrightarrow \text{diamminedichloroplatinum(II)}$$

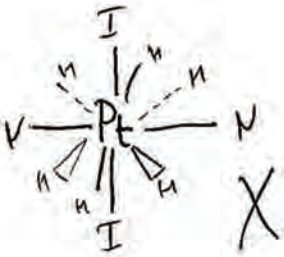
Fig. 4.1

Compound **X** has the composition by mass Pt 40.37%, I 52.59%, N 5.80% and H 1.24% and a relative molecular mass of 483.

(a) Calculate the molecular formula of **X**, draw its two possible structures and indicate the ligand-platinum-ligand bond angle.

Pt	I	N	H
0.207	0.414	0.414	1.24
1	2	2	6

∴ molecular formula = $PtI_2N_2H_6$ ✓



X

2

[6]

(b) Cobalt forms both octahedral and tetrahedral complexes. Give the identities of one complex ion of cobalt with each shape and, in each case, state the ligand-cobalt-ligand bond angle.

octahedral $[Co(OH_4)(H_2O)_4]^{2-}$ X

bond angle 90° ✓

tetrahedral $Co(OH_4)^{2-}$ X

bond angle 109.5°

1

[3]

(c) With reference to the **3-D orientation** of d orbitals in an octahedral transition metal complex explain why such complexes are usually coloured. ($d_{xy}/d_{xz}/d_{yz}$)

3 of the 3d orbitals have lower energy orbitals, the other 2 (dz^2/dx^2-y^2) are at high energy due to their alignment along the axes. If a transition metal complex has empty orbitals or full orbitals (🔲) no colours will be shown. If it does have e⁻ however, the right frequency of radiation/light can take the lower energy e⁻ to the high energy state and when it comes back down, that energy is emitted as light energy giving a colour. This leads to the complexes being coloured. [4]

2

[Total: 13]

5

Examiner Comment

Overall a Merit level script with this response on a par with the overall performance.

Again there was no progression from the empirical formula to the molecular formula shown in part **(a)** and unfortunately this candidate failed to recognise that N_2H_6 represented two NH_3 groups so was unable to make a sensible suggestion for the structure.

Part **(b)** illustrates the need for candidates to remember some example material for reference in questions. The concept of split energy levels was remembered in part **(c)** but then the origin of colour was explained in terms of emission rather than absorption.

Example Candidate Response – Pass

4 The complex compound diamminedichloroplatinum(II) has two isomeric forms, one of which can be prepared from potassium tetrachloroplatinate(II) as shown in the reaction sequence in Fig. 4.1.

$$K_2[PtCl_4] \rightarrow K_2[PtI_4] \rightarrow \mathbf{X} \rightarrow [Pt(H_2O)_2(NH_3)_2](NO_3)_2 \rightarrow \text{diamminedichloroplatinum(II)}$$

Fig. 4.1

Compound **X** has the composition by mass Pt 40.37%, I 52.59%, N 5.80% and H 1.24% and a relative molecular mass of 483.

(a) Calculate the molecular formula of **X**, draw its two possible structures and indicate the ligand-platinum-ligand bond angle.

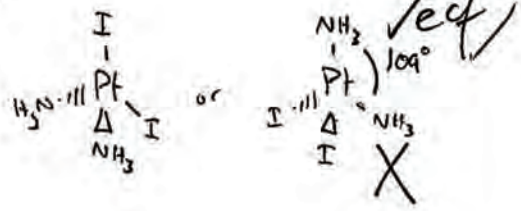
Pt : I : N : H

$\frac{40.37}{195} : \frac{52.59}{127} : \frac{5.80}{14.0} : \frac{1.24}{1}$

0.207 : 0.414 : 0.414 : 1.24

1 : 2 : 2 : 6

$[PtI_2(NH_3)_2]$



[6] 3

(b) Cobalt forms both octahedral and tetrahedral complexes. Give the identities of one complex ion of cobalt with each shape and, in each case, state the ligand-cobalt-ligand bond angle.

octahedral $[Co(H_2O)_6]$

bond angle 90°

tetrahedral $[CoCl_4]$

bond angle 109°

[3] 1

With reference to the **3-D orientation** of d orbitals in an octahedral transition metal complex explain why such complexes are usually coloured.

Because of the orbitals being at certain wavelengths distance from other orbitals below ~~wavelengths~~ and then, ~~the~~ there are these gaps which the light passes through, but only the light of the certain wavelengths can get through. Because of the 3-D nature of these orbitals, all light has to travel through and the wavelength distance between the 3-d orbitals and the ones below it causes the complex to be the same colour that fits the wavelength. [4]

[Total: 13]

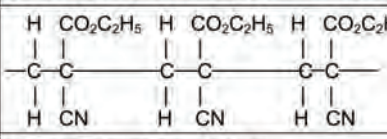
Examiner Comment

Overall this script was just below the Merit borderline and this response exemplified the overall performance.

Specific recall of some platinum complex ion chemistry is expected (syllabus B2.4 (d)) but the candidate represented the complex as tetrahedral. The presence of only two different groups should also have served as a clue that a representation of optical isomerism would be inappropriate here. The other mark lost was for failing to show that the molecular formula was the same as the empirical formula, by reference to the relative molecular mass.

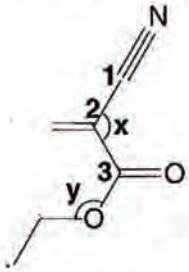
Omission of charges in part **(b)** was costly and part **(c)** required the specific recall of a principle that needs committing to memory.

Question 5 Mark Scheme

5	(a)	$C_6H_7NO_2$	1	
	(b)	**x** = 120° **y** = 104.5°	2	allow 104 – 105 for **y**
	(c)	**1** = carboxylic Acid Level **2** = hydrocarbon Level **3** = carboxylic Acid Level	2	three = 2 two = 1
	(d) (i)	donates pair of electrons to form covalent bond	1 + 1	
	(ii)		2	
	(e)	**Q** = CH_2=C(CH_2NH_2)CH_2OH **R** = CH_3CH_2OH **S** = CH_2=C($CH_2NHOCCH_3$)CH_2OCOCH_3 **T** = $CH_3CH_2OCOCH_3$ **U** = $CH_3CH(CH_2NH_2)CO_2CH_2CH_3$ Reactions of **Q** and **R** with ethanoyl chloride: 2:1 ratio with **Q** as both NH_2 and OH acylated/ 1:1 ratio with **R** as only one OH group acylated (1) Reaction with NH_2 produces (secondary) amide (+HCl) (1) Reaction with OH produce ester (+HCl) (1) ^{1}H NMR of **T**: three signals indicate / due to 3 H environments (1) triplet @ ~1.3 is protons on CH_3 adj to CH_2 (1) quartet @ ~ 4.1 is protons on CH_2 (adj to CH_3) (1) singlet @ ~ 2.0 is protons on CH_3 on C=O (1) ^{13}C NMR of **T**: two signals near 20 = Cs in the two CH_3 groups (1) signal at ~ 60 is C in CH_2 (1) signal at ~170 is C in C=O (1) ^{1}H NMR of **U**: six signals indicate / due to 6 H environments (1) disappearing signal due to labile protons on NH_2 (2)	1 1 1 1 1 1 1 1 max 3 1 1 1 1 1 + 1	do not allow 'peptide' ^{1}H NMR marks are independent of structures drawn except first mark ^{13}C NMR marks are independent of structures drawn
			[26]	

Example Candidate Response – Merit

5 Cyanoacrylate is the generic name for cyanoacrylate based fast-acting glues such as ethyl 2-cyanoacrylate. The skeletal formula of ethyl 2-cyanoacrylate is given in Fig. 5.1.



$C_6H_7N_1O_2$

CN C(CH₂)C OH

Fig. 5.1

(a) Give the molecular formula of ethyl 2-cyanoacrylate.

~~$C_5H_5NO_2$~~ ~~C_5H_7ON~~ $C_6H_7NO_2$ ✓ [1]

(b) Give the bond angles labelled **x** and **y**.

bond angle **x** 120° ✓

bond angle **y** ~~120°~~ 109.5° X [2]

(c) Write the **names** of the functional group levels of the carbon atoms numbered **1**, **2**, and **3**.

1 carboxylic acid level

2 carbonyl level X ✓

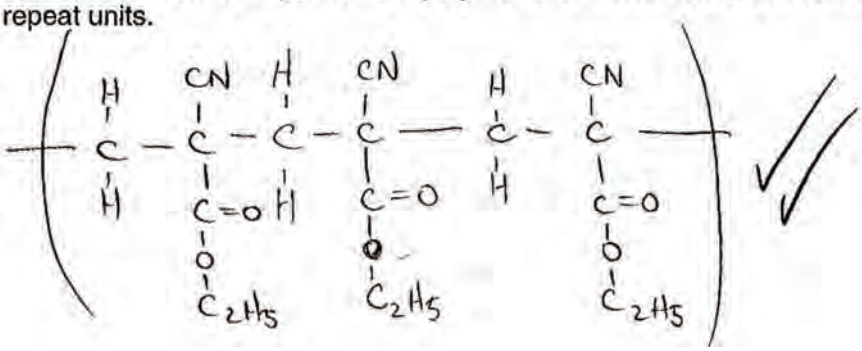
3 carboxylic acid level [2]

(d) Ethyl 2-cyanoacrylate rapidly undergoes addition polymerisation in the presence of a suitable nucleophile to form long, strong chains which join the bonded surfaces together. The presence of moisture can therefore cause the glue to set, so exposure to moisture in the air can cause a tube or bottle of glue to become unusable over time.

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

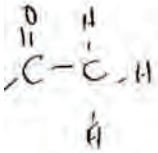
A lone pair donor ✓ [2]

(ii) Draw the structure of part of the polymer chain that would be formed, showing **three** repeat units.



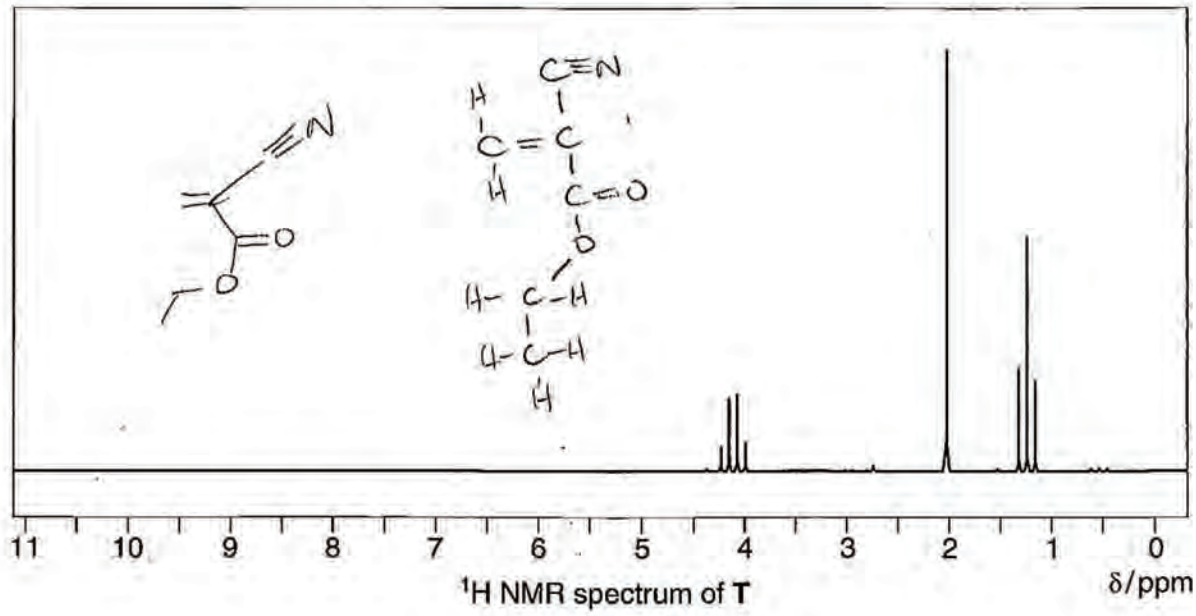
✓✓ [2] 2

(e) The reduction of ethyl 2-cyanoacrylate with $LiAlH_4$ in ether produces two compounds, **Q** and **R**. **Q** reacts with ethanoyl chloride in a 1:2 molar ratio to form **S**. **R** reacts with ethanoyl chloride in a 1:1 ratio to form **T**. The ^1H NMR spectrum of **T** is shown in Fig. 5.2 and the ^{13}C NMR spectrum of **T** is shown in Fig. 5.3.



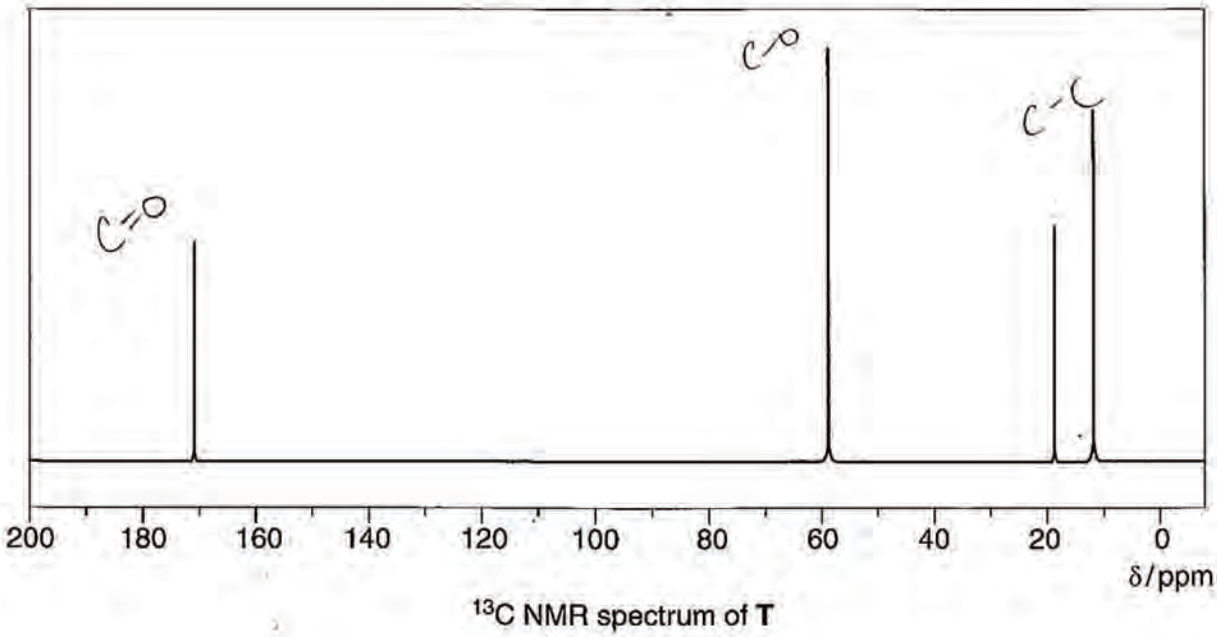
If ethyl 2-cyanoacrylate is instead reduced with hydrogen using a nickel catalyst then there is only a single product, **U**. The ^1H NMR spectrum of **U** has six signals, one of which disappears on shaking with D_2O.

Draw the structural formula of each of the compounds **Q**, **R**, **S**, **T** and **U**. Explain the reactions and the forms of the spectra in Fig. 5.2 and Fig. 5.3. This should include the identification of the atoms or groups of atoms responsible for each signal.



^1H NMR spectrum of **T**

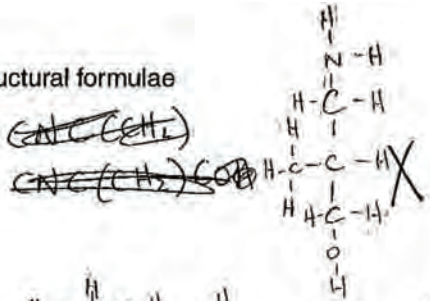
Fig. 5.2

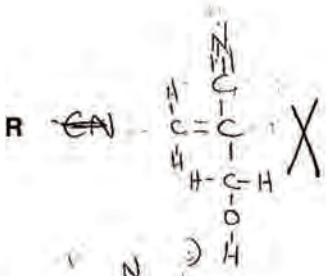


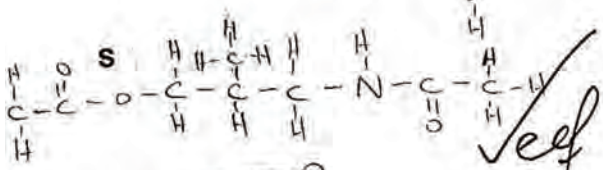
^{13}C NMR spectrum of **T**

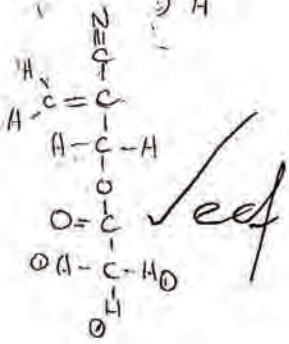
Fig. 5.3

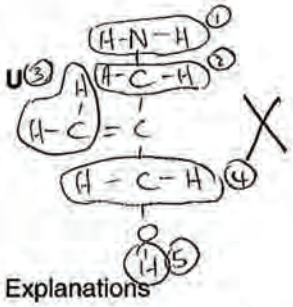
Structural formulae

Q 

R 

S 

T 

U 

[5]

Explanations

Reactions of **Q** and **R** with ethanoyl chloride These are condensation reactions forming an ester bond. There is the elimination of HCl through the process with Q and R Peptide bond is also formed in that with Q [3]

^{1}H NMR of **T** The signal with no splittings just above 2 ppm is due to the protons labelled ① in T as the adjacent carbon has no hydrogens on it. Signal with 3 splittings above 1 ppm is due to protons labelled ② as adjacent carbon has two protons [3]

^{13}C NMR of **T** The peak at 170 ppm is due to the C=O bond and the one at around 59 ppm is due to the C-O bond. The other two peaks below 20 ppm are due to C-C bonds CON [3]

^{1}H NMR of **U** The signal that disappears is due to the presence of a hydrogen isotope. Otherwise, the five other signals are due to the different groups of protons in five different environments, each in a differently numbered circle in U. CON [3]

[Total: 26]

Examiner Comment

Parts **(a)** – **(d)** were generally well answered as was the case for most candidates. A Distinction level candidate would have been able to identify all three functional group levels in part **(c)** and both bond angles in part **(b)**.

Part **(e)** was definitely a high level discriminator. Only 2 marks were gained for the structures and they came from ecf from incorrect original structures as the true nature of the reduction process was not recognised. Failing to distinguish between a peptide bond and an amide cost a mark early on in the description.

References to NMR spectra need to be clear and specific and the most often seen problem with references to ^{13}C spectra was, as here, with candidates who seemed to be referring to bonds as being responsible for the spectrum rather than to carbon atoms/nuclei. This could have been due to confusion with UV spectroscopy or simply poorly phrased answers.

Example Candidate Response – Merit

5 Cyanoacrylate is the generic name for cyanoacrylate based fast-acting glues such as ethyl 2-cyanoacrylate. The skeletal formula of ethyl 2-cyanoacrylate is given in Fig. 5.1.

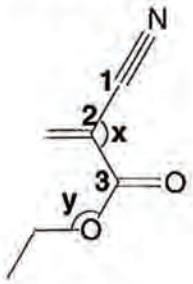


Fig. 5.1

(a) Give the molecular formula of ethyl 2-cyanoacrylate.

$C_6H_7NO_2$ [1]

(b) Give the bond angles labelled **x** and **y**.

bond angle **x** 120° ✓

bond angle **y** 104° ✓ [2]

(c) Write the **names** of the functional group levels of the carbon atoms numbered **1**, **2**, and **3**.

1 carboxylic acid level

2 carbonyl level ✗

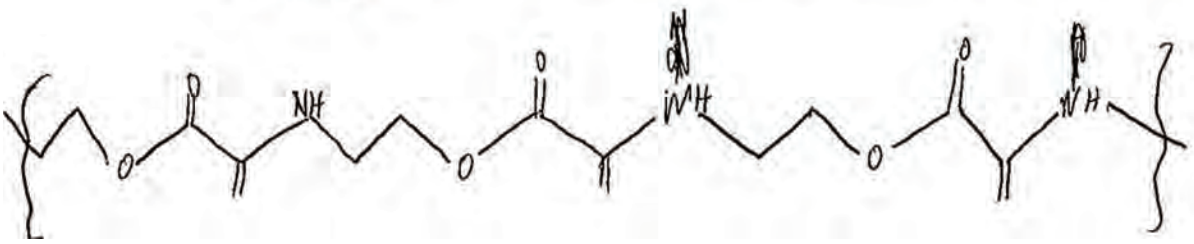
3 carboxylic acid level ✓ [2]

(d) Ethyl 2-cyanoacrylate rapidly undergoes addition polymerisation in the presence of a suitable nucleophile to form long, strong chains which join the bonded surfaces together. The presence of moisture can therefore cause the glue to set, so exposure to moisture in the air can cause a tube or bottle of glue to become unusable over time.

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

An electron pair donator, something that attracts the electrophiles. [2]

(ii) Draw the structure of part of the polymer chain that would be formed, showing **three** repeat units.

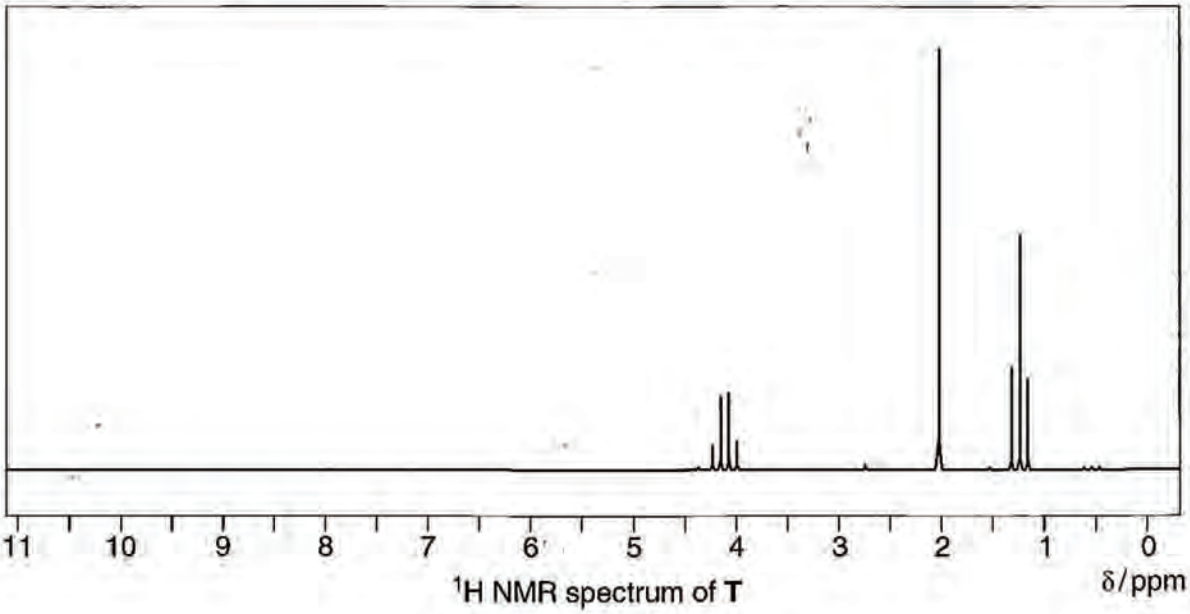


[2]

(e) The reduction of ethyl 2-cyanoacrylate with $LiAlH_4$ in ether produces two compounds, **Q** and **R**. **Q** reacts with ethanoyl chloride in a 1:2 molar ratio to form **S**. **R** reacts with ethanoyl chloride in a 1:1 ratio to form **T**. The ^1H NMR spectrum of **T** is shown in Fig. 5.2 and the ^{13}C NMR spectrum of **T** is shown in Fig. 5.3.

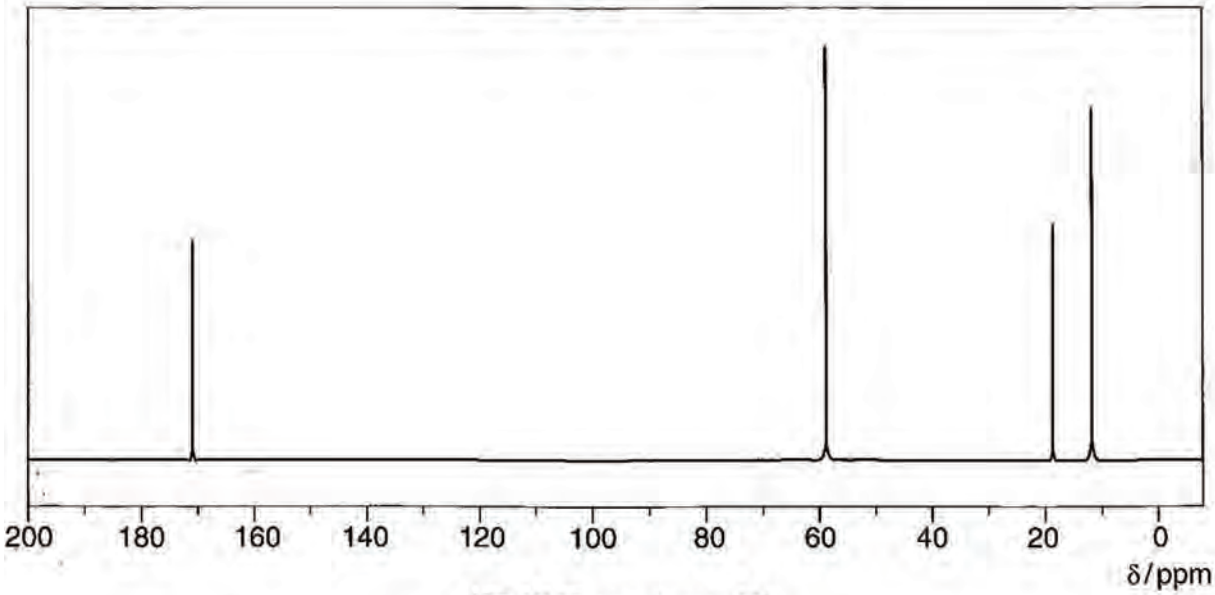
If ethyl 2-cyanoacrylate is instead reduced with hydrogen using a nickel catalyst then there is only a single product, **U**. The ^1H NMR spectrum of **U** has six signals, one of which disappears on shaking with D_2O.

Draw the structural formula of each of the compounds **Q**, **R**, **S**, **T** and **U**. Explain the reactions and the forms of the spectra in Fig. 5.2 and Fig. 5.3. This should include the identification of the atoms or groups of atoms responsible for each signal.



^1H NMR spectrum of **T**

Fig. 5.2

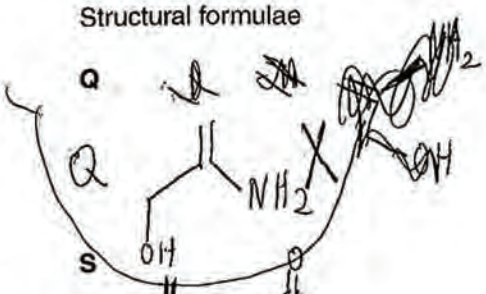


^{13}C NMR spectrum of **T**

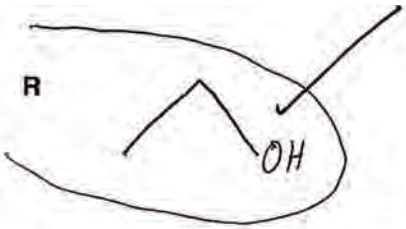
Fig. 5.3

Structural formulae

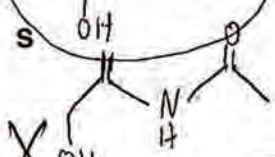
Q



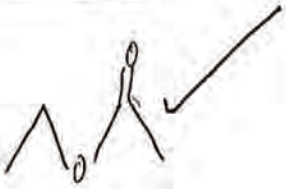
R



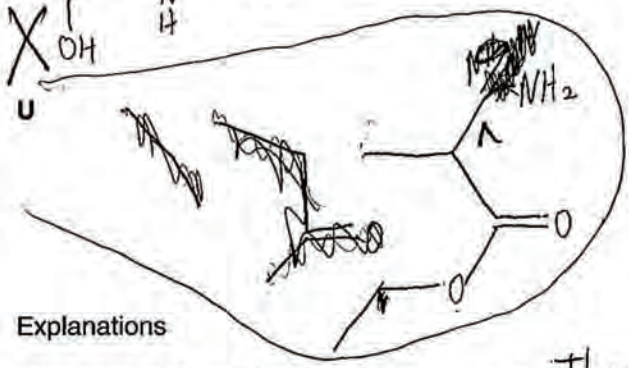
S



T



U



[5] 2

Explanations

Reactions of **Q** and **R** with ethanoyl chloride .... These reactions simply add a carbonyl group to the compound through the mechanism of nucleophilic substitution as the carbocation of the ethanoyl chloride replaces the Hydrogens from NH_2 (ethanol) and the Hydrogen from OH ..... X [3] 0

^{1}H NMR of **T** .... It is clear that there are 3 different Hydrogen environments, 1 of which there are two of with no other Hydrogens on the adjacent carbons. 1 of which there are two of with 2 Hydrogens on the adjacent Carbon. ..... [3] 1

^{13}C NMR of **T** .... There are 4 different carbon environments shown in the ^{13}C NMR of T. The peaks at 170 showing a carbon bonded to 2 Oxygens and a CH_3 group. The peak at 60 showing the C bonded to an oxygen and a CH_3 group. 20 showing C bonded to a C(X)0 group. [3] And 11 showing the C bonded to a CH_2 group. 2

^{1}H NMR of **U** .....

.....

.....

..... [3] 0

[Total: 26]

11

Examiner Comment

As with many candidates a reasonable attempt was made at parts **(a)** – **(d)** although the clue in the stem of referring to addition polymerisation was overlooked as this candidate attempted some form of condensation polymer in part **(d) (ii)**.

Correct identification of R in part **(e)** should have led to a correct structure of Q but a mistake was made with regard to the chain length.

The explanations incorrectly referred to an acyl group as a carbonyl group and again lacked specificity when referring to proton NMR although the ^{13}C NMR was well explained.

Paper 4 Practical

Mark Scheme

Skill	Total marks	Breakdown of marks		Qu. 1	Qu. 2	Qu. 3
Manipulation, measurement and observation	17 marks	Successful collection of data and observations	13 marks	2	8	3
		Quality of measurements or observations	2 marks	2	0	0
		Decisions relating to measurements or observations	2 marks	0	2	0
Presentation of data and observations	6 marks	Recording data and observations	2 marks	2	0	0
		Display of calculations and reasoning	2 marks	2	0	0
		Data layout	2 marks	1	0	1
Analysis, conclusions and evaluation	17 marks	Interpretation of data or observations and identifying sources of error	5 marks	5	0	0
		Drawing conclusions	10 marks	1	6	3
		Suggesting improvements	2 mark	2	0	0

MMO = manipulation, measurement and observation
collection = successful collection of data and observations
quality = quality of measurements or observations
decisions = decisions relating to measurements or observations

PDO = presentation of data and observations
recording = recording data and observations
display = display of calculations and reasoning
layout = data layout

ACE = analysis, conclusions and evaluation
interpretation = interpretation of data or observations and identifying sources of error
conclusions = drawing conclusions
improvements = suggesting improvements

The examiner is to check (and correct if necessary) all subtractions on the Supervisor and candidate scripts where accuracy marks are concerned.

When awarding accuracy marks in Question 1 the candidate's value for the ratio of corrected mass water: corrected mass residue should be listed on the blank page of the Supervisor script or on a sheet of paper securely attached to it.

Where Supervisor results are considered to be suspect (fewer than half the candidates score more than 1 mark), a value derived from the consistent results of the candidates may be used.

Question 1 Mark Scheme

		Sections	Learning outcomes	Indicative material	Mark
1	(a)	PDO layout	Use the appropriate presentation medium to produce a clear presentation of the data	**All** balance readings clearly shown in a single table including mass of residue and mass of water lost	[1]
		PDO recording	Record raw readings of a property to the same degree of precision	All values of mass given to the same number of decimal places	[1]
		PDO recording	Use column headings that include both the quantity and the unit and that conform to accepted scientific conventions	All masses are labelled clearly with units. Must use solidus, brackets or describe units fully in words.	[1]
		MMO collection	Follow instructions given in the form of written instructions or diagrams	Final masses within 0.05 g (Award 1 mark if readings within 0.10 g)	[2]
		ACE interpretation	Calculate other quantities from data	Calculates correctly the mass of water and mass of residue (Examiner to note corrected values)	[1]
		MMO quality	Make accurate and consistent measurements and observations	Examiner to check/calculate the ratio of corrected mass water: corrected mass residue. Award 2 marks if difference is within ±0.05 of Supervisor value Award 1 mark if difference is within ±0.10 of Supervisor value.	[2]

	(b)	PDO display	Show their working in calculations, and the key steps in their reasoning	Mass of residue/120.4	[1]
		PDO display	Show their working in calculations, and the key steps in their reasoning	Mass of water/18.(0)	[1]
		ACE interpretation	Calculates other quantities from data	Calculates ratio of moles water to moles of magnesium sulfate	[1]
		ACE conclusion	Draw conclusions from interpretations of observations, data and calculated values.	States *x* as an integer	[1]
	(c) (i)	ACE interpretation	Estimate, quantitatively the uncertainty in quantitative measurements	± 0.005 g (or 0.0005 g) (Allow ± 0.01g (or 0.001g) as long as this value is not doubled in **(ii)**)	[1]
	(c) (ii)	ACE interpretation	Express such uncertainty in a measurement as an actual or percentage error	Value from **(c)(i)** × 2 ANS / mass of water × 100	[1] [1]
	(d)	ACE improvement	Suggest modifications to an experimental arrangement that will improve the accuracy of the experiment	Any sensible answer with explanation. e.g. more gentle heating or use of lid during the early stages of heating to reduce loss of solid	[1] [1]
					[Total: 17]

Example Candidate Response – Distinction

1 Epsom salts occur naturally and are a hydrated form of magnesium sulfate, $MgSO_4.xH_2O$.
In the following experiment you will determine the value of x.
Read all of the following instructions before you start any experimental work.

You are provided with the following:
FA 1 hydrated magnesium sulfate, $MgSO_4.xH_2O$

Method

1. Weigh a clean, dry crucible.
2. In the crucible place the entire sample of Epsom salts, **FA 1**.
3. Reweigh the crucible.
4. Place the crucible in a pipe-clay triangle on top of a tripod.
5. Heat the crucible **gently** for about 1 minute and then more strongly for a further 4 minutes.
6. Allow the crucible to cool for about 1 minute and then use a pair of tongs to place the crucible on a heat proof mat.
7. Leave the crucible to cool for approximately three minutes, then reweigh the crucible and its contents.
8. Repeat the cycle of heating and weighing, as described in steps 4 to 7, until consecutive recorded masses do not differ by more than 0.05 g.

(a) In a suitable table, record all masses.
Calculate the mass of the residue and the mass of the water lost. Record both of these masses in the table.

	mass of crucible + residue /g	mass of residue /g	mass of water lost /g
initial mass (no residue)	22.09	0.00	0.00
not heated	23.60	1.51	0.00
heated once	22.82	0.73	0.78
heated twice	22.82	0.73	0.78
heated 3 times	22.82	0.73	0.78
~~4th heating~~			

range = 1.07
1.06
δ = 0.01

[8]

8

(b) From the measurements you have made, determine the value of x in the formula $MgSO_4.xH_2O$.

Show your working.

$m(H_2O)_{lost} = 0.78\,g$

$\Rightarrow n(H_2O) = \frac{m(H_2O)}{M_r(H_2O)} = \frac{0.78}{18} = 0.0433\ mol$

$m(residue)_{final} = 0.73\,g$

$n(residue)_{final} = \frac{m(residue)_{final}}{M_r(residue)_{final}}$

$= \frac{0.73}{24.3+32.1+(16\times4)}$

$n(residue) = 6.0831\times10^{-3}\ mol$

$x = \frac{n(H_2O)}{n(residue)} = 7.1470 \approx 7$

$x = 7$ .....[4]

(c) **(i)** State the uncertainty in the measurement of each mass in this experiment.

uncertainty = ± 0.005 g [1]

(ii) Calculate the percentage error in the mass of water that is lost.

Show your working.

$\frac{0.005}{0.78} \times 100 = 0.641\ \%$

0.641 % .....[2]

(d) Suggest an improvement that a student might make to the experiment and explain why this would lead to the determination of a more accurate value of x.

~~repeat the experiment at least once with a new sample of Epsom salts. These results would hopefully confirm the value of x to be 7.~~

[2]

[Total: 17]

If more accurate scales were used, the masses calculated and measured would be more accurate and this would lead to a higher level of accuracy when calculating x.

XX

4

1

1

0

14

Examiner Comment

(a) The candidate scored all 8 marks in the opening part although it was not necessary to record the mass of residue and the mass of water lost following each period of heating as was done here.

(b) Again the candidate gained full marks here. Although they do not state the relative formula mass of $MgSO_4$, they have clearly shown how the value is obtained and gain the mark.

(c) The correct uncertainty was given in part **(i)** but the candidate did not double this value in part **(ii)** as it was not appreciated that two masses were needed to work out the mass of water lost, these being the combined mass of the crucible and FA 1, along with the combined mass of the crucible and the residue.

(d) This answer was too vague to merit any credit. The candidate goes someway to suggesting the use of a higher precision balance but this does not merit credit.

Example Candidate Response – Distinction

1 Epsom salts occur naturally and are a hydrated form of magnesium sulfate, $MgSO_4.xH_2O$.
In the following experiment you will determine the value of x.
Read all of the following instructions before you start any experimental work.

You are provided with the following:
FA 1 hydrated magnesium sulfate, $MgSO_4.xH_2O$

Method

1. Weigh a clean, dry crucible.
2. In the crucible place the entire sample of Epsom salts, **FA 1**.
3. Reweigh the crucible.
4. Place the crucible in a pipe-clay triangle on top of a tripod.
5. Heat the crucible **gently** for about 1 minute and then more strongly for a further 4 minutes.
6. Allow the crucible to cool for about 1 minute and then use a pair of tongs to place the crucible on a heat proof mat.
7. Leave the crucible to cool for approximately three minutes, then reweigh the crucible and its contents.
8. Repeat the cycle of heating and weighing, as described in steps 4 to 7, until consecutive recorded masses do not differ by more than 0.05 g.

(a) In a suitable table, record all masses.
Calculate the mass of the residue and the mass of the water lost. Record both of these masses in the table.

	Mass /g		
Crucible	22.36		
Crucible + hydrate $MgSO_4$ (before heating)	23.88		
Hydrated $MgSO_4$	1.52		
Crucible + $MgSO_4$ (after heating)	23.10	23.10	23.09
Anhydrous $MgSO_4$	0.73		
Water	0.79		

rahb = 1.08
1.06
δ=0.02

Mass of anhydrous $MgSO_4$ = (Crucible + $MgSO_4$ [after heating]) − Crucible
= 23.09g − 22.36g
= 0.73g

Mass of water = (Mass of hydrated $MgSO_4$) − (Mass of anhydrous $MgSO_4$)
= 1.52g − 0.73g
= 0.79g

[8]

8

For Examiner's Use

(b) From the measurements you have made, determine the value of x in the formula $MgSO_4.xH_2O$.

Show your working.

$n(H_2O) = \frac{m(H_2O)}{Mr(H_2O)} = \frac{0.79g}{18 g mol^{-1}} = 0.439\ mol$ ecf

$\frac{n(H_2O)}{n(MgSO_4)} = 7.238$ (water of crystallisation) bod

$n(MgSO_4) = \frac{m(MgSO_4)}{Mr(MgSO_4)} = \frac{0.73}{120.4 g\ mol^{-1}} = 6.06 \times 10^{-3}\ mol$

$\therefore MgSO_4.7H_2O$ (to nearest whole number)

7 [4]

4

(c) **(i)** State the uncertainty in the measurement of each mass in this experiment.

uncertainty = ± 0.05 g [1]

0.

(ii) Calculate the percentage error in the mass of water that is lost.

Show your working.

$\frac{0.05}{0.79} \times 100 = 6.33\%$ ecf

6.33% [2]

1

(d) Suggest an improvement that a student might make to the experiment and explain why this would lead to the determination of a more accurate value of x.

Allow the crucible to cool in a dessicator in between heating so that moisture from the air does not add to the mass of the dehydrated $MgSO_4$. [2]

2

[Total: 17]

15

Examiner Comment

(a) The candidate scored all 8 marks on the opening part. All the results were clearly displayed in a single table including the mass of residue and that of water lost. The data was noted to an appropriate level of precision. The headings were clear and units given. In addition, the final masses lie sufficiently close together and the results are in excellent agreement with those of the Supervisor.

(b) The second mark for showing the mass of water lost divided by the relative formula mass of water given despite the slip of quoting the answer as 0.439 rather than 0.0439. The ratio was allowed despite the incorrect rounding of the answer which uses the two calculator values for the amount of water and residue rather than the values noted in the working.

(c) As the candidate was using a balance that read to two decimal places, the answer should have been given as ±0.005 g. Another mark was lost by not doubling the value from part **(i)** in the following calculation. The candidate did not appreciate that two masses are required to work out the mass of water lost.

(d) An excellent suggestion for an improvement and furthermore, the candidate gave a clear explanation of why the suggested improvement would lead to a more accurate value of *x*.

Example Candidate Response – Merit

1 Epsom salts occur naturally and are a hydrated form of magnesium sulfate, $MgSO_4.xH_2O$.
In the following experiment you will determine the value of x.
Read all of the following instructions before you start any experimental work.

You are provided with the following:
FA 1 hydrated magnesium sulfate, $MgSO_4.xH_2O$

Method

1. Weigh a clean, dry crucible.
2. In the crucible place the entire sample of Epsom salts, **FA 1**.
3. Reweigh the crucible.
4. Place the crucible in a pipe-clay triangle on top of a tripod.
5. Heat the crucible **gently** for about 1 minute and then more strongly for a further 4 minutes.
6. Allow the crucible to cool for about 1 minute and then use a pair of tongs to place the crucible on a heat proof mat.
7. Leave the crucible to cool for approximately three minutes, then reweigh the crucible and its contents.
8. Repeat the cycle of heating and weighing, as described in steps 4 to 7, until consecutive recorded masses do not differ by more than 0.05 g.

(a) In a suitable table, record all masses.
Calculate the mass of the residue and the mass of the water lost. Record both of these masses in the table.

Mass of crucible = 18.644g

Mass of crucible + FA1 = 20.121g

Final mass = 19.335g

	Time/mins	Mass /g
1st heating	0	20.121
2nd heating	9	19.349
3rd heating	18	19.339
4th heating	27	19.335

Mass lost = 0.786g
water
residue = 0.691
ratio = 1.14
δ = 0.06
1.08

X ✓ ✓ ✓ ✓ X ✓ X

5

[8]

(b) From the measurements you have made, determine the value of x in the formula $MgSO_4.xH_2O$.

Show your working.

Initial mass of FA1 = 1.477g

Final mass of FA1 = 0.691g

Mass lost = 0.786g

moles of H_2O = $\frac{0.786}{18}$ = 0.0436

moles of $MgSO_4$ = $\frac{0.691}{120.4}$ = 0.00573

7.6 : 1 ratio of moles, ✓

round to nearest integer

$x = 8$ = $MgSO_4 8H_2O$

$x = 8$ ✓ .....[4]

4

(c) (i) State the uncertainty in the measurement of each mass in this experiment.

uncertainty = ± 0.05 X g [1]

0.

(ii) Calculate the percentage error in the mass of water that is lost.

Show your working. ± 0.05g

1. Mass lost = 0.836g

moles of H_2O = $\frac{0.836}{18}$ = 0.0464

moles of $MgSO_4$ = $\frac{0.641}{120.4}$ = 0.00532

ratio = 1 : 8.72

2. mass lost = 0.736g

$\frac{0.736}{18}$ = 0.0408

$\frac{0.741}{120.4}$ = 0.00615

ratio = 1 : 6.64

$\frac{6.64}{8.72}$ = 0.76

XX

= 0.76%. .....[2]

0.

(d) Suggest an improvement that a student might make to the experiment and explain why this would lead to the determination of a more accurate value of x.

Heat for shorter periods of time, This will show more accurate losses of mass/time ∴ showing when the heating mass is constant. .....[2]

XX

0.

[Total: 17]

9

NB: You could increase the mass of x but assume that FA1 is all you have you cannot do this

Examiner Comment

(a) The candidate scored both recording marks by recording the mass to the appropriate number of decimal places and by including the correct units in the column headings. The column recording the time was superfluous. Two further marks were awarded for the candidate recording final masses after heating that fell within 0.05 g of one another. The final mark achieved for this section came from the level of agreement between the candidate's ratio of mass of water lost to mass of residue with that of the Supervisor's value. The agreement was not sufficiently close to award the second available mark. The candidate did not record all their results in a single table nor did they calculate the mass of the residue.

(b) The candidate used their values from part **(a)** to correctly calculate an integer value of x. They have also clearly shown their working and so gained all 4 marks.

(c) **(i)** The candidate may have interpreted this question as asking for the uncertainty in a single recording of mass or the uncertainty in the value of one of the masses. Acceptable answers for this candidate, who used a balance that read to three decimal places, would be either ±0.0005 g or ±0.001 g.

(ii) The candidate approached the question incorrectly by working out the maximum and minimum values of x that would arise from their quoted uncertainty in the mass of water lost.

(d) The candidate's final comment was correct in that a more accurate value of x could be obtained by increasing the mass of FA 1. However, an incorrect answer had already been given in suggesting that accuracy could be improved by heating for shorter periods of time.

Example Candidate Response – Merit

1 Epsom salts occur naturally and are a hydrated form of magnesium sulfate, $MgSO_4.xH_2O$.
In the following experiment you will determine the value of x.
Read all of the following instructions before you start any experimental work.

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You are provided with the following:
FA 1 hydrated magnesium sulfate, $MgSO_4.xH_2O$

Method

1. Weigh a clean, dry crucible. 16.7484 g
2. In the crucible place the entire sample of Epsom salts, **FA 1**.
3. Reweigh the crucible. 18.237
4. Place the crucible in a pipe-clay triangle on top of a tripod.
5. Heat the crucible **gently** for about 1 minute and then more strongly for a further 4 minutes.
6. Allow the crucible to cool for about 1 minute and then use a pair of tongs to place the crucible on a heat proof mat.
7. Leave the crucible to cool for approximately three minutes, then reweigh the crucible and its contents.
8. Repeat the cycle of heating and weighing, as described in steps 4 to 7, until consecutive recorded masses do not differ by more than 0.05 g.

(a) In a suitable table, record all masses.
Calculate the mass of the residue and the mass of the water lost. Record both of these masses in the table.

Mass of the crucible only / g	Mass of the crucible and FA1 before heating / g	Mass of the crucible + FA1 after heating / g	
		1st	2nd
16.744	18.237	17.466	17.462
Mass of FA1 without the crucible only / g	1.493	0.722	0.718

mass of residue = 0.718
" " water = 0.775

ratio = 1.08

S = 0

1.08

[8]

6

(b) From the measurements you have made, determine the value of x in the formula $MgSO_4.xH_2O$.

Show your working.

Mass of $MgSO_4 \cdot xH_2O$ = 18.237 − 16.744 = 1.493g

RMM of $MgSO_4$ = 24.3 + 32.1 + (4×16) = 120.4

Mass of $MgSO_4 \cdot xH_2O$ after repeat of heating = 17.462 − 16.744 = 0.718g

RMM of H_2O = 18

Mass change = 1.493 − 0.718 = 0.775g

(H_2O) mole = $\frac{g}{RMM} = \frac{0.775}{18} = 0.043$

$(MgSO_4)$ mole = $\frac{0.718}{120.4} = 0.00596 \simeq 0.006$

∴ $\frac{0.043}{0.006} = 7.17$

s.f. x = 7 c.f. [4]

(c) (i) State the uncertainty in the measurement of each mass in this experiment.

uncertainty = ± 0.0005 g [1]

(ii) Calculate the percentage error in the mass of water that is lost.

Show your working.

$\frac{0.0005}{0.775} \times 100 =$ ~~0.000645 %~~ (3 s.f.)

0.0645 % (3 s.f.)

≃ 0.065 %

~~0.000645 %~~

~~0.0645 %~~

0.065 % [2]

(d) Suggest an improvement that a student might make to the experiment and explain why this would lead to the determination of a more accurate value of x.

repeat the whole experiment a few times. By doing so, you will get value of x 3 times. If they all round up or down to the same number than you have the right value for x. If they round up or down to different number, something is wrong with your experiment [2]

also, I if I heated for shorter time I would have got more data and more accurate results. From the table, it seems that most water vapour already evaporated even before repeating the procedure 4 to 7 to get 2nd data. Heating for shorter time will give me better idea of the mass of $MgSO_4$. ∴ can work out more accurate value of x.

[Total: 17]

3 3 1 1 1 1 1 0 0 11 11

Examiner Comment

(a) This candidate did not record the mass of water lost as instructed and so did not gain the first mark. This also meant that they were unable to gain the sixth marking point for correctly calculating the mass of water lost and the mass of residue. The marks for recording all mass readings to an appropriate level of precision and with the correct units were awarded, as were the marks for heating to near constant mass. This candidate also scored both marks for the quality of their data compared to that of the Supervisor.

(b) The candidate's method was correct but at one stage the candidate rounded the number of moles of magnesium sulfate to just one significant figure which leads to an incorrect ratio using the data from part **(a)**.

(c) The uncertainty was correctly given in part **(i)** but the candidate did not appreciate that in order to work out the mass of water lost, two measurements of mass are required and so the uncertainty must be doubled before being used in the calculation in part **(ii)**.

(d) The suggestion to repeat the experiment was a response given by a number of candidates but did not merit any credit as it does not necessarily lead to a more accurate value of x.

Question 2 Mark Scheme

FA 2: NaOH **FA 3**: K_2CrO_4 **FA 4**: H_2SO_4 **FA 5**: $BaCl_2$ **FA 6**: $Pb(NO_3)_2$					
2	**(a)**	MMO collection	Use their apparatus to collect an appropriate quantity of data or observations, including differences in colour, solubility or quantity of materials	Observation for **FA 2**: white ppt with **FA 6** (award only if no reaction recorded with **FA 3**, **FA 4** and **FA 5**. Ignore slight ppt if recorded with **FA 5**) ppt is soluble in excess Observations for **FA 3**: turns orange in **FA 4** yellow ppt with **FA 5** bright yellow ppt with **FA 6** (must have a comparison between the 2 yellow ppts) Observations for **FA 4** white ppt with **FA 5** white ppt with **FA 6** Observation for **FA 5**: white ppt with **FA 6**	[1] [1] [1] [1] [1] [1] [1] [1]
	(b)	ACE conclusion	Draw conclusion from interpretation of observations	H^+: **FA 4** CrO_4^{2-}: **FA 3** SO_4^{2-}: **FA 4** Pb^{2+}: **FA 6** Ba^{2+}: **FA 5** OH^-: **FA 2**	[1] [1] [1] [1] [1] [1]
	(c)	MMO decision	Identify where confirmatory tests are appropriate and the nature of such tests	Heat with hydroxide and aluminium foil and test gas with damp red litmus paper No pale brown gas liberated by dilute acids	[1] [1]
					[Total: 16]

Example Candidate Response – Distinction

2 **FA 2**, **FA 3**, **FA 4**, **FA 5** and **FA 6** contain a number of different ions. By making observations when each pair of solutions is mixed it is possible to determine which solution contains which ion. The following ions are present: H^+, CrO_4^{2-}, SO_4^{2-}, Pb^{2+}, Ba^{2+} and OH^-.

(a) Complete the following table by recording your observations on mixing each pair of solutions.

	FA 3	FA 4	FA 5	FA 6
FA 2	Solution stays the same yellow colour. There is the slight formation of an oil on shaking	No observation. Solution remains colourless	white ppt. formed Dissolves after a few minutes (soluble in excess)	white ppt formed which dissolved almost immediately to give a colourless solution
FA 3		solution turns from yellow to orange in colour	yellow ppt gelatinous formed	Bright yellow gelatinous ppt formed
FA 4			white gelatinous ppt. formed	white gelatinous ppt. formed
FA 5				white ppt formed

[8]

7

(b) From your observations, identify which of the solutions contain the following ions.

ion	H^+	CrO_4^{2-}	SO_4^{2-}	Pb^{2+}	Ba^{2+}	OH^-
solution	FA 4 ✓	FA 3 ✓	FA 4 ✓	FA 6 ✓	FA 5 ✓	FA 2 ✓

[6]

6

(c) **FA 6** is an aqueous solution of a nitrate. Explain how you would confirm the presence of the nitrate anion. **Do not carry out any experimental work.**

Heat a boiling tube containing FA6 with OH⁻ (aq) and Al foil and test the gas liberated with damp red litmus paper. If the litmus paper turns blue, the solution contained the nitrate anion. [2]

1

[Total: 16]

14

Examiner Comment

(a) Overall this is a very good answer with clear recordings of all observations and sound use of the appropriate technical terms. The only mark not to be awarded was the one for noting that the white precipitate formed by mixing FA 2 with FA 6 was soluble in an excess of FA 2. It was apparent from this candidate's answer that they added too much FA 2 in the first place so their initial white precipitate dissolved almost at once.

(b) All the ions were correctly assigned.

(c) As occurred on many of the scripts only the first mark could be awarded here. The second mark in this part relied on candidates realising that both nitrate and nitrite salts evolve ammonia on warming with aluminium and sodium hydroxide solution. To be certain that a nitrate was present it would be necessary to note that no pale brown gas was liberated when the sample was treated with dilute acid.

Example Candidate Response – Merit

2 **FA 2**, **FA 3**, **FA 4**, **FA 5** and **FA 6** contain a number of different ions. By making observations when each pair of solutions is mixed it is possible to determine which solution contains which ion. The following ions are present: H^+, CrO_4^{2-}, SO_4^{2-}, Pb^{2+}, Ba^{2+} and OH^-.

(a) Complete the following table by recording your observations on mixing each pair of solutions.

	FA 3	FA 4	FA 5	FA 6
FA 2	Solution is clear pale yellow from FA3; no change on mixing.	Colourless solution; no change on mixing.	Pale white precipitate (from colourless) on mixing i	Solution is colourless; white ppt ~~change~~ on mixing ^ bright
FA 3		~~Yellow~~ Orange clear ppt on mixing (from ~~colourless~~ deep pale yellow)	Pale Cream/off-white opaque ppt on mixing (from clear pale yellow)	Opaque yellow ppt on mixing (from clear pale yellow)
FA 4			Opaque white ppt on mixing (from colourless)	Opaque white ppt on mixing (from colourless) ~~white precipitate~~
FA 5				Solid white ~~precipitate~~ produced on mixing

[8]

4

(b) From your observations, identify which of the solutions contain the following ions.

ion	H^+	CrO_4^{2-}	SO_4^{2-}	Pb^{2+}	Ba^{2+}	OH^-
solution	FA 4 ✓	FA 3 ✓	FA 4 ✓	FA 6 ✓	FA 5 ✓	FA 2 ✓

[6]

6

(c) **FA 6** is an aqueous solution of a nitrate. Explain how you would confirm the presence of the nitrate anion. **Do not carry out any experimental work.**

Mix the solution with dil. NaOH(aq) and place aluminium foil in the resulting solution and heat gently ; ~~confirmation of the NO_3^- ion~~ [2]

~~presence is achieved when $NH_3(g)$ is produced~~ [Total: 16]

~~which can be detected by damp red litmus paper which turns blue in the presence of $NH_3(g)$.~~

~~damp~~ When $NH_3(g)$ is evolved, test for $NH_3(g)$ with damp red litmus paper, if $NH_3(g)$ is present (i.e. if it is NO_3^-) it will turn blue.

1

11

Examiner Comment

(a) The candidate observed the correct initial products when combining FA 2 with the other unknown solutions but does not go on to note that the white precipitate formed on mixing FA 2 with FA 6 is soluble in an excess of FA 2. No precipitate results from the mixing of FA 3 and FA 4 as recorded by the candidate and only shades of yellow were acceptable as descriptions for the colour of barium chromate, formed by mixing FA 3 and FA 5. Despite not being awarded the mark for the colour of barium chromate, the use of bright to describe the colour of lead chromate was sufficient to merit the mark for the comparison of the two shades of yellow. Overall the candidate uses slightly confusing terms to describe the observations. For example, it is not necessary to describe a precipitate as being opaque although this did not mean the loss of any marks. In the final part, however, with the mixing of FA 5 and FA 6, the candidate stated that a white saturate was produced which was deemed insufficient to convey the sense of a precipitate.

(b) All ions were correctly assigned.

(c) The second mark in this part relied on candidates realising that both nitrate and nitrite salts evolve ammonia on warming with aluminium and sodium hydroxide solution. To be certain that a nitrate was present it would be necessary to note that no pale brown gas was liberated when the sample was treated with dilute acid.

Example Candidate Response – Merit

2 FA 2, FA 3, FA 4, FA 5 and FA 6 contain a number of different ions. By making observations when each pair of solutions is mixed it is possible to determine which solution contains which ion. The following ions are present: NH_4^+, CrO_4^{2-}, SO_4^{2-}, Pb^{2+}, Ba^{2+} and OH^-.

(a) Complete the following table by recording your observations on mixing each pair of solutions.

	FA 3	FA 4	FA 5	FA 6
FA 2	The FA3 colur remains on addition slight emulsion form he dissapears.	no change	white percipitate particles form white ppt	white emulsion is formed. white ppt is formed
FA 3		orange coloured emulsion is formed	lime green yellow emulsion formed. lime green emulsion formed	yellow yellow ppt formed.
FA 4			creamy emulsion formed. white ppt formed	creamy emulsion formed white percipitate formed
FA 5				creamy emulsion formed. white percipitate formed.

[8]

5

(b) From your observations, identify which of the solutions contain the following ions.

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ion	H^+	CrO_4^{2-}	SO_4^{2-}	Pb^{2+}	Ba^{2+}	OH^-
solution	FA4	FA3 ~~FA6~~	FA5	FA6	FA2	~~FA4~~ FA2

[6]

(c) **FA 6** is an aqueous solution of a nitrate. Explain how you would confirm the presence of the nitrate anion. **Do not carry out any experimental work.**

NH_3 is liberated when reacted with OH^- and ~~you can~~ NH_3 turns damp red litmus blue. [2]

[Total: 16]

4
4
0
0
9
9

Examiner Comment

(a) All the marks were awarded for the observations of FA 2 with each of the other unknowns, apart from the solubility of lead hydroxide in an excess of FA 2. For the observation on combining FA 3 and FA 4, although the colour was given correctly, the description of the solution as an emulsion meant that the mark was not awarded. The candidate also described the colour of barium chromate as lime green which is incorrect. The mark for noting the colour of lead chromate was awarded as the candidate has recorded it as being different to the colour of barium chromate.

(b) The candidate incorrectly assigned the barium ion to FA 2 despite noting correctly that FA 2 did not form a precipitate with FA 3 which was correctly identified as containing the chromate ion. The candidate also incorrectly assigned the sulfate ion to FA 5 despite having correctly assigned FA 4 as containing H^+ which would not have given a white precipitate on mixing with sulfate. The source of these errors lies in the observation of a white precipitate with FA 2 and FA 5 which can occur if the solutions are not pure.

(c) The candidate failed to pick up either mark here. They forgot to note that aluminium as well as sodium hydroxide solution must be added before warming if ammonia gas is to be liberated. The second and much more challenging mark was for noting the need to distinguish between nitrate and nitrite which the candidate does not do.

Example Candidate Response – Merit

2 FA 2, FA 3, FA 4, FA 5 and FA 6 contain a number of different ions. By making observations when each pair of solutions is mixed it is possible to determine which solution contains which ion. The following ions are present: H^+, CrO_4^{2-}, SO_4^{2-}, Pb^{2+}, Ba^{2+} and OH^-.

For Examiner Use

(a) Complete the following table by recording your observations on mixing each pair of solutions.

	FA 3 CrO_4^{2-}	FA 4 H^+	FA 5 Ba^{2+}	FA 6 Pb^{2+}
FA 2	The solution remains yellow no visible change.	No visible change. Solution stays colourless.	The solution goes milky. Formation of a white precipitate.	Formation of a white precipitate ✓
FA 3		The solution changes colour to orange. ✓	The solution gives a yellow precipitate. ✓	A bright yellow precipitate forms. ✓
FA 4			A white precipitate forms. ✓	A white precipitate forms. ✓
FA 5				A ~~white~~ milky ~~precipitate~~ solution ~~which dissolves~~ on ~~when adding excess~~ ~~FA 6~~ ✗

[8]

6

(b) From your observations, identify which of the solutions contain the following ions.

ion	H^+	CrO_4^{2-}	SO_4^{2-}	Pb^{2+}	Ba^{2+}	OH^-
solution	FA 4 ✓	FA 3 ✓	FA 2 X	FA 6 ✓	FA 5 ✓	FA5 X

[6]

4

(c) **FA 6** is an aqueous solution of a nitrate. Explain how you would confirm the presence of the nitrate anion. **Do not carry out any experimental work.**

I would pour about 2cm³ of FA6 into a boiling tube and add about 5 drops of NaOH (aq.). Then put a small Al foil and heat the tube with a Bunsen burner. NH_3 should come out which can be tested with a damp red litmus paper. The gas coming off should turn the litmus paper blue. ✓ [2] [Total: 16]

11

Examiner Comment

(a) Two marks were not awarded in part **(a)**. The candidate did not test the solubility of the precipitate of lead hydroxide, formed by mixing FA 2 and FA 6, in an excess of FA 2 and so did not observe that it was soluble. On mixing FA 5 and FA 6 the candidate records a milky solution rather than a white precipitate or white solid.

(b) The candidate assigned the hydroxide ion to be present in FA 5 despite noting correctly that FA 4 and FA 5 when mixed give a white precipitate. FA 2 was stated as containing sulfate ions. This error arose from not having noted the solubility of the lead hydroxide in an excess of hydroxide solution which would rule out the white solid as being lead sulfate.

(c) The candidate correctly describes a positive test for nitrates or nitrites but then does not go on to say how adding dilute acid and looking for the presence of brown fumes can distinguish between them.

Question 3 Mark Scheme

FA 7: butanal **FA 8**: butan-1-ol **FA 9**: butanone

3	(a)	PDO layout	Use the appropriate presentation medium to produce a clear presentation of the data	Draws up a clear table showing at least 3 observations	[1]
		MMO collection	Use their apparatus to collect an appropriate quantity of data or observations, including differences in colour, solubility or quantity of materials	Observations for **FA 7**: colour change to green with acidified dichromate (not green ppt) AND silver mirror / black or dark brown solution or ppt with Tollens'	[1]
				Observations for **FA 8**: colour change to green with acidified dichromate (not green ppt but do not penalise again if mentioned in test for **FA 7**) AND no reaction with Tollens'	[1]
				Observations for **FA 9**: no reaction with either reagent	[1]
	(b)	ACE conclusion	Draw conclusion from interpretation of observations	**FA 8** is butan-1-ol Must refer to positive test with dichromate and no reaction with Tollens'	[1]
				FA 7 is batanal Sufficient to refer only to positive result with Tollens' so long as positive test was observed with dichromate and no other positive tests for Tollens' were observed	[1]
				FA 9 is butanone Sufficient to refer only to negative result with dichromate so long as no reaction with Tollens' was observed and no other negative results are recorded for dichromate. No ecf. Explanation must be based on correct observations	[1]
					[Total: 7]

	dichromate	Tollens'
FA 7 butanal	✓	✓
FA 8 butan-1-ol	✓	x
FA 9 butanone	x	x

Example Candidate Response – Distinction

Before starting question 3, half-fill a 250 cm^3 beaker with water and heat it with a Bunsen burner to between 50 °C and 70 °C. You will use this as a hot water-bath in this question. Turn off the Bunsen burner.

3 **FA 7**, **FA 8** and **FA 9** each contain a single compound which could be butan-1-ol, butanal or butanone. By reacting each of the compounds first with acidified potassium dichromate(VI) and then with Tollens' reagent you should identify each of the three samples.

Tollens' reagent must be prepared immediately before use.

Method

Test with acidified potassium dichromate(VI)

1. Into separate test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
2. Add approximately 1 cm depth of dilute sulfuric acid to each test-tube.
3. Add a few drops of aqueous potassium dichromate(VI).
4. If no initial reaction is seen, warm the test-tube in the hot water-bath.

Preparation of Tollens' reagent

5. Pour aqueous silver nitrate into a boiling tube to a depth of approximately 2 cm.
6. Add approximately 0.5 cm depth of aqueous sodium hydroxide.
7. Add aqueous ammonia a little at a time with continuous shaking until the brown precipitate **just** dissolves. Be careful not to add an excess of aqueous ammonia.

Test with Tollens' reagent

8. Into separate, clean, dry test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
9. Add a few drops of Tollens' reagent.
10. If no initial reaction is seen, warm the test-tube in the hot water-bath. ✓✓✓✓

(a) Record all your observations in a single table.

Procedure	Observations with FA7	FA 8	FA 9
Test with acidified $K_2Cr_2O_7$	Mixture turns pale yellow/ green slowly. Becomes pale blue after heating in water bath.	Mixture stays orange until it is heated in water bath. It then turns green/blue.	Mixture stays orange even when heated in water bath.
Test with Tollens' reagent	Forms black ppt, some of which coats test tube. Turns more shiny on heating.	No observable reaction, even when heated in water bath.	No observable reaction even when heated in water bath.

[4]

4

(b) Identify each sample. In each case explain the observations leading to your conclusion.

FA ..8... contains butan-1-ol.

explanation ....Because it is oxidised by dichromate (slowly) but Tollens' reagent cannot oxidise it. ✓ .....[1]

FA ..7.... contains butanal.

explanation ..Because it is oxidised quickly to butanoic acid by dichromate and gives a positive result for the silver mirror test ✓ .....[1]

FA ....9.. contains butanone.

explanation ..Because there is no oxidation with either dichromate or Tollens' reagent so it cannot be butan-1-ol or butanal ✓ ....[1]

[Total: 7]

7

Examiner Comment

(a) The candidate set out the results in a very clear format. It was not necessary to note the colours both before and after warming each solution with acidified dichromate but so doing clearly indicates a student who is observing closely and working carefully through the series of tests. All observations were correct so the candidate gained full marks for this part.

(b) The identities were given correctly and there was a sound explanation of how each assignment matches the observations made in the opening part.

Example Candidate Response – Merit

Before starting question 3, half-fill a 250 cm^3 beaker with water and heat it with a Bunsen burner to between 50 °C and 70 °C. You will use this as a hot water-bath in this question. Turn off the Bunsen burner.

3 **FA 7**, **FA 8** and **FA 9** each contain a single compound which could be butan-1-ol, butanal or butanone. By reacting each of the compounds first with acidified potassium dichromate(VI) and then with Tollens' reagent you should identify each of the three samples.

Tollens' reagent must be prepared immediately before use.

Method

Test with acidified potassium dichromate(VI)

1. Into separate test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
2. Add approximately 1 cm depth of dilute sulfuric acid to each test-tube.
3. Add a few drops of aqueous potassium dichromate(VI).
4. If no initial reaction is seen, warm the test-tube in the hot water-bath.

Preparation of Tollens' reagent

5. Pour aqueous silver nitrate into a boiling tube to a depth of approximately 2 cm.
6. Add approximately 0.5 cm depth of aqueous sodium hydroxide.
7. Add aqueous ammonia a little at a time with continuous shaking until the brown precipitate **just** dissolves. Be careful not to add an excess of aqueous ammonia.

Test with Tollens' reagent

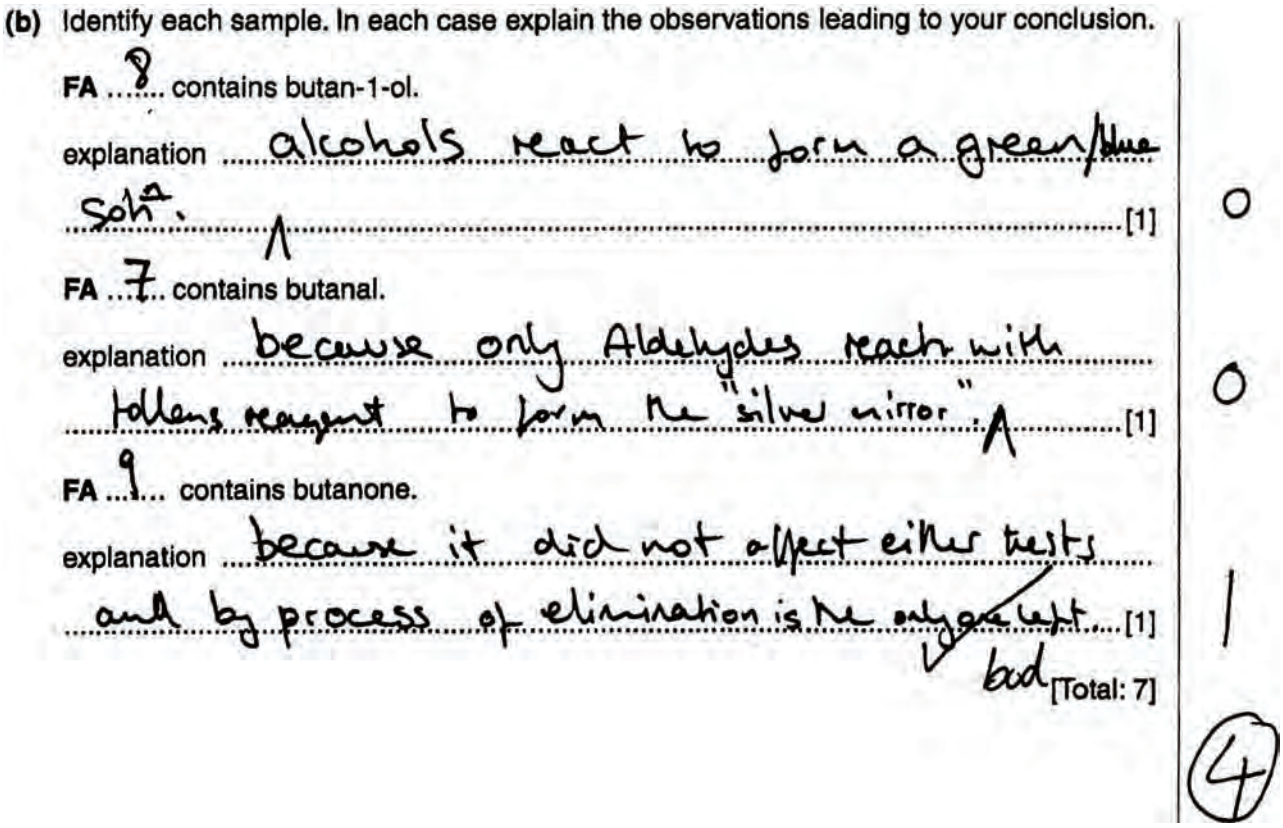
8. Into separate, clean, dry test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
9. Add a few drops of Tollens' reagent.
10. If no initial reaction is seen, warm the test-tube in the hot water-bath.

(a) Record all your observations in a single table.

FA	Acidified Potassium Dichromate	Tollen's Reagent
7	two clear layers to slightly yellow clear layers. X	grey deposit
8	two clear layers turns to dark green/dark blue sol.	N/A
9	two clear layers no orange layers.	N/A

[4]

3



(b) Identify each sample. In each case explain the observations leading to your conclusion.

FA 8 contains butan-1-ol.

explanation alcohols react to form a green/blue soln. [1] 0

FA 7 contains butanal.

explanation because only Aldehydes react with Tollens reagent to form the "silver mirror". [1] 0

FA 9 contains butanone.

explanation because it did not affect either tests and by process of elimination is the only one left [1] bad 1

[Total: 7] 4

Examiner Comment

(a) The candidate constructed a clear table for the results and so gained the first mark. Although the observation was correct for FA 7 and Tollen's reagent, it appears that there was no reaction between FA 7 and the acidified dichromate solution. Here the candidate's background knowledge let them down as clearly none of the possible compounds could give such a result. The other observations with acidified dichromate were correct although no detail was given about whether the change happened before or after warming. The use of N/A to indicate no reaction is not recommended when describing what happens on mixing each reagent with Tollen's solution.

(b) The assignments were correct but credit can only be given when they are supported by the correct observations. Hence, it is insufficient to say that FA 8 is an alcohol simply because it reacted with the acidified dichromate as this would also be true for the aldehyde. The assignment of FA 7 is not supported by the observation of no reaction with acidified dichromate in part **(a)**. Consequently, only the mark for assigning FA 9 to the ketone was awarded.

Example Candidate Response – Unclassified

Before starting question 3, half-fill a 250 cm^3 beaker with water and heat it with a Bunsen burner to between 50 °C and 70 °C. You will use this as a hot water-bath in this question. Turn off the Bunsen burner.

3 **FA 7**, **FA 8** and **FA 9** each contain a single compound which could be butan-1-ol, butanal or butanone. By reacting each of the compounds first with acidified potassium dichromate(VI) and then with Tollens' reagent you should identify each of the three samples.

Tollens' reagent must be prepared immediately before use. ✓

Method

Test with acidified potassium dichromate(VI) 1°, 2°-alcohol

1. Into separate test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
2. Add approximately 1 cm depth of dilute sulfuric acid to each test-tube.
3. Add a few drops of aqueous potassium dichromate(VI).
4. If no initial reaction is seen, warm the test-tube in the hot water-bath.

Preparation of Tollens' reagent

5. Pour aqueous silver nitrate into a boiling tube to a depth of approximately 2 cm.
6. Add approximately 0.5 cm depth of aqueous sodium hydroxide.
7. Add aqueous ammonia a little at a time with continuous shaking until the brown precipitate **just** dissolves. Be careful not to add an excess of aqueous ammonia.

Test with Tollens' reagent

8. Into separate, clean, dry test-tubes, to a depth of approximately 1 cm, pour **FA 7**, **FA 8** and **FA 9**.
9. Add a few drops of Tollens' reagent.
10. If no initial reaction is seen, warm the test-tube in the hot water-bath.

(a) Record all your observations in a single table. ✓ XXX

	Observation with Potassium dichromate(VI)	Observation with Tollens reagent
FA 7	Orange solution turns to a ~~blue~~ light blue solution.	~~It a black~~ clear colourless ~~precipitate~~ solution is formed X
FA 8	Orange solution stays ~~the~~ a ~~light~~ orange solution X	a clear solution remains (no change) ✓
FA 9	Orange solution stays an orange colour.	a ~~clear solution~~ reaction a silver mirror is produced X [4]

(b) Identify each sample. In each case explain the observations leading to your conclusion.

FA ...7... contains butan-1-ol.

explanation ...as it showed a positive test with the potassium dichromate showing a ~~primary alcohol~~ blue solution which is a primary alcohol ...[1]

FA ...9... contains butanal.

explanation ...because there is a positive test with tollens reagent (~~black precipitate~~) (silver mirror ...[1]

FA ...8... contains butanone.

explanation ...by process of elimination, it had no positive results for either tests ...[1]

[Total: 7]

0

0

0

1

Examiner Comment

(a) The first mark was awarded for presenting the results in a single table. The candidate did not gain any of the 3 remaining marks as one of the pair of observations for each unknown was incorrect. The candidate's background knowledge was clearly unsound as the observations for FA 9 could not be true for any of the possible unknowns.

(b) No marks could be awarded here as in each case the assignment does not match the observations made in the opening section.

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