AQA A-LEVEL CHEMISTRY

CHEMISTRY



EXAM QUESTION PACK

UNIT 4 OLD SPECIFICATION PAPERS

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AQA

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Centre number | | | | | | Candidate number | | | | |

Surname _____

Forename(s) _____

Candidate signature _____

A-level CHEMISTRY

Unit 4 Kinetics, Equilibria and Organic Chemistry

Tuesday 14 June 2016 Afternoon Time allowed: 1 hour 45 minutes

Materials

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information

- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice

- You are advised to spend about 80 minutes on **Section A** and about 25 minutes on **Section B**.

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Section A

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

1 Nitric acid (HNO_3) is a strong acid. Ethanoic acid (CH_3COOH) is a weak acid.

1 (a) Write an equation to show how ethanoic acid behaves as a weak acid in its reaction with water.

[1 mark]

1 (b) When pure ethanoic acid reacts with pure nitric acid, ethanoic acid acts as a base.

Write an equation for this reaction.

[1 mark]

1 (c) Two beakers, **A** and **B**, each contain 100.0 cm^3 of 0.0125 mol dm^{-3} nitric acid.

1 (c) (i) Calculate the pH of the solution formed after 50.0 cm^3 of distilled water are added to beaker **A**.
Give your answer to 2 decimal places.

[2 marks]

1 (c) (ii) Calculate the pH of the solution formed after 50.0 cm^3 of 0.0108 mol dm^{-3} aqueous sodium hydroxide are added to beaker **B**.
Give your answer to 2 decimal places.

[4 marks]

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1 (d) A third beaker, **C**, contains 100.0 cm^3 of 0.0125 mol dm^{-3} ethanoic acid.
The acid dissociation constant K_a for ethanoic acid has the value 1.74×10^{-5} mol dm^{-3} at 25 ºC.

1 (d) (i) Write an expression for K_a for ethanoic acid and use it to calculate the pH of the ethanoic acid solution in beaker **C**.
Show your working. Give your answer to 2 decimal places.

[4 marks]

K_a _____

_____

Calculation _____

_____

_____

_____

1 (d) (ii) Aqueous sodium hydroxide is added to beaker **C** until the pH of the solution becomes 4.84

Name the salt formed in the reaction of ethanoic acid with sodium hydroxide.

[1 mark]

_____

1 (d) (iii) Calculate the value of $\frac{[\text{salt}]}{[\text{ethanoic acid}]}$ in the solution with the pH of 4.84

[3 marks]

_____

_____

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1 (e) Explain why chloroethanoic acid is a stronger acid than ethanoic acid.

[2 marks]

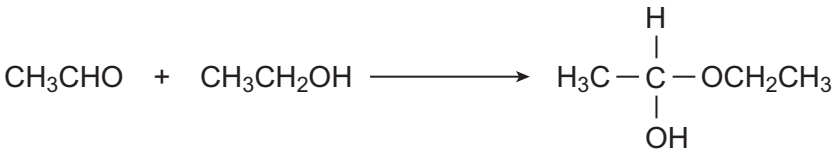
1 (f) Explain why data books do not usually contain values of K_a for strong acids.

[2 marks]

20

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2 Hemiacetals and acetals are compounds formed by the reaction of aldehydes with alcohols, such as the reaction of ethanal with ethanol.



a hemiacetal

2 (a) (i) Use your knowledge of carbonyl mechanisms to suggest the name of the mechanism of this reaction.

[1 mark]

2 (a) (ii) Outline how an ethanol molecule reacts with an ethanal molecule in the first step of this mechanism. Include two curly arrows to show the movement of electron pairs.

[2 marks]

2 (b) The reaction produces a racemic mixture of chiral molecules.

2 (b) (i) Explain the meaning of the term racemic mixture.

[1 mark]

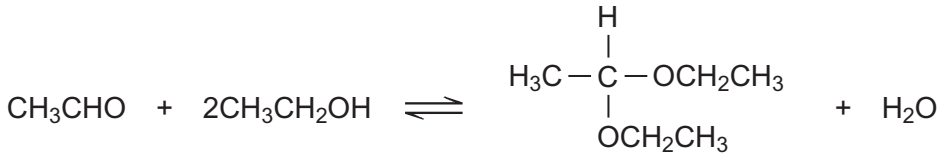
2 (b) (ii) State the relationship between two chiral molecules with the same structural formula.

[1 mark]

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2 (c) In the presence of an acid catalyst such as dry hydrogen chloride, ethanal reacts with an excess of ethanol to form an acetal.

The overall reaction of ethanal with an excess of ethanol forms an equilibrium mixture as shown. All reactants and products are liquids.



an acetal

A mixture of 0.75 mol of ethanal and 5.00 mol of ethanol was left to reach equilibrium in the presence of dry hydrogen chloride at a given temperature. The equilibrium mixture contained 0.42 mol of the acetal.

2 (c) (i) Calculate the amount, in moles, of ethanal and of ethanol in this equilibrium mixture.

[2 marks]

Amount of ethanal _____ mol

Amount of ethanol _____ mol

Space for working _____

_____

_____

_____

Do not write outside the box

2 (c) (ii) In a different experiment using the same reaction as in part **(c)**, an equilibrium mixture was established at a given temperature.
This mixture contained 0.58 mol of ethanal, 3.76 mol of ethanol, 0.37 mol of the acetal and 0.65 mol of water in a total volume of 310 cm^3.

Write an expression for the equilibrium constant K_c for this reaction.
Calculate a value for K_c at this temperature. Give units with your answer.

[4 marks]

K_c _____

_____

Calculation _____

_____

_____

_____

_____

_____

_____

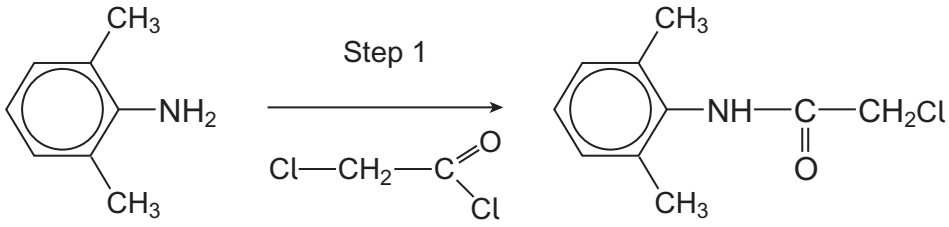
2 (d) Draw the structure of the acetal ($C_4H_8O_2$) formed by the reaction of ethanal with ethane-1,2-diol.

[1 mark]

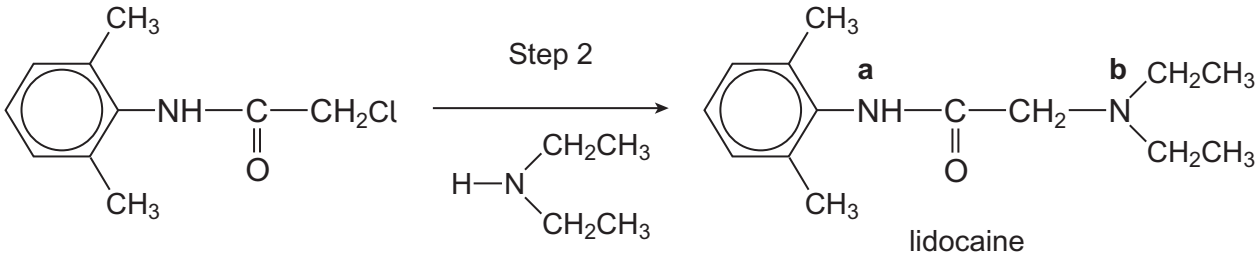
12

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3 Lidocaine is a local anaesthetic used in dentistry and in minor surgical operations. The synthesis of lidocaine in 2 steps from 2,6-dimethylphenylamine is shown.



X



lidocaine

Y

3 (a) (i) Give the IUPAC name of reagent **X** in Step 1.

[1 mark]

3 (a) (ii) Outline a mechanism for Step 1.
In your answer, use RNH_2 to represent 2,6-dimethylphenylamine.

[4 marks]

3 (b) Name the mechanism for Step 2.

[1 mark]

Do not write outside the box

3 (c) Which of these is the total number of peaks in the ^{13}C n.m.r spectrum of lidocaine?

Tick (✓) one box.

[1 mark]

8 ☐ 9 ☐ 11 ☐ 12 ☐

3 (d) Calculate the percentage by mass of hydrogen in a molecule of lidocaine.

[2 marks]

3 (e) Give the name, including the classification, of the functional group that contains the nitrogen atom labelled **b**.

[1 mark]

3 (f) Lidocaine is used medically as the salt lidocaine hydrochloride.

3 (f) (i) Suggest which one of the nitrogen atoms labelled **a** or **b** is protonated in lidocaine hydrochloride. Explain your answer.

[3 marks]

Nitrogen atom protonated _____

Explanation _____

3 (f) (ii) Suggest why lidocaine hydrochloride is used medically in preference to lidocaine. Explain your answer.

[2 marks]

15

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4 Compound **X** ($ClCH_2COCl$) is used as a reagent in organic synthesis.

4 (a) The mass spectrum of **X** contains several molecular ion peaks.

4 (a) (i) Chlorine exists as the isotopes ^{35}Cl and ^{37}Cl in a 3:1 ratio.

Calculate the *m*/*z* value of the most abundant molecular ion peak in the mass spectrum of **X**.

[1 mark]

4 (a) (ii) The most abundant fragment ion in the mass spectrum of **X** has *m*/*z* = 77.

Draw the **displayed** formula of this fragment ion.

[1 mark]

4 (a) (iii) A molecular ion of **X** that contains one ^{35}Cl atom and one ^{37}Cl atom undergoes fragmentation to form an ion with *m*/*z* = 65 and one other species.

Write an equation for this fragmentation. Show which isotope of chlorine is present in each product species.

[2 marks]

4 (b) One important reaction of **X** is in the preparation of compound **P** as shown.



X **P**

Do not write outside the box

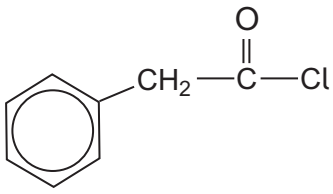
4 (b) (i) Draw the structure of the electrophile formed by the reaction of **X** with $AlCl_3$

[1 mark]

4 (b) (ii) Outline the mechanism for the reaction of the electrophile from part **(b)(i)** with benzene in the preparation of **P**.

[3 marks]

4 (c) Compound **Q** is an alternative product that could be formed when **X** reacts with benzene.



Q

Describe how you could distinguish between **P** and **Q** by a test-tube reaction.
Give the reagent used and the observation with each compound.

[3 marks]

Reagent _____

Observation with **P** _____

Observation with **Q** _____

Do not write outside the box

4 (d) **X** is also used to make the compound $HOCH_2COOH$. This compound is polymerised to form the polymer known as PGA. PGA is used in surgical sutures (stitches).

4 (d) (i) Draw the repeating unit of PGA.

[1 mark]

4 (d) (ii) Production of PGA occurs via a cyclic compound. Two $HOCH_2COOH$ molecules react together to form the cyclic compound and two molecules of water.

Draw the structure of this cyclic compound.

[1 mark]

4 (e) Poly(propene) is also used in surgical sutures.

4 (e) (i) Draw the repeating unit of poly(propene).

[1 mark]

Do not write outside the box

4 (e) (ii) Suggest an advantage of surgical sutures made from PGA rather than from poly(propene).
Explain your answer.

[2 marks]

_____

_____

_____

_____

16

Turn over for the next question

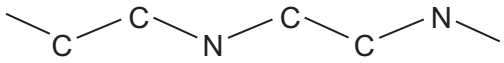
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5 Proteins contain sequences of amino acids joined by peptide links.
Amino acid chains (polypeptides) are attracted to each other by hydrogen bonding.

5 (a) (i) A section of a protein is formed from one molecule of each of the amino acids glycine (H_2NCH_2COOH) and alanine ($H_2NCH(CH_3)COOH$).

Add bonds and atoms to the diagram to complete a structural formula for this section of the protein.

[2 marks]

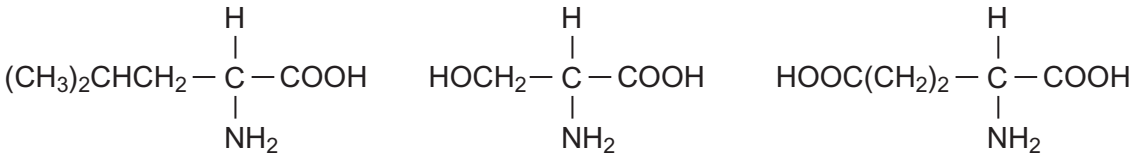


5 (a) (ii) Draw a diagram to show how an amino acid chain can form a hydrogen bond with another amino acid chain.
Your diagram need only show the relevant atoms from one amino acid in each chain.

[1 mark]

Do not write outside the box

5 (b) Leucine, serine and glutamic acid are naturally-occurring amino acids.



leucine serine glutamic acid

5 (b) (i) Give the IUPAC name of leucine.

[1 mark]

5 (b) (ii) Draw the structure of the zwitterion of serine.

[1 mark]

5 (b) (iii) Draw the structure of the ester formed by two molecules of serine.

[1 mark]

5 (b) (iv) Draw the structure of the species formed by glutamic acid at low pH.

[1 mark]

7

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6 The initial rate of the reaction between gases **D** and **E** was measured in a series of experiments at a constant temperature. The results are shown in **Table 1**.

Table 1

Expt	Initial [D] / mol dm^{-3}	Initial [E] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.25×10^{-2}	5.81×10^{-1}	1.16×10^{-2}
2	1.88×10^{-2}	8.73×10^{-1}	3.92×10^{-2}
3	1.88×10^{-2}	1.75	1.57×10^{-1}

6 (a) Deduce the order of reaction with respect to **D** and the order with respect to **E**.

[2 marks]

Order with respect to **D** _____

Order with respect to **E** _____

Space for working _____

6 (b) Suggest why initial rates of reaction are used to determine these orders rather than rates of reaction at other times during the experiments.

[1 mark]

6 (c) State how the initial rate is obtained from a graph of the concentration of the product against time.

[2 marks]

5

Turn over ▶

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7 The reaction between propanone and iodine in the presence of hydrochloric acid was studied at a constant temperature.

$$CH_3COCH_3 + I_2 \longrightarrow CH_3COCH_2I + HI$$

The following rate equation was deduced.

$$\text{rate} = k\,[CH_3COCH_3][H^+]$$

7 (a) Suggest why the order with respect to iodine is zero.

[1 mark]

7 (b) In an experiment the initial concentrations of propanone, iodine and hydrochloric acid were as shown in **Table 2**. The initial rate of reaction in this experiment was 8.64×10^{-7} mol dm^{-3} s^{-1}.

Table 2

	Initial concentration / mol dm^{-3}
CH_3COCH_3	5.82×10^{-2}
I_2	1.78×10^{-3}
H^+	4.76×10^{-1}

Use the data in **Table 2** and the rate equation to calculate a value for the rate constant at this temperature.
Give units with your answer.

[2 marks]

Do not write outside the box

7 (c) A series of experiments was carried out using concentrations of propanone approximately 100 times the concentrations of iodine and hydrochloric acid.

Suggest the rate equation under these conditions.
Explain your answer.

[2 marks]

5

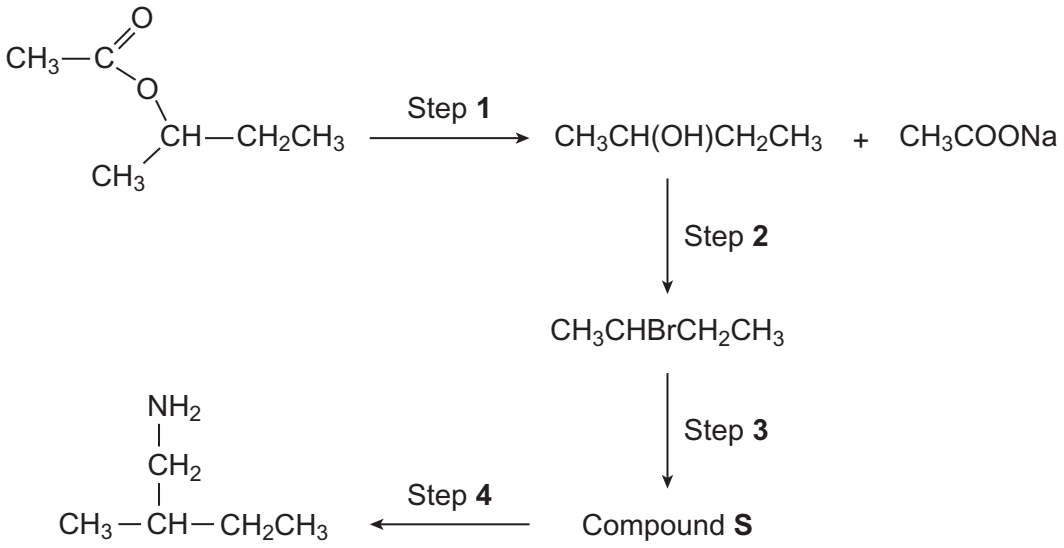
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Section B

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

8 A four-step synthesis of compound **T** is shown.



Compound **T**

8 (a) Give the reagent and conditions for Step **1**.
State how you could obtain a sample of the alcohol from the reaction mixture formed in Step **1**.

[3 marks]

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8 (b) Draw the structure of compound **S**.
For each of Steps **3** and **4**, give a reagent and one condition, other than heat.

[5 marks]

8

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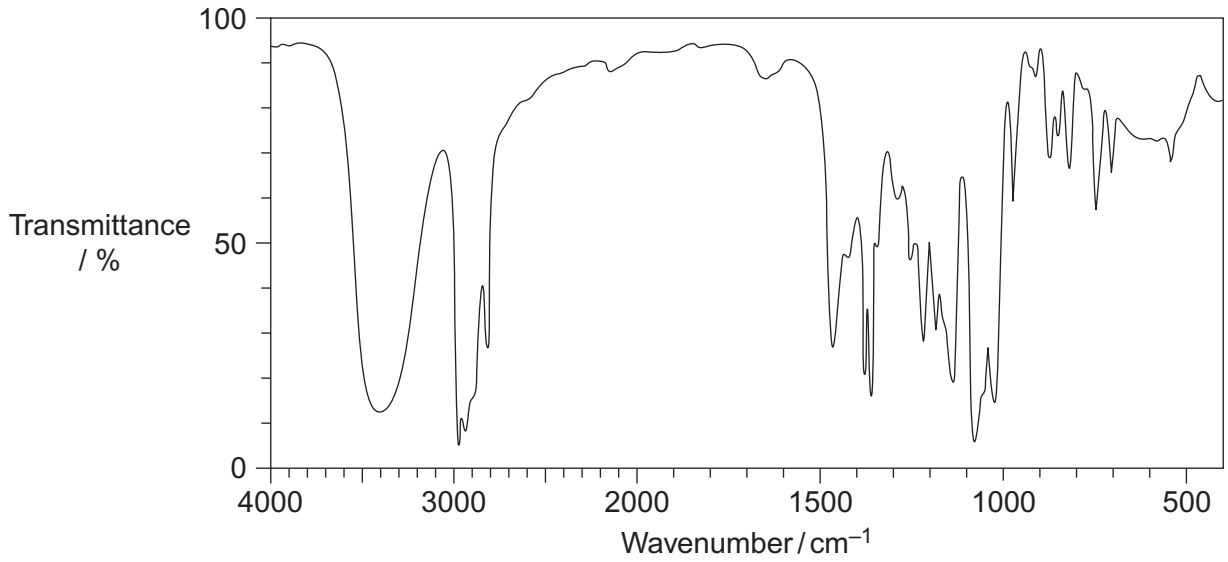
9 Compound **R** contains 61.0% carbon and 11.9% hydrogen by mass. The remainder is oxygen.
The mass spectrum of **R** contains a molecular ion peak at $m/z = 118$

9 (a) Use these data to show that the molecular formula of **R** is $C_6H_{14}O_2$

[3 marks]

9 (b) The infrared spectrum of **R** ($C_6H_{14}O_2$) is shown in **Figure 1**.

Figure 1



The proton n.m.r. spectrum of **R** contains five peaks. The chemical shift values, integration ratios and splitting patterns of these peaks are given in **Table 3**.

Table 3

Chemical shift/ppm	3.8	3.2	3.1	1.4	1.1
Integration ratio	2	3	1	2	6
Splitting patterns	triplet	singlet	singlet	triplet	singlet

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When **R** is warmed with acidified potassium dichromate(VI) a green solution is formed.

Use **Table A** and **Table B** on the data sheet and all of the data provided in the question to deduce the structure of **R**.
In your answer, explain how you have used the data provided in the question.

[9 marks]

12

END OF QUESTIONS

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AQA Qualifications

A-LEVEL

Chemistry

CHEM4 Kinetic, Equilibria and Organic Chemistry
Mark scheme

2420
June 2016

Version: 1.0 Final

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Question	Answers	Mark	Additional Comments/Guidance	ID detail
1a	$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ OR $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	1	Must show ⇌ allow CH_3CO_2H, $CH_3CO_2^-$ Ignore state symbols	
1b	$CH_3COOH + \underline{HNO_3} \rightarrow CH_3COOH_2^+ + NO_3^-$	1	Ignore ⇌ Allow CH_3CO_2H, $CH_3CO_2H_2^+$, $CH_3C^+(OH)_2$	

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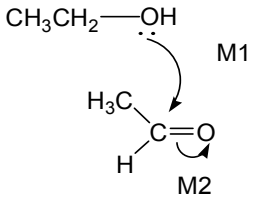
1c(i) marked with 1c(ii)	(new $[HNO_3] = [H^+] = \frac{100}{150} \times 0.0125$) M1 $[H^+] = 8.3(3) \times 10^{-3}$ (mol dm^{-3}) M2 pH = –log M1 OR 2.08	 1 1	OR new $[HNO_3] = \frac{\text{mol } HNO_3}{\text{total vol}} = \frac{1.25 \times 10^{-3}}{150 \times 10^{-3}}$ Must be 2 dp Allow correct pH conseq to their $[H^+]$ concentration	
1c(ii) marked with 1c(i)	M1 mol NaOH (= $50 \times 10^{-3} \times 0.0108$) = 5.40×10^{-4} M2 Subtraction of M1 from moles of HNO_3 (1.25×10^{-3} or conseq from 1c(i)) Excess mol $H^+ = 7.10 \times 10^{-4}$ M3 $[H^+] = \frac{M2}{150 \times 10^{-3}}$ OR $\frac{7.10 \times 10^{-4}}{150 \times 10^{-3}} = 4.73 \times 10^{-3}$ M4 pH = –log M3 OR 2.32	1 1 1 1	 M2 allow ecf for subtraction of mol **If no subtraction, no further marks** M3 **if no use of volume, no further marks** (pH=3.15) If incorrect volume used, can score M4 M4 Allow 2.33 Must be 2 dp	

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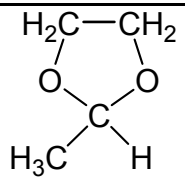
1d(i)	M1 $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ M2 $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or with HA M3 $[H^+] = [\sqrt{(1.74 \times 10^{-5} \times 0.0125)}] = 4.66 \times 10^{-4}$ M4 pH = 3.33	1 1 1 1	penalise ( ) once here Not [H+][A-] / [HA] if K_a expression wrong – Allow correct pH conseq to their $[H^+]$ concentration M4 only mark for answer Must be 2 dp Allow correct pH conseq to their $[H^+]$ concentration (pH = 3.83 can score M1, M2 and M4)	
G 1d(ii)	<u>sodium ethanoate</u>	1	Ignore formula allow sodium acetate	
1d(iii)	M1 $[H^+] = 1.45 \times 10^{-5}$ M2 $\frac{[salt]}{[acid]}$ (OR $\frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{Ka}{[H^+]}$)= $\frac{1.74 \times 10^{-5}}{1.45 \times 10^{-5}}$ M3 1.2(0)	1 1 1	Accept 1.445×10^{-5} or 1.4×10^{-5} If M1 incorrect CE=0 Inclusion of 0.0125 in calculation can only score M1 ignore units 1.4×10^{-5} gives 1.24	
1e	M1 (Electronegative) chlorine withdraws electrons M2 Stabilises/reduces charge on COO- **OR** weakens <u>O-H</u> bond **OR** makes <u>O-H</u> more polar	1 1	Allow Cl has negative inductive effect Ignore chloroethanoic acid dissociates more readily Mark independently	

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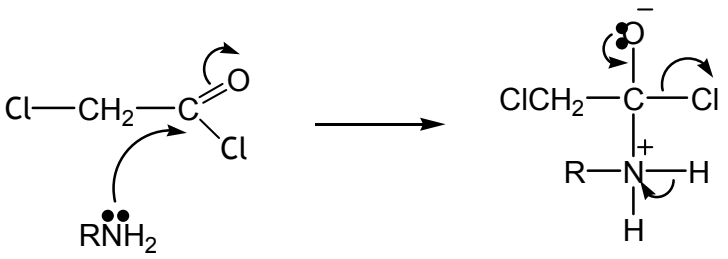
1f	M1	Strong acids (almost) completely dissociated/ionised **OR** not an equilibrium **OR** equilibrium lies <u>far</u> to the right	1 1	Cannot have $\underline{K_a}$ value for a reaction not in equilibrium scores both marks	
	M2	$\underline{K_a}$ value for strong acids tends to infinity/is very large **OR** can't divide by zero in $\underline{K_a}$			
Total			**20**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
G 2a(i)	<u>Nucleophilic addition</u>	1	any extra loses the mark allow minor spelling errors e.g. nucleophyllic	
2a(ii)		1 1	M1 for arrow from lone pair on oxygen in ethanol to C of C=O (or to space half way between O and C) M2 for arrow from C=O bond to oxygen in ethanal Do not allow M2 as first step without nucleophilic attack, but can allow M1 for attack on C+ produced + rather than δ+ on C=O loses M2 Ignore any further steps Mark independently	
2b(i)	<u>Equal</u> mixture of enantiomers/optical isomers OWTTE	1		
2b(ii)	(non-superimposable) mirror images	1	Ignore rotates light in opposite directions Ignore stereoisomers	

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2c(i)	Ethan**al** 0.33 Ethan**ol** 4.16	1 1	 Allow 4.2 for ethanol	
2c(ii)	$K_c = \frac{[acetal][H_2O]}{[CH_3CHO][CH_3CH_2OH]^2}$ or with names $\frac{(0.37/0.31)(0.65/0.31)}{(0.58/0.31)(3.76/0.31)^2}$ **OR** $\frac{(0.37)(0.65)}{(0.58)(3.76)^2} \times 0.31$ 9.1×10^{-3} $mol^{-1}dm^3$	M1 M2 M3 M4	Ignore slips in acetal structure or formula $C_6H_{14}O_2$ If K_c wrong, allow M4 only for units conseq to their K_c If volume omitted (gives 2.93×10^{-2}) may only score M1 and M4 If volume used = 310 cm^3 allow M2 then award M3 for 9.08 – 9.23 only and M4 for $mol^{-1}cm^3$ only Treat error in converting 310 cm^3 to dm^3 as AE Allow range 9.08×10^{-3} – 9.23×10^{-3} Not $moles^{-1}dm^3$	
2d		1		
Total		**12**		

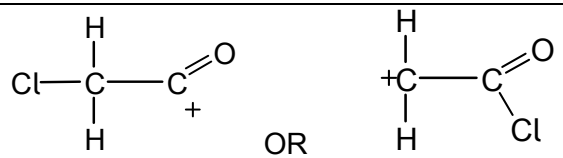
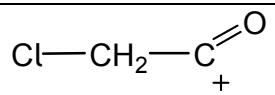
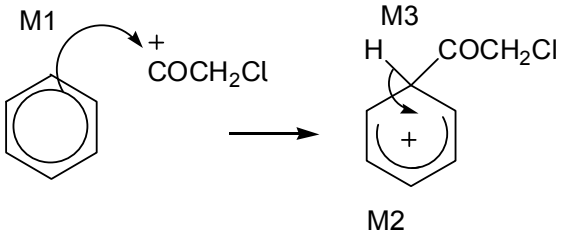
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Question	Answers	Mark	Additional Comments/Guidance	
3a(i)	(2-)chloroethan (-1-) oyl chloride	1	2 not required but penalise 1- or other numbers at start. Ignore 1 in ethanoyl Ignore hyphens, commas, spaces	
3a(ii)		4	M1 for arrow from lp on N to C (or to space half way between N and C) If full amine drawn, ignore slips except in $-NH_2$ M2 for arrow from C=O bond to O Not score M2 as an independent first step, but can allow M1 for attack on C+ produced If Cl lost at this stage, Max 1 for M1 M3 for structure of ion including 2 charges M4 for 3 arrows and lp on O - may be scored in two steps Ignore use of RNH_2 to remove H+ in M4, but penalise use of Cl^-	
3b **G**	nucleophilic substitution	1	allow minor spelling errors e.g. nucleophyllic	
3c **A**	9	1		

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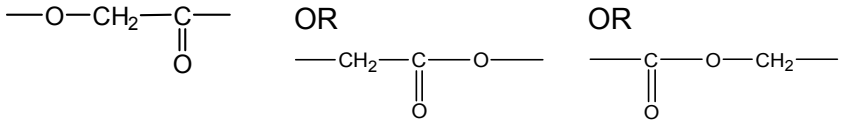
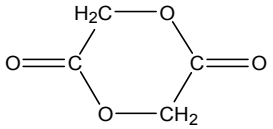
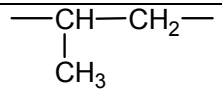
3d	M_r = 234(.0) % H = 9.4(0)	1 1	9.4 scores 2 marks M2 = $\frac{22}{M1} \times 100$ If M_r = 234 not shown, can score M1 if their answer × 234 = their no of H	
3e	tertiary amine OR 3° amine OR III° amine	1	Ignore N- substituted	
3f(i)	If ***a*** given: CE=0, can only score if answer given is **b** M1 lp on N^{b} or on **b** M2 alkyl groups donate electron density or positive inductive effect or electron donating groups attached M3 (lp on N^{b}) more available or protonated amine stabilised or better lp donor/H^+ acceptor Ignore reference to nucleophiles	 1 1 1	NOTE – there is NO mark for **b** alone Alternatives: M1 lp on N^{a} or on **a** M2 lp or electrons (on N^{a}) delocalised into ring /towards O in C=O M3 (lp on N^{a}) less available (to bond to H^+/accept proton)	
3f(ii)	Salt is ionic (more) soluble (in blood/body fluids/water)	1 1	Independent marks	
Total		**15**		

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Question	Answers	Mark	Additional Comments/Guidance	
4a(i)	112(.0)	1	Not 112.5 ignore working	
4a(ii)	 OR	1	<u>Must be displayed and show + on relevant carbon</u> Penalise extra dots or [ ]$^+$ penalise ^{37}Cl	
4a(iii)	$[ClCH_2COCl]^{+\cdot} \rightarrow [^{35}ClCH_2]^{\cdot} + [CO^{37}Cl]^+$	 1 1	Allow without brackets M1 for molecular ion M2 for both fragments with mass numbers Allow dot or + anywhere on formula	
4b(i)		1	Allow $[ClCH_2CO]^+$	
4b(ii)		1 1 1	M1 Arrow from inside hexagon to C or + on C on correct electrophile M2 Structure of intermediate • horseshoe centred on C1; • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6) M3 Arrow from bond to H into ring • Allow M3 arrow independent of M2 structure • + on H in intermediate loses M2 not M3 • Ignore Cl^- removing H^+ (different from Qu3a(ii))	

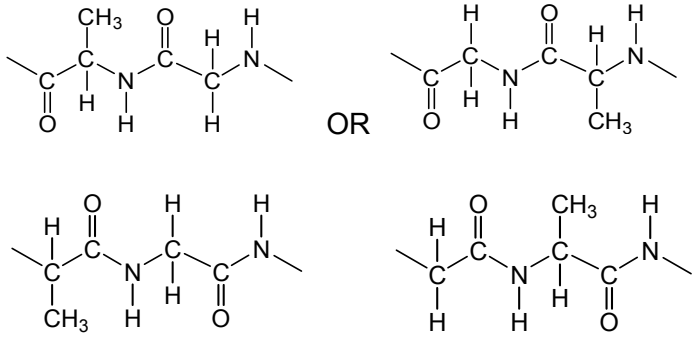
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4c	reagent	water	(Aqueous) silver nitrate	NaOH followed by acidified silver nitrate	(Water +) named indicator	1	Named alcohol	Na_2CO_3 or $NaHCO_3$	ammonia	
	P	no reaction	no reaction (or slow formation of ppt)	no reaction (or slow formation of ppt)	No colour change	1	NVC	NVC	no reaction	Do NOT award No observation
	Q	Steamy /misty/ white fumes	white precipitate (immediately formed)	white precipitate (immediately formed)	Indicator turns to correct acid colour	1	Fruity or sweet smell or misty fumes	Fizzing or effervescence (not just gas produced)	white smoke	

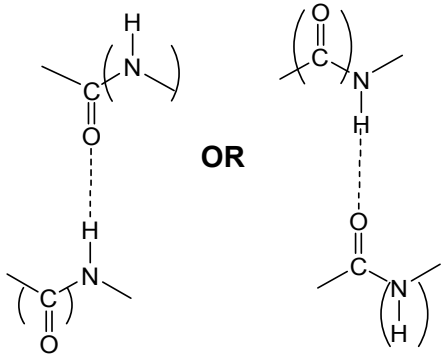
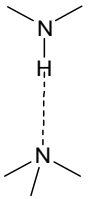
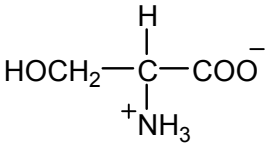
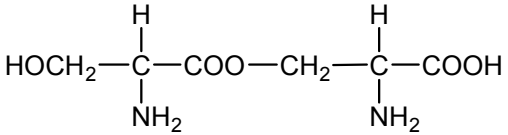
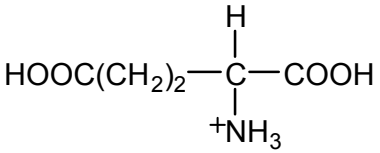
4d(i)		1	One unit only must have trailing bonds ignore n and brackets allow —O—CH_2—CO—	
4d(ii)		1	Allow CO for C=O	
4e(i)		1	One unit only must have trailing bonds ignore n and brackets	

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4e(ii)	PGA sutures react/dissolve/break down/are biodegradable/ are hydrolysed / attacked by water or nucleophiles /no need to remove (Ester links have) <u>polar bonds</u>	1 1	OR Polypropene not biodegradeable/ not hydrolysed / not attacked by water/nucleophiles polypropene contains <u>non-polar bonds</u> ignore intermolecular forces	
Total		**16**		

Question	Answers	Mark	Additional Comments/Guidance	ID details
5a(i)	 OR	2	Only one molecule of each used M1 for 2 amide links M2 CH_2 and $CH(CH_3)$ Allow 1 mark after one error Dipeptide max 1 Treat both trailing bonds missing as one error Ignore *n*	

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5a(ii)	 **OR**	1	No need to show lp The covalent bond and the hydrogen bond either side of the H must be linear. Allow 	
5b(i)	2-amino-4-methylpentan(-1-)oic acid	1	Ignore hyphens, commas, spaces	
5b(ii)		1	Allow $-NH_3^+$	
5b(iii)		1		
5b(iv)		1	Allow $-NH_3^+$	
Total				**7**

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Question	Answers	Mark	Additional Comments/Guidance	ID details
G 6a	Order wrt **D** = 1 OR first OR [D] OR [D]^1 Order wrt **E** = 2 OR second OR [E]^2	1 1	Ignore working	
6b	(At time zero/start) the concentrations are known	1		
6c	M1 (Calculate) gradient (of tangent/curve/graph) M2 at t=0 or at start of graph/curve	1 1	Allow description of gradient calculation: Change in conc / time M2 scored only if M1 gained Ignore the word initial	
Total		**5**		

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Question	Answers	Mark	Additional Comments/Guidance	ID details
7a	Iodine is not involved in (or before) the rate determining / slow(est) / limiting step (in the mechanism)	1	Ignore, iodine does not appear in the rate equation or iodine concentration does not affect the rate	
7b	$k = \left(\frac{8.64\times10^{-7}}{(5.82\times10^{-2})\times(4.76\times10^{-1})}\right) = 3.1(2)\times10^{-5}$ $\underline{mol^{-1}\ dm^{+3}\ s^{-1}}$	1 1	Mark for answer Mark units separately, i.e. only these units but can be in any order	
7c	rate = k $[H^+]$ (large excess of propanone) so $\underline{[CH_3COCH_3]\ is}$ (effectively) $\underline{constant}$	1 1	If wrong or missing CE = 0	
Total		**5**		

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Question	Answers	Mark	Additional Comments/Guidance	ID details
8a	M1 NaOH	1	Only score M2 if M1 gained, but mark on from hydroxide. Mention of acid loses M1 & M2	
	M2 Aqueous/(warm)	1	ignore alcoholic / conc / dil.	
	M3 (Fractional) distillation or described	1	Not just evaporation; not reflux Allow chromatography	
8b	M1 S is $CH_3CH(CN)CH_2CH_3$	1	Allow without brackets	
	Step 3			
	M2 KCN (mark on from CN^-)	1	Not HCN, not KCN with acid	
	M3 Alcoholic (/aqueous)	1	Allow ethanolic can only score M3 if M2 gained	
	Step 4			
	M4 H_2 / $LiAlH_4$ / Na	1	can only score M5 if M4 gained	
	M5 Ni or Pt or Pd / Ethoxyethane or ether / ethanol	1	NOT $NaBH_4$ OR Sn/HCl penalise other extras as list $LiAlH_4$ with acid loses both M4 and M5 Ignore 'followed by acid' ignore pressure or temperature	
Total		**8**		

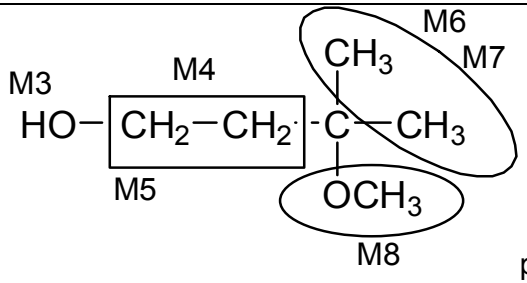
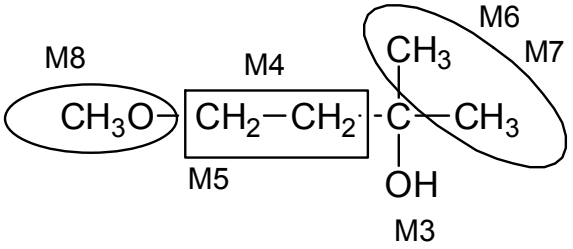
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Question	Answers	Mark	Additional Comments/Guidance	ID details
9a	Method 1 M1 % O = 27.1 $\frac{61.0}{12.0}$ $\frac{11.9}{1.0}$ $\frac{27.1}{16.0}$ = 5.08 = 11.9 = 1.69 M2 3 7 1 M3 C_3H_7O = 59 which is half of M_r so MF = 2EF **OR** Method 2 M1 61% of 118 = 72.0 and 11.9 % of 118 = 14.0 M2 72 + 14 = 86 so oxygen = 32 out of 118 OR 27.1% of 118 = 32.0 M3 $\frac{72.0}{12.0}$ $\frac{14.0}{1.0}$ $\frac{32.0}{16.0}$ = 6 = 14 = 2	3	Method 3 Alternative using given molecular formula M1 C = $\frac{12\times6}{118}\times 100$ = 61.0% M2 H = $\frac{14\times1}{118}\times 100$ = 11.9% M3 O = $\frac{16\times2}{118}\times 100$ = 27.1%	

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Question	Additional Comments/Guidance	
9b	For this question, marks can be awarded either for a description of how the structure is derived or from the given structure itself. The maximum mark to be awarded is nine from the ten marks listed. Marks fall into three sections: • Infrared evidence : two marks are available for use of the infrared evidence, (M1 and M10) • Chemical evidence: one mark is available for use of the chemical evidence (M2) • N.m.r. evidence: six marks are available for use of the n.m.r. evidence (M3 – M8 inclusive) plus one mark (M9) for a completely correct structure. **Suggested procedure for marking** First look at the infrared spectrum: marks M1 and M10 may be scored there or in the written answer. Then look for use of the acidified potassium dichromate(VI) evidence, (M2). Then look at the final structure: this may lead to the award of marks M3 to M9 as shown on the structures below. Beware contradictions, e.g. using the chemical evidence they may state that **R** is a primary or secondary alcohol but then draw a tertiary alcohol. This will lose M2 but may score M3. The written 'evidence' frequently simply contains extracts from the Table **B** on the Data Sheet and, if only this is given, is unlikely to score many marks.	

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Q9b	Described	Or drawn
M1	infrared peak/absorbance at 3400 (cm^{-1}) = O-H alcohol (reference to ir spectrum needed)	Note: please check the spectrum If peak at 3000 (cm^{-1}) is identified as acid then cannot score M1 (contradiction)
M10	**Either** No peak between 1680-1750 (cm^{-1}) so no C=O or not aldehyde/acid **OR** peak at 1000-1300 (cm^{-1}) so C–O present	Apply list principle to IR analysis for M10
M2	(Acidified potassium dichromate(VI) turns green) so primary alcohol or secondary alcohol or not tertiary alcohol	Ignore aldehyde here Lose M2 if just tertiary alcohol in structure
M3	δ = 3.1 singlet or integration =1 is O-H	Award M3 if structure has 1 O-H group only (can be primary, secondary or tertiary). Lose M3 if more than one OH group shown
M4	two triplets at 1.4 & 3.8 = $-CH_2-CH_2-$	Allow $-CH_2-CH_2-CH_2-$
M5	δ = 3.8 means CH_2 attached to O (in ether NOT ester) δ = 1.4 means CH_2 attached to C (but not to C=O)	Allow $O-CH_2-CH_2-CH_2-C$
M6	δ = 1.1 (singlet) integration 6 = 2 × equivalent CH_3 on same C	$-C(CH_3)_2-$
M7	δ = 1.1 singlet so no H attached to $-C(CH_3)_2-$	$R-C(CH_3)_2-R$
M8	δ = 3.2 singlet integration 3 = $-OCH_3$	$-OCH_3$
M9	For completely correct	If no structure given then Max 8
R is  plus M9		This close alternative  would not score M9, but could score up to 8 marks

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2015

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 10 June 2015 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

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Section A

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

1 Gases **A** and **B** react as shown in the following equation.

$$2\mathbf{A}(g) + \mathbf{B}(g) \longrightarrow \mathbf{C}(g) + \mathbf{D}(g)$$

The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{A}]^2$$

An incomplete table of data for the reaction between **A** and **B** is shown in **Table 1**.

Table 1

Experiment	Initial [A] / mol dm^{-3}	Initial [B] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.2×10^{-3}	2.8×10^{-3}	3.3×10^{-5}
2	7.9×10^{-3}	2.8×10^{-3}	
3		5.6×10^{-3}	1.8×10^{-4}

1 (a) Use the data from Experiment **1** to calculate a value for the rate constant, *k*, at this temperature.
Deduce the units of *k*.

[3 marks]

Calculation .....

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Units .....

.....

Do not write outside the box

1 (b) Use your value of *k* from Question **1(a)** to complete **Table 1** for the reaction between **A** and **B**.
(If you have been unable to calculate an answer for Question **1 (a)**, you may assume a value of 2.3 This is **not** the correct answer.)

[2 marks]

1 (c) The reaction is zero order with respect to **B**.

State the significance of this zero order for the mechanism of the reaction.

[1 mark]

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6

Turn over for the next question

Do not write outside the box

2 Sulfur dioxide reacts with oxygen to form sulfur trioxide according to the equation

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

2 (a) Write an expression for the equilibrium constant, K_c, for this reaction and deduce its units.

[2 marks]

K_c .....

.....

Units .....

.....

2 (b) Samples of sulfur dioxide, oxygen and sulfur trioxide were added to a flask of volume 1.40 dm^3 and allowed to reach equilibrium at a given temperature.
The flask contained 0.0550 mol of sulfur dioxide and 0.0720 mol of sulfur trioxide at equilibrium.
K_c has the numerical value of 27.9 under these conditions.

Calculate the amount, in moles, of oxygen gas in this equilibrium mixture.

[3 marks]

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Do not write outside the box

2 (c) The experiment in Question **2 (b)** was repeated with the same amounts of sulfur dioxide, oxygen and sulfur trioxide at the same temperature but in a smaller flask.
The mixture was allowed to reach equilibrium.

2 (c) (i) State the effect, if any, of using a smaller flask on the value of K_c

[1 mark]

.....

2 (c) (ii) State the effect, if any, of using a smaller flask on the amount of sulfur trioxide at equilibrium.
Explain your answer.

[3 marks]

Effect .....

Explanation .....

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9

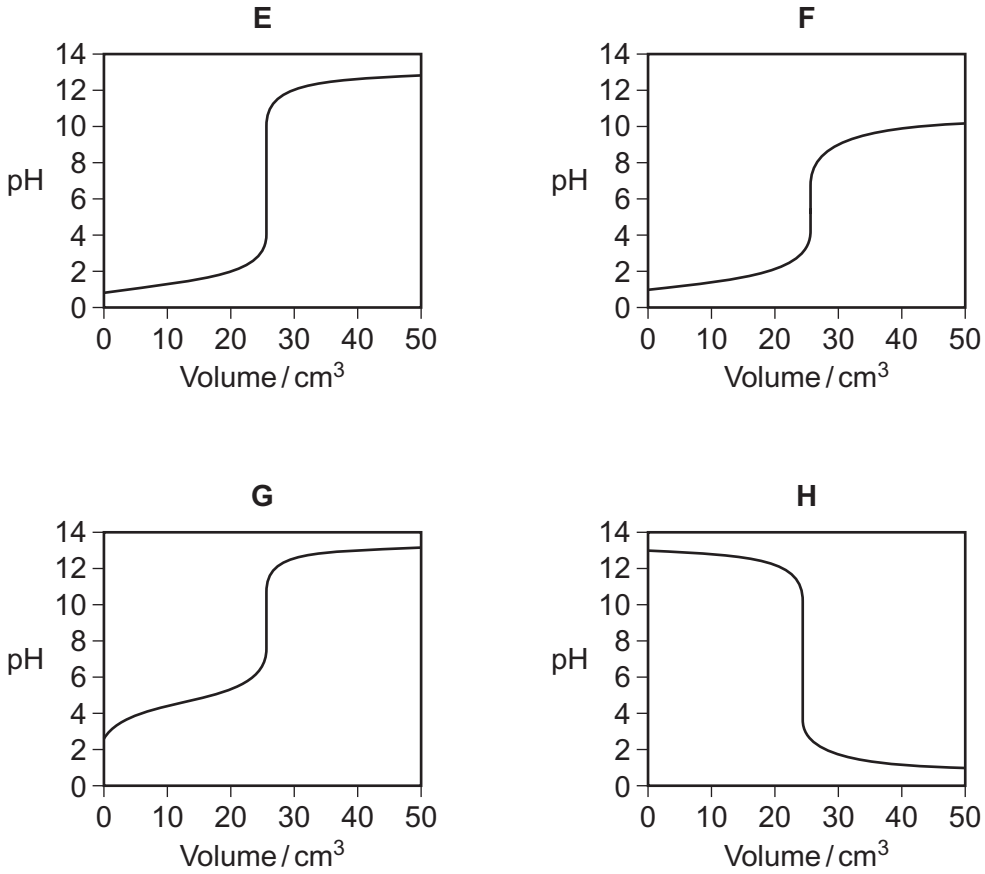
Turn over for the next question

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3 Titration curves, labelled **E**, **F**, **G** and **H**, for combinations of different aqueous solutions of acids and bases are shown in **Figure 1**.

All solutions have concentrations of 0.1 mol dm^{-3}.

Figure 1



3 (a) In this part of the question, write the appropriate letter in each box.

From the curves **E**, **F**, **G** and **H**, choose the curve produced by the addition of

3 (a) (i) sodium hydroxide to 25 cm^3 of ethanoic acid

[1 mark]

3 (a) (ii) ammonia to 25 cm^3 hydrobromic acid

[1 mark]

3 (a) (iii) hydrochloric acid to 25 cm^3 of potassium hydroxide

[1 mark]

Do not write outside the box

3 (b) **Table 2** shows information about some acid-base indicators.

Table 2

Indicator	pH range	Lower pH colour	Higher pH colour
pentamethoxy red	1.2–3.2	violet	colourless
naphthyl red	3.7–5.0	red	yellow
4-nitrophenol	5.6–7.0	colourless	yellow
cresol purple	7.6–9.2	yellow	purple

3 (b) (i) Which indicator in **Table 2** could be used for the titration that produces curve **E** but **not** for the titration that produces curve **F**?

[1 mark]

Tick (✓) **one** box.

pentamethoxy red ☐

naphthyl red ☐

4-nitrophenol ☐

cresol purple ☐

3 (b) (ii) Give the colour change at the end point of the titration that produces curve **H** when naphthyl red is used as the indicator.

[1 mark]

.....

3 (b) (iii) A beaker contains 25 cm^3 of a buffer solution at pH = 6.0
Two drops of each of the four indicators in **Table 2** are added to this solution.

State the colour of the mixture of indicators in this buffer solution.
You should assume that the indicators do **not** react with each other.

[1 mark]

.....

6

Do not write outside the box

4 Water dissociates slightly according to the equation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

The ionic product of water, K_w, is given by the expression

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

K_w varies with temperature as shown in **Table 3**.

Table 3

Temperature / ºC	K_w / mol^2 dm^{-6}
25	1.00×10^{-14}
50	5.48×10^{-14}

4 (a) Explain why the expression for K_w does **not** include the concentration of water.

[2 marks]

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4 (b) Explain why the value of K_w increases as the temperature increases.

[2 marks]

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Do not write outside the box

4 (c) Calculate the pH of pure water at 50 °C.
Give your answer to 2 decimal places.

[3 marks]

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4 (d) Calculate the pH of 0.12 mol dm^{-3} aqueous NaOH at 50 °C.
Give your answer to 2 decimal places.

[3 marks]

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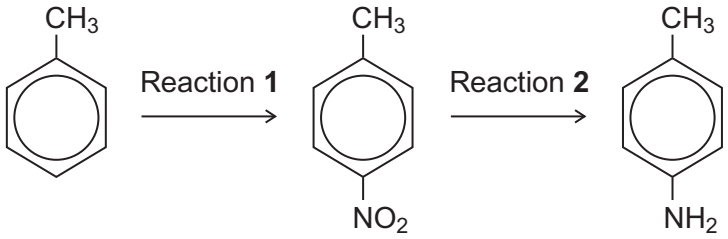
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10

Turn over for the next question

Do not write outside the box

5 Consider the following reaction sequence starting from methylbenzene.



J

5 (a) Name the type of mechanism for reaction **1**.

[1 mark]

.....

5 (b) Compound **J** is formed by reduction in reaction **2**.

5 (b) (i) Give a reducing agent for this reaction.

[1 mark]

.....

5 (b) (ii) Write an equation for this reaction. Use [H] to represent the reducing agent.

[1 mark]

.....

5 (b) (iii) Give a use for **J**.

[1 mark]

.....

Do not write outside the box

5 (c) Outline a mechanism for the reaction of bromomethane with an excess of compound **J**. You should represent **J** as RNH_2 in the mechanism.

[4 marks]

5 (d) Compound **K** ($C_6H_5CH_2NH_2$) is a structural isomer of **J**.

Explain why **J** is a weaker base than **K**.

[3 marks]

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Do not write outside the box

6 Esters are used as raw materials in the production of soaps and biodiesel.

6 (a) A student prepared an ester by two different methods.

Method **1** alcohol + acid anhydride

Method **2** alcohol + acyl chloride

6 (a) (i) An ester was prepared using method **1**, by reacting $(CH_3)_2CHOH$ with $(CH_3CO)_2O$

Write an equation for this reaction and give the IUPAC name of the ester formed.

[2 marks]

Equation

.....

IUPAC name of the ester .....

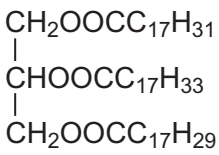
6 (a) (ii) The same ester was prepared using method **2** by reacting $(CH_3)_2CHOH$ with CH_3COCl

Outline a mechanism for this reaction.

[4 marks]

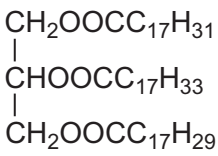
Do not write outside the box

6 (b) The ester shown occurs in vegetable oils.
It can be hydrolysed to make soap and can also be used to produce biodiesel.



6 (b) (i) Write an equation for the reaction of this ester with sodium hydroxide to form soap.

[2 marks]



.....

6 (b) (ii) Give the formula of the biodiesel molecule with the highest M_r that can be produced by reaction of this ester with methanol.

[1 mark]

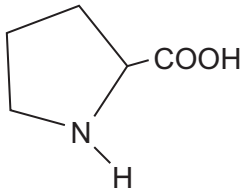
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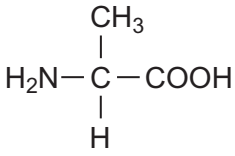
Turn over for the next question

Do not write outside the box

7 (a) The structures and common names of two amino acids are shown.



proline



alanine

7 (a) (i) Draw the structure of the zwitterion of proline.

[1 mark]

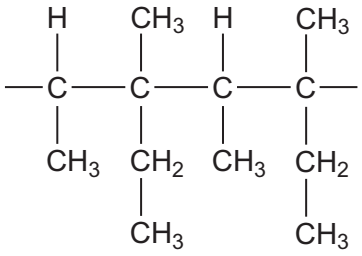
7 (a) (ii) Draw the structure of the tripeptide formed when a proline molecule bonds to two alanine molecules, one on each side.

[2 marks]

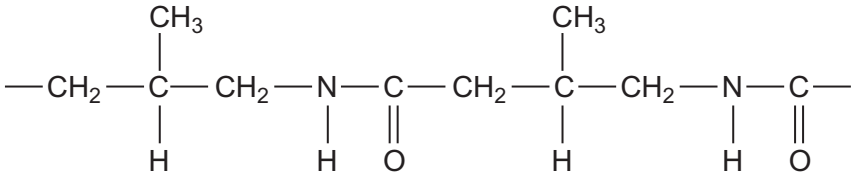
Do not write outside the box

7 (b) Sections of two polymers, **L** and **M**, are shown.

L



M



7 (b) (i) Give the IUPAC name of a monomer that forms polymer **L**.

[1 mark]

.....

7 (b) (ii) Give the IUPAC name of the monomer that forms polymer **M**.

[1 mark]

.....

7 (b) (iii) Draw the section of a polymer made from a dicarboxylic acid and a diamine that is isomeric with the section of polymer **M** shown.

[1 mark]

7 (b) (iv) Explain why polymer **L** is non-biodegradable.

[1 mark]

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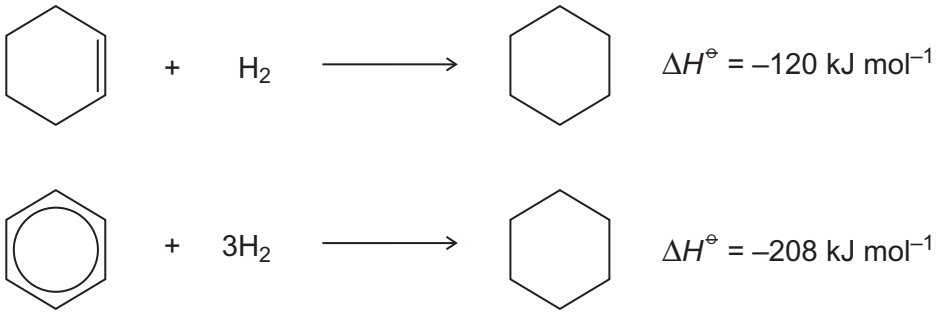
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Turn over ▶

Do not write outside the box

8 Equations for the hydrogenation of cyclohexene and of benzene, together with the enthalpies of hydrogenation, are shown.



8 (a) (i) Use these data to show that benzene is 152 kJ mol^{-1} more stable than the hypothetical compound cyclohexa-1,3,5-triene.

[1 mark]

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8 (a) (ii) State, in terms of its bonding, why benzene is more stable than cyclohexa-1,3,5-triene.

[1 mark]

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8 (b) Three carbon-carbon bonds are labelled on the structures shown.
These bonds are of different lengths.



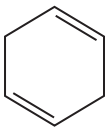
Write the letters **w**, **x** and **y** in order of **increasing** bond length.

[1 mark]

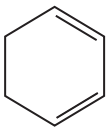
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Do not write outside the box

8 (c) The structures of two cyclic dienes are shown.



cyclohexa-1,4-diene



cyclohexa-1,3-diene

8 (c) (i) Use the enthalpy of hydrogenation data given opposite to calculate a value for the enthalpy of hydrogenation of cyclohexa-1,4-diene.

[1 mark]

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8 (c) (ii) Predict a value for the enthalpy of hydrogenation of cyclohexa-1,3-diene.

[1 mark]

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8 (c) (iii) Explain your answers to Questions **8 (c) (i)** and **8 (c) (ii)** in terms of the bonding in these two dienes.

[3 marks]

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8

Turn over ▶

Do not write outside the box

Section B

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

9 The acid dissociation constant, K_a, for ethanoic acid is given by the expression

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

The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C.

9 (a) A buffer solution is prepared using ethanoic acid and sodium ethanoate. In the buffer solution, the concentration of ethanoic acid is 0.186 mol dm^{-3} and the concentration of sodium ethanoate is 0.105 mol dm^{-3}.

Calculate the pH of this buffer solution.
Give your answer to 2 decimal places.

[3 marks]

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Do not write outside the box

9 (b) In a different buffer solution, the concentration of ethanoic acid is 0.251 mol dm^{-3} and the concentration of sodium ethanoate is 0.140 mol dm^{-3}.

A sample of hydrochloric acid containing 0.015 mol of HCl is added to 1000 cm^3 of this buffer solution.

Calculate the pH of the buffer solution after the hydrochloric acid has been added.
You should ignore any change in total volume.
Give your answer to 2 decimal places.

[5 marks]

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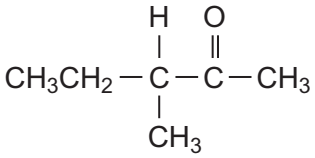
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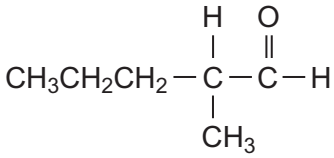
Turn over for the next question

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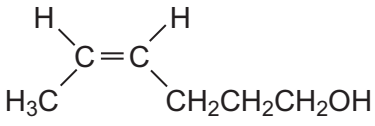
10 The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



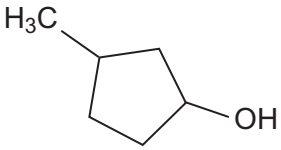
P



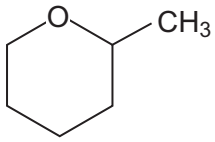
Q



R



S



T

10 (a) A simple test-tube reaction can be used to distinguish between isomers **P** and **S**.

Identify a reagent (or combination of reagents) you could use.
State what you would observe when both isomers are tested separately with this reagent or combination of reagents.

[3 marks]

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Do not write outside the box

10 (b) A simple test-tube reaction can be used to distinguish between isomer **Q** and all the other isomers.

Identify a reagent (or combination of reagents) you could use.
State what you would observe when **Q** is tested with this reagent or combination of reagents.

[2 marks]

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10 (c) State which **one** of the isomers, **P**, **Q**, **R**, **S** and **T**, has the least number of peaks in its ^{1}H n.m.r. spectrum.
Give the number of peaks for this isomer.

[2 marks]

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10 (d) Write the **molecular** formula of the standard used in ^{13}C n.m.r. spectroscopy.
Give **two** reasons why this compound is used.

[3 marks]

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Question 10 continues on the next page

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10 (e) **Figure 2** and **Figure 3** show the ^{13}C n.m.r. spectra of two of the five isomers.

Figure 2

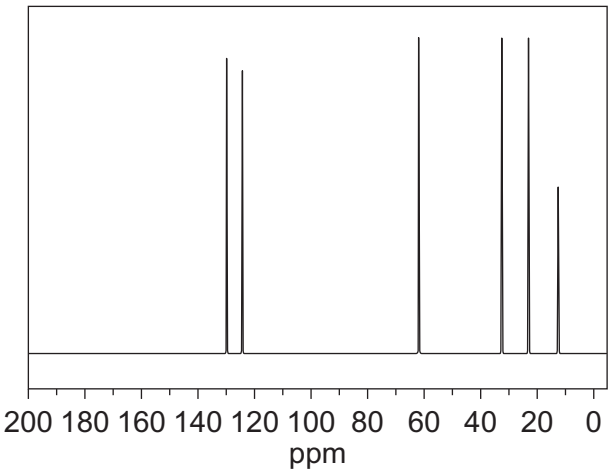
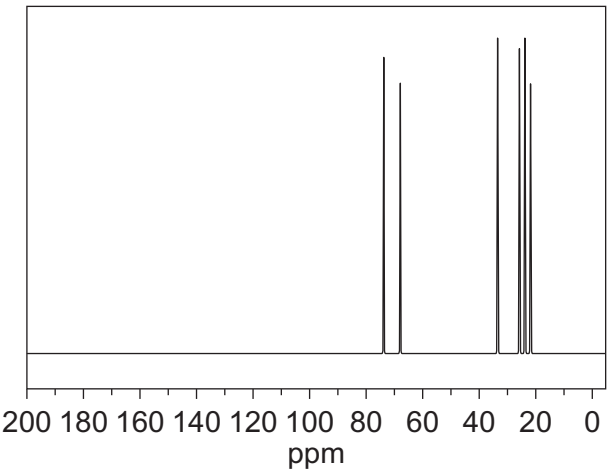
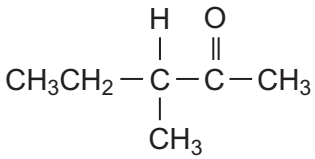


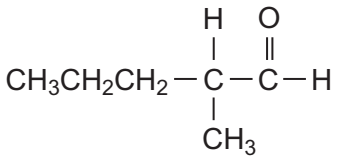
Figure 3



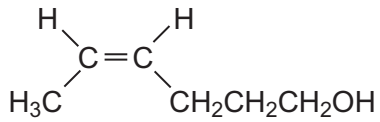
The structures of the five isomers are repeated to help you answer this question.



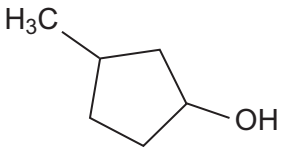
P



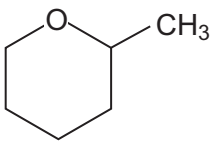
Q



R



S



T

Do not write outside the box

State which isomer produces the spectrum in **Figure 2** and which isomer produces the spectrum in **Figure 3**.

Explain your answer.

You do not need to identify every peak in each spectrum.
Use **Table C** on the Data Sheet to answer the question.

[5 marks]

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10 (f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.
The ^{1}H n.m.r. spectrum of **U** consists of two singlets.
V is a cyclic alcohol that exists as optical isomers.

Draw the structure of **U** and the structure of **V.**

[2 marks]

U **V**

17

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11 The N-substituted amide $C_6H_{13}NO$ can be formed from but-2-ene in a three-step synthesis.

$$H_3CCH{=}CHCH_3 \xrightarrow{\text{Reaction 1}} C_4H_9Br \xrightarrow{\text{Reaction 2}} C_4H_{11}N \xrightarrow{\text{Reaction 3}} C_6H_{13}NO$$

For each reaction
- state a reagent
- give the structure of the product
- name the mechanism of the reaction.

Detailed mechanisms are **not** required.

[9 marks]

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END OF QUESTIONS

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AQA Qualifications

A- LEVEL

CHEMISTRY

CHEM4 Kinetics, Equilibria and Organic Chemistry

Mark scheme

2420

June 2015

Version 1: Final

Mark schemes are prepared by the Lead Assessment Writer and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all associates participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the students' responses to questions and that every associate understands and applies it in the same correct way. As preparation for standardisation each associate analyses a number of students' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, associates encounter unusual answers which have not been raised they are required to refer these to the Lead Assessment Writer.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of students' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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Question	Marking Guidance	Mark	Comments
1(a) Marked with 1(b)	k = rate / $[A]^2$ or $\frac{3.3\times10^{-5}}{(4.2\times10^{-3})^2}$ = 1.87 or 1.9 $mol^{-1}dm^3s^{-1}$	1 1 1	 Answer scores 2 1.90 scores first mark only (incorrect rounding) Any order and independent of calculation
1(b) Marked with 1(a)	Expt 2 rate = $1.167 \times 10^{-4} - 1.2 \times 10^{-4}$ (mol dm^{-3} s^{-1}) Expt 3 [A] = $9.7 \times 10^{-3} - 9.8(1) \times 10^{-3}$ (mol dm^{-3}) Using alternative value for *k* Expt 2 rate = $1.4(4) \times 10^{-4}$ (mol dm^{-3} s^{-1}) Expt 3 [A] = 8.85×10^{-3} (mol dm^{-3})	1 1	If answers in table are not those given here, check their value of k in part 1(a) or use of alternative k. If their k is incorrect in part 1(a) mark 1(b) consequentially e.g. if k = 7.9×10^{-3} due to lack of squaring in 1(a) expt 2 4.9×10^{-7} expt 3 1.5×10^{-1} (expt 2 6.24×10^{-5} x their k) (expt 3 0.0134 / √k)
1(c)	Slow step or rds involves only A ***OR*** B does not appear in the slow step or the rds ***OR*** B only appears after the slow step or the rds	1	Not B has no effect on the rate or B is not in the rate equation Allow "it" for B

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Question		Marking Guidance	Mark	Comments
2(a) Marked with 2(b)		$K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ units = $mol^{-1}\ dm^3$	1 1	Penalise ( ) in part (a) but can score units; mark on in (b) If K_c expression wrong no marks in (a) but can score M1 & M3 in (b)
2(b) Marked with 2(a)	M1	$[O_2] = \dfrac{[SO_3]^2}{[SO_2]^2 K_c}$ or $\dfrac{(0.072/1.4)^2}{(0.055/1.4)^2 \times 27.9}$ or $\dfrac{(0.072)^2}{(0.055)^2 \times 27.9}$	1	Correct answer scores three marks Ignore ( ) in part (b) Penalise contradiction in M1
	M2	0.061(4)		If K_c expression wrong in (a) can score M1 here for rearrangement of their K_c & M3 for multiplication by 1.4
	M3	mol O_2 = 0.0614 × 1.4 = 0.086 (allow 0.085–0.087)	1 1	If K_c or rearrangement wrong here score only M3 for multiplication by 1.4 M3 = correct answer of (M2 × 1.4)
2(c)(i) **G**		No effect **OR** none **OR** no change **OR** stays the same	1	

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2(c)(ii)	M1	Effect: Increase or more SO_3	Increase or more SO_3	1	If wrong effect, no further marks, but M2 and M3 are independent of each other
	M2	Fewer mole(cule)s on RHS or 3 moles to 2 moles or (eqm shifts) to side with fewer moles	(V^3 or) residual V decreases in numerator of K_c expression	1	
	M3	<u>Equilibrium moves/shifts</u> to reduce the pressure/oppose the increase in pressure	to keep K_c constant, ratio $\frac{(\text{mol } SO_3)^2}{(\text{mol } SO_2)^2(\text{mol } O_2)}$ must increase	1	Allow to oppose the change only if increase pressure mentioned

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Question	Marking Guidance	Mark	Comments
3(a)(i) **A**	G	1	
3(a)(ii) **A**	F	1	
3(a)(iii) **A**	H	1	
3(b)(i) **A**	cresol purple	1	
3(b)(ii) **G**	yellow to red	1	both colours needed and must be in this order
3(b)(iii) **G**	Yellow or pale yellow	1	Not allow any other colour with yellow

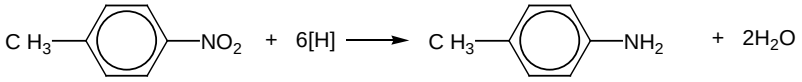
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Question		Marking Guidance	Mark	Comments
4(a)	M1	$[H_2O]$ is very high (compared with $[H^+]$ and $[OH^-]$) **OR** Very few H^+ and OH^- ions **OR** Only / very slightly dissociates **OR** Equilibrium lies far to the left	1	Not partially dissociates
	M2	$[H_2O]$ is (effectively) constant OR is incorporated into the constant K	1	Allow changes by only a very small amount
4(b)		(Dissociation OR breaking bonds) is endothermic	1	
		∴ Equilibrium moves to RHS (at higher T) to absorb heat or to lower T or oppose increase in T	1	Allow to oppose change only if increase T mentioned

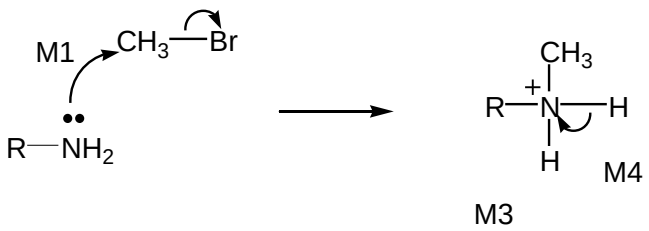
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4(c) Marked with 4(d)	$[H^+]$ = $\sqrt{K_w}$ (or = $\sqrt{5.48 \times 10^{-14}}$) If wrong method no marks = 2.34×10^{-7} pH = 6.63	1 1 1	Correct pH answer scores 3 Using alternative K_w (1.00×10^{-14}) gives pH = 7.00 which scores 1 Final answer must have 2dp
4(d) Marked with 4(c)	$[H^+]$ = $K_w / [OH^-]$ or (= $5.48 \times 10^{-14}/0.12$) If wrong method no marks = 4.566×10^{-13} pH = 12.34	1 1 1	Correct pH answer scores 3 If use alternative K_w (1.00×10^{-14}) again, do not penalise repeat error so pH = 13.08 scores 3 If use alternative K_w (1.00×10^{-14}) **not** as a repeat error, pH = 13.08 scores 1 If AE in K_w value made in part (c) is repeated here, do not penalise again. Final answer must have 2dp, but if dp penalised in 4(c) allow more than 2dp here but not fewer.

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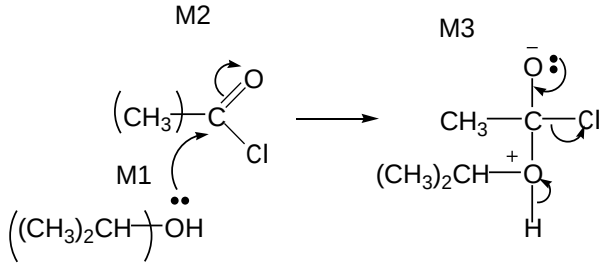
Question	Marking Guidance	Mark	Comments
5(a) **G**	Electrophilic substitution	1	Both words needed Ignore minor misspellings
5(b)(i)	Sn/HCl **OR** H_2/Ni OR H_2/Pt **OR** Fe/HCl **OR** Zn/HCl **OR** $SnCl_2$/HCl	1	Ignore conc or dil with HCl, Allow (dil) H_2SO_4 but not conc H_2SO_4 Not allow HNO_3 or H^+ Ignore NaOH after Sn/HCl Ignore catalyst
5(b)(ii)	$CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$ **OR** 	1	Allow molecular formulae as structures given $C_7H_7NO_2 + 6[H] \rightarrow C_7H_9N + 2H_2O$ Qu states use [H], so penalised $3H_2$
5(b)(iii)	making dyes ***OR*** making quaternary ammonium salts ***OR*** making (cationic) surfactants ***OR*** making hair conditioner ***OR*** making fabric softener ***OR*** making detergents	1	

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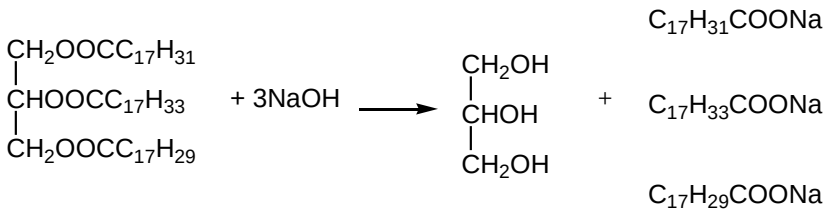
5(c)	M2  NO Mark for name of mechanism	4	Allow SN1 M1 for lone pair on N and arrow to C or mid point of space between N and C M2 for arrow from bond to Br M3 for structure of protonated secondary amine M4 for arrow from bond to N or + on N For M4: ignore RNH_2 or NH_3 removing H^+ but penalise Br-

5(d)	M1	<u>lone or electron pair on N</u>	1	If no mention of lone pair CE=0 If lone pair mentioned but not on N then lose M1 and mark on
	M2	in **J** spread/delocalised into ring (or not delocalised in K)	1	Ignore negative inductive effect of benzene
	M3	less available (for protonation or donation in **J**)	1	Allow interacts with ***π*** cloud for M2
		OR		
	M2	in **K** there is a positive inductive effect / electron releasing)		
	M3	more available (for protonation or donation in **K**)		

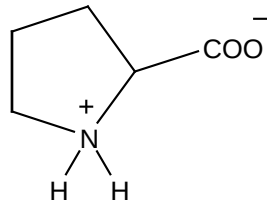
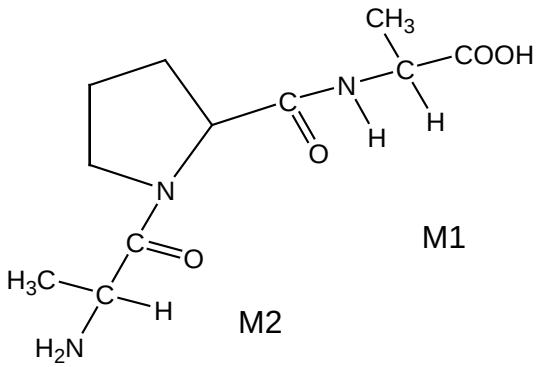
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Question	Marking Guidance	Mark	Comments
6(a)(i)	$(CH_3)_2CHOH + (CH_3CO)_2O \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$ (1)-methylethyl ethanoate OR Propan-2-yl ethanoate	1 1	**Allow** $CH_3CO_2CH(CH_3)_2$ and CH_3CO_2H Ignore $(CH_3)_2$–C in equation Ignore extra or missing spaces, commas or hyphens
6(a)(ii)	M2 M3  M4 for 3 arrows and lp NO Mark for name of mechanism	4	M1 for lone pair on O and arrow to C or to mid-point of space between O and C M2 for arrow from C=O bond to O • M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • If Cl lost with C=O breaking, max1 for M1 M3 for correct structure with charges (penalise wrong alcohol here) but lone pair on O is part of M4 Penalise $(CH_3)_2$–C in M3 M4 for lone pair on O and three arrows • only allow M4 after correct/very close M3 • M4 can be gained over more than one structure • Ignore Cl- removing H^+

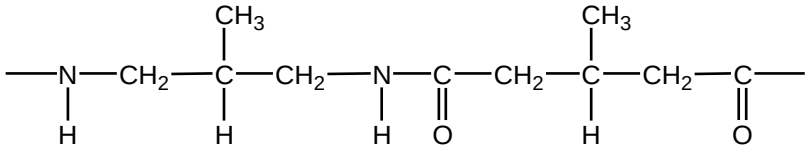
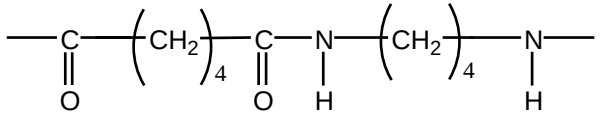
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6(b)(i)		LHS 1 RHS 1	Penalise covalent Na e.g. -O-Na
6(b)(ii)	$C_{17}H_{33}COOCH_3$	1	Allow $C_{19}H_{36}O_2$

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Question	Marking Guidance	Mark	Comments
7(a)(i)		1	Allow CO_2^- and NH_2^+
7(a)(ii)	NOTE – **Two** marks for this clip  M1 M2	1 1	M1 for alanine section bonded through N M2 for alanine section bonded through C But penalise error in proline ring Allow MAX 1 for correct tripeptide in polymer structure
7(b)(i)	3-methylpent-2-ene	1	Ignore *E-Z*, commas, spaces or missing hyphens
7(b)(ii)	4-amino-3-methylbutanoic acid	1	Ignore commas, spaces or missing hyphens

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7(b)(iii)		1	or any polyamide section containing 8 carbons plus two C=O plus two N-H, such as  Trailing bonds are required
7(b)(iv)	Non polar OR no polar groups/bonds (for attack by water / acids / alkalis / nucleophiles or for hydrolysis) C-C bonds are strong	1	

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Question	Marking Guidance	Mark	Comments
8(a)(i)	3(-120) – (-208) = -152 OR 3(120) – 208 = 152 (kJ mol^{-1})	1	Must show <u>working</u> and answer and maths must be correct, but ignore sign
8(a)(ii)	Electrons <u>delocalised</u> OR <u>delocalisation</u> (QOL) Or allow reference to <u>resonance</u> (QOL)	1	
8(b) **G**	x, y, w	1	Must be in this order
8(c)(i) **G**	-240 (kJ mol^{-1})	1	Must have minus sign
8(c)(ii)	between -239 and -121 (kJ mol^{-1})	1	Must have minus sign
8(c)(iii)	Must specify which diene: M1 Proximity – for 1,3 C=C bonds are close together M2 Delocalisation – for 1,3 some delocalisation OR some overlap of electrons, π clouds or p orbitals M3 some extra stability for the 1,3- isomer	 1 1 1	 allow converse for 1,4 diene allow converse for 1,4 diene

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Question		Answers	Mark	Comments
9(a)	M1	$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]}$ or $= 1.74 \times 10^{-5} \times \frac{0.186}{0.105}$	1	Allow ( )
	M2	$= 3.08 \times 10^{-5}$	1	If $[HX]/[X^-]$ or $\frac{0.186}{0.105}$ upside down, or any addition or subtraction lose M1 & M2.
	M3	pH = 4.51 (correct answer scores 3)	1	Can score M3 for correct pH conseq to their $[H^+]$, so pH = 5.01 scores one Must be to 2 dp
9(b)	M1	mol HX after addition (= 0.251 + 0.015) = 0.266	1	For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3
	M2	mol X^- after subtraction (= 0.140 – 0.015) = 0.125	1	For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3
	M3	$[H^+] = \left(\frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} \right) = \frac{1.74 \times 10^{-5} \times 0.266}{0.125}$	1	If errors above in both addition AND subtraction can only score M3 for insertion of their numbers in rearranged expression. One exception, if addition and subtraction reversed then pH =4.58 scores 2
	M4	$[H^+] = 3.703 \times 10^{-5}$ (mol dm^{-3})	1	If $[HX]/[X^-]$ upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their $[H^+]$, so if M1 & M2 correct, pH = 5.09 scores 3.
	M5	pH = 4.43 Correct use of HX and X^- values from 9(a) gives pH= 4.41 and scores 4	1	If wrong method, e.g √ or no use of rearranged K_a expression, may score M1 & M2 but no more. Allow more but not fewer than 2dp here.

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Questio	Answers		Mar	Comments
	Alternative using Henderson-Hasselbach Equation			
9(a)	M1	pH = pKa – log[HX]/X^-] = -log(1.74 × 10^{-5}) – log($\frac{0.186}{0.105}$)	1	Allow ( )
	M2	pKa = 4.76 – 0.248	1	If [HX]/[X^-] or $\frac{0.186}{0.105}$ upside down, can only score 1
	M3	pH = = 4.51	1	so pH = 5.01 Must be to 2 dp
9(b)	M1	mol acid after addition = 0.251 + 0.015 = 0.266	1	For HX, if no addition or error in addition (other than AE) (or subsequent extra add or sub) MAX 3
	M2	mol salt after addition = 0.140 – 0.015 = 0.125	1	For X^- if no subtraction or error in subtraction (other than AE) (or subsequent extra add or sub) MAX 3
	M3	pH = (pKa – log[HX]/[X^-]) = -log(1.74 × 10^{-5}) – log(0.266/0.125)	1	If errors above in both addition AND subtraction can only score M3 for insertion of their numbers - except if addition and subtraction reversed then pH =4.58 scores 2
	M4	pH = 4.76 – 0.328	1	
	M5	pH = = 4.43	1	If [HX]/[X^-] upside down, lose M3 & M4 (or next two marks) but can score M5 for correct pH conseq to their working, so if M1 & M2 correct, pH = 5.09 scores 3. Allow more but not fewer than 2dp here.

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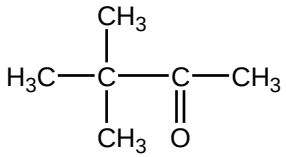
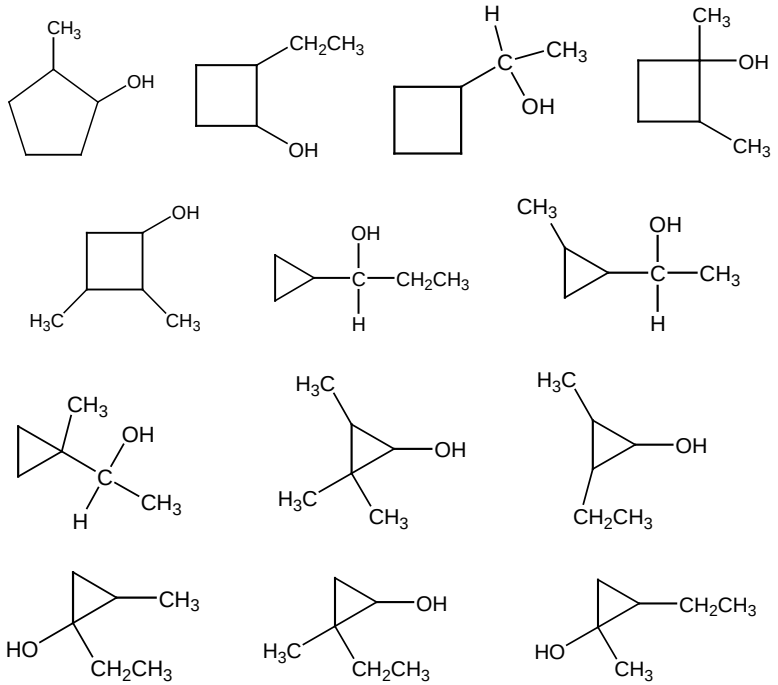
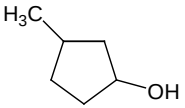
Question	Marking Guidance						Mark	Comments
10(a)	Reagent **P** (ketone) **S** (2° alcohol)	Acidified $K_2Cr_2O_7$ no reaction (orange to) green	Acidified $KMnO_4$ no reaction (purple to) colourless	I_2/NaOH Yellow ppt no reaction	Named RCOOH with HCl or H_2SO_4 no reaction fruity or sweet smell	Named RCOCl no reaction Misty fumes	1 1 1	Allow names including potassium permanganate Wrong or no reagent CE=0 Penalise incorrect formulae or incomplete reagent, such as $K_2Cr_2O_7$ or acidified dichromate, but mark on. Allow no change or nvc but penalise *nothing or no observation* If 2 reagents added sequentially or 2 different reagents used for P and S then CE=0
10(b)	Tollens' silver mirror/solid	Fehling's / Benedicts red ppt					1 1	
10(c) **G**	P 5 OR five						1 1	If not P then no marks for clip

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10(d)	$C_4H_{12}Si$ Any **two** from • <u>One or single</u> peak OR all (four) carbon atoms are equivalent or one environment • upfield from others or far away from others or far to right • non toxic OR inert • low boiling point or volatile or easy removed from sample	1 1 1	Must be molecular formula Wrong substance CE=0 for clip Ignore and don't credit single peak linked to 12 equivalent H or has a peak at $\delta = 0$ but use list principle for wrong statements

10 (e)				
	M1	Figure 2 is **R**	1	If not **R** cannot score M2
	M2	90-150 (ppm) or value in range is (two peaks for) C=C/alkene	1	
	M3	Figure 3 is **T**	1	If not **T** cannot score M4 or M5
	M4	50-90 (ppm) or value in range is C—O or alcohol or ether	1	
	M5	two peaks (so not S which would have only one)	1	

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10(f)	**U** $C_6H_{12}O_6$ 	1	
	Answers include **V** $C_6H_{12}O_6$ 	1	Not allow **S**  because **V** must be an isomer of **S**

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Question	Marking Guidance			Mark	Comments
11	Step 1	M1	HBr	1	In any step, if wrong reagent or extra wrong reagent, can only score mechanism mark, but if $AlCl_3$ added in Step 3, lose M7 but can score M8 & M9
		M2	CH_3CH_2—$CHCH_3$ (Br)	1	
		M3	electrophilic addition	1	If 1-bromobutane structure given for M2 then 1-aminobutane structure for M5, penalise M2 and M5 but mark M8 consequentially
	Step 2	M4	NH_3	1	
		M5	CH_3CH_2—$CHCH_3$ (NH_2)	1	If 1-bromobutane structure given for M2 then 2-aminobutane structure for M5, penalise M2, M5 and M8
		M6	nucleophilic substitution	1	If 2-bromobutane structure given for M2 then 1-aminobutane structure, penalise M5 and M8
	Step 3	M7	CH_3COCl or $(CH_3CO)_2O$	1	Allow C_2H_5 for CH_3CH_2
		M8	CH_3CH_2—$CHCH_3$ (NH—C(=O)—CH_3)	1	
		M9	(nucleophilic) addition-elimination	1	Not allow (electrophilic) addition-elimination

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General principles applied to marking CHEM4 papers by CMI+ (June 2015)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are <u>required information</u> to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a student gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

NB Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. <u>Spelling</u>

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

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NB Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the student to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a student provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

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F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

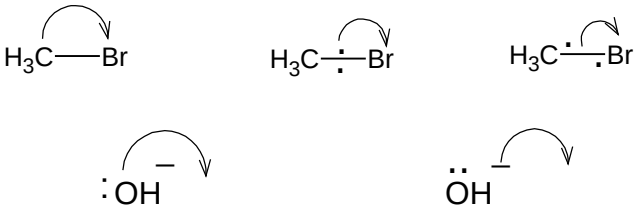
G. Marking calculations

In general

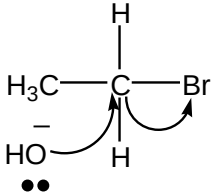
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



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When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

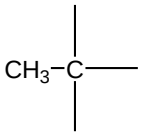
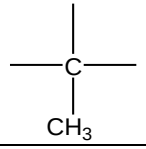
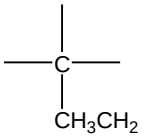
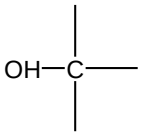
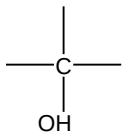
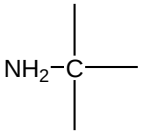
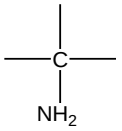
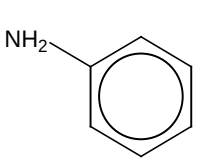
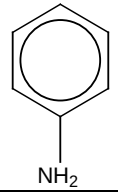
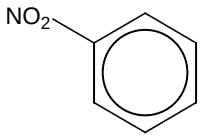
I. Organic structures

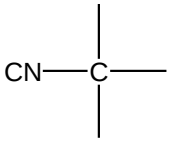
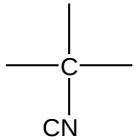
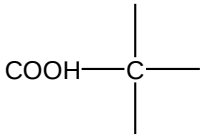
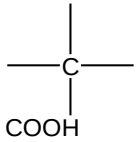
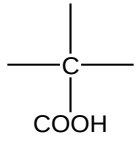
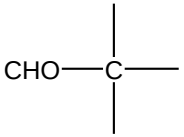
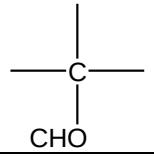
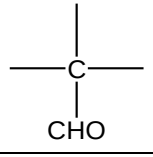
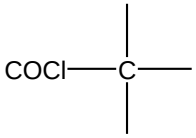
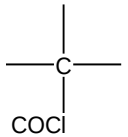
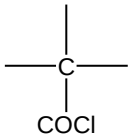
In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Structures must not be ambiguous, e.g. 1-bromopropane should be shown as $CH_3CH_2CH_2Br$ and not as the molecular formula C_3H_7Br which could also represent the isomeric 2-bromopropane.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if students show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.

  By way of illustration, the following would apply.

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allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

					
not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

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- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Representation of CH_2 by $C–H_2$ will be penalised

- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

NB Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
ethan-1,2-diol	should be **ethane-1,2-diol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
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8	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2014

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Monday 9 June 2014 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a ruler with millimetre measurements
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

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Section A

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

1 This question is about the gaseous equilibrium between compounds **E**, **F** and **G** as shown in the equation.

$$\mathbf{E}(g) + 2\mathbf{F}(g) \rightleftharpoons 2\mathbf{G}(g) \qquad \Delta H = -50 \text{ kJ mol}^{-1}$$

1 (a) A 2.0 mol sample of **E** was heated in a sealed container with a 1.0 mol sample of **F**. Equilibrium was established at a given temperature and the equilibrium mixture formed contained 0.80 mol of **G**.

Calculate the amount, in moles, of **E** and of **F** in this equilibrium mixture.

[2 marks]

Moles of **E** .....

Moles of **F** .....

1 (b) Write an expression for the equilibrium constant K_c for this equilibrium.
State the units of K_c

[2 marks]

Expression .....

.....

.....

Units .....

.....

Do not write outside the box

1 (c) A different mixture of **E** and **F** reached equilibrium at temperature T_1 in a container of volume 1.50 dm^3. This equilibrium mixture contained 2.50 mol of **E**, 1.20 mol of **F** and 0.85 mol of **G**.

Calculate a value of K_c for the equilibrium at temperature T_1

[2 marks]

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1 (d) The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature T_1 in a different container of volume 3.00 dm^3.

State whether the amount of **G** in the equilibrium mixture will increase, decrease or stay the same. Explain your answer.

[3 marks]

Effect on the amount of **G** .....

Explanation .....

.....

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1 (e) The mixture in Question **1 (c)** was allowed to reach equilibrium at temperature T_2 in the original container of volume 1.50 dm^3.

The value of K_c for the equilibrium was found to have increased.

State and explain which of T_1 or T_2 is the higher temperature.

[3 marks]

Higher temperature .....

Explanation .....

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12

Do not write outside the box

2 This question is about alkalis and carboxylic acids.

In this question, all data are quoted at 25 ºC.

2 (a) Carboxylic acids are weak acids.

State the meaning of the term **weak** as applied to carboxylic acids.

[1 mark]

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2 (b) Write an equation for the reaction of propanoic acid with sodium carbonate.

[1 mark]

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2 (c) Calculate the pH of a 0.0120 mol dm^{-3} solution of calcium hydroxide.
The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6}.
Give your answer to 2 decimal places.

[3 marks]

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[Extra space].....

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Do not write outside the box

2 (d) The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

2 (d) (i) Write an expression for the acid dissociation constant K_a for benzenecarboxylic acid.

[1 mark]

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2 (d) (ii) Calculate the pH of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid. Give your answer to 2 decimal places.

[3 marks]

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[Extra space] .....

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Question 2 continues on the next page

Do not write outside the box

2 (d) (iii) A buffer solution with a pH of 4.00 is made using benzenecarboxylic acid and sodium benzenecarboxylate.

Calculate the mass of sodium benzenecarboxylate (M_r = 144.0) that should be dissolved in 1.00 dm^3 of a 0.0120 mol dm^{-3} solution of benzenecarboxylic acid to produce a buffer solution with a pH of 4.00

The value of the acid dissociation constant K_a for benzenecarboxylic acid (C_6H_5COOH) is 6.31×10^{-5} mol dm^{-3}.

[5 marks]

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[Extra space] .....

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Do not write outside the box

2 (e) Two solutions, one with a pH of 4.00 and the other with a pH of 9.00, were left open to the air.

The pH of the pH 9.00 solution changed more than that of the other solution.

Suggest what substance might be present in the air to cause the pH to change.
Explain how and why the pH of the pH 9.00 solution changes.

[3 marks]

Substance present in air .....

Explanation .....

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17

Turn over for the next question

Do not write outside the box

3 (a) **Table 1** shows the results of three experiments to investigate the rate of reaction between compounds **A** and **B** dissolved in a given solvent.
All three experiments were carried out at the same temperature.

Table 1

	Experiment 1	**Experiment 2**	**Experiment 3**
Initial concentration of A / mol dm^{-3}	1.60×10^{-2}	2.40×10^{-2}	3.60×10^{-2}
Initial concentration of B / mol dm^{-3}	4.20×10^{-2}	6.30×10^{-2}	6.30×10^{-2}
Initial rate / mol dm^{-3} s^{-1}	8.00×10^{-5}	1.80×10^{-4}	4.05×10^{-4}

3 (a) (i) Deduce the order of reaction with respect to **A**.
Tick (✓) **one** box.

[1 mark]

Order of reaction with respect to A	**Tick (✓)**
0	
1	
2	

3 (a) (ii) Deduce the order of reaction with respect to **B**.
Tick (✓) **one** box.

[1 mark]

Order of reaction with respect to B	**Tick (✓)**
0	
1	
2	

Do not write outside the box

3 (b) The reaction between two different compounds, **C** and **D**, is studied at a given temperature.
The rate equation for the reaction is found to be

$$\text{rate} = k[\mathbf{C}][\mathbf{D}]^2$$

3 (b) (i) When the initial concentration of **C** is 4.55×10^{-2} mol dm^{-3} and the initial concentration of **D** is 1.70×10^{-2} mol dm^{-3}, the initial rate of reaction is 6.64×10^{-5} mol dm^{-3} s^{-1}.

Calculate the value of the rate constant at this temperature and deduce its units.

[3 marks]

Calculation .....

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Units of rate constant .....

.....

3 (b) (ii) The experiment in Question **3 (b) (i)** is repeated at the same temperature but after the addition of extra solvent so that the total volume of the mixture is doubled.

Deduce the new initial rate of reaction.

[1 mark]

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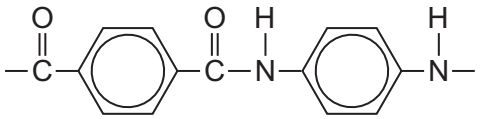
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6

Turn over for the next question

Do not write outside the box

4 Kevlar is a polymer used in protective clothing.
The repeating unit within the polymer chains of Kevlar is shown.



4 (a) Name the strongest type of interaction between polymer chains of Kevlar.

[1 mark]

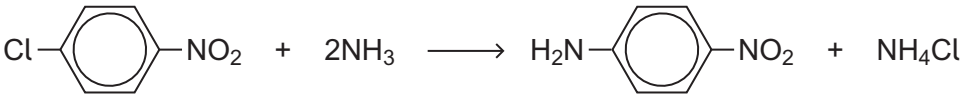
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4 (b) One of the monomers used in the synthesis of Kevlar is



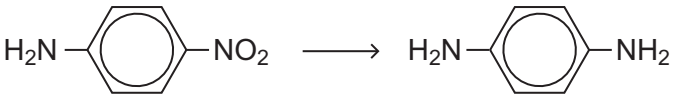
An industrial synthesis of this monomer uses the following two-stage process starting from compound **X**.

Stage **1**



X

Stage **2**



4 (b) (i) Suggest why the reaction of ammonia with **X** in Stage **1** might be considered unexpected.

[2 marks]

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Do not write outside the box

4 (b) (ii) Suggest a combination of reagents for the reaction in Stage **2**.

[1 mark]

.....

4 (b) (iii) Compound **X** can be produced by nitration of chlorobenzene.

Give the combination of reagents for this nitration of chlorobenzene.
Write an equation or equations to show the formation of a reactive intermediate from these reagents.

[3 marks]

Reagents .....

.....

Equation(s) .....

.....

4 (b) (iv) Name and outline a mechanism for the formation of **X** from chlorobenzene and the reactive intermediate in Question **4 (b) (iii)**.

[4 marks]

Name of mechanism .....

Mechanism

Turn over for the next question

11

Do not write outside the box

5 The carbonyl compound CH_3CH_2CHO reacts very slowly with HCN

5 (a) Name and outline a mechanism for the reaction of CH_3CH_2CHO with HCN

[5 marks]

Name of mechanism .....

Mechanism

5 (b) The reaction in Question **5 (a)** produces a pair of enantiomers.

5 (b) (i) Draw the structure of each enantiomer to show how they are related to each other.

[2 marks]

Do not write outside the box

5 (b) (ii) State and explain how you could distinguish between the two enantiomers.

[2 marks]

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5 (c) Give the IUPAC name of the product of the reaction in Question **5 (a)**.

[1 mark]

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5 (d) In practice, KCN rather than HCN is added to the carbonyl compound.

Given that K_a for HCN = 4.0×10^{-10} mol dm^{-3}, suggest why the reaction with HCN is very slow.

[2 marks]

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Question 5 continues on the next page

Do not write outside the box

5 (e) Acrylic fibres are used as a substitute for wool. Acrylics are copolymers of acrylonitrile with other compounds.

Acrylonitrile is the common name for the following compound.

$$H_2C=CH-C\equiv N$$

5 (e) (i) Acrylonitrile can be formed from propene.

Write an equation for the reaction of propene with ammonia and oxygen to form acrylonitrile and one other product.

[1 mark]

.....

5 (e) (ii) The term copolymer is used to describe the product obtained when two or more different monomers form a polymer.

Draw the repeating unit of the acrylic copolymer that contains 75% acrylonitrile monomer and 25% chloroethene monomer.

[1 mark]

5 (e) (iii) Name the type of polymerisation involved in Question **5 (e) (ii)**.

[1 mark]

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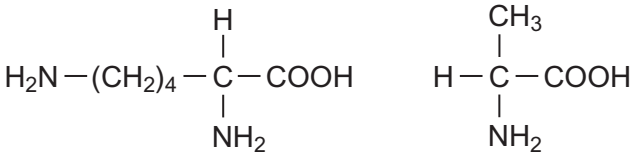
15

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED

Do not write outside the box

6 Lysine and alanine are two amino acids.



lysine

alanine

6 (a) Give the IUPAC name of lysine.

[1 mark]

.....

6 (b) Draw structures to show the product formed in each case when lysine reacts with

6 (b) (i) an excess of aqueous HCl

[1 mark]

6 (b) (ii) an excess of aqueous NaOH

[1 mark]

6 (b) (iii) methanol in the presence of a small amount of concentrated H_2SO_4

[1 mark]

Do not write outside the box

6 (c) The mass spectrum of alanine gives a major peak at $m/z = 44$

Write an equation for the fragmentation of the molecular ion of alanine to give an ion that produces this peak.
In your answer, draw the displayed formula for this fragment ion.

[2 marks]

6 (d) Draw a dipeptide formed from one molecule of lysine and one molecule of alanine.

[1 mark]

6 (e) The dipeptide in Question **6 (d)** is hydrolysed in acid conditions and the mixture produced is analysed by column chromatography. The column is packed with a resin which acts as a polar stationary phase.

Suggest why lysine leaves the column after alanine.

[2 marks]

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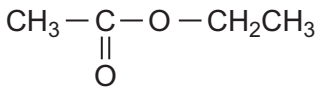
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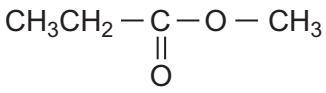
Section B

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

7 (a) **Ester 1** and **Ester 2** were studied by ^{1}H n.m.r. spectroscopy.

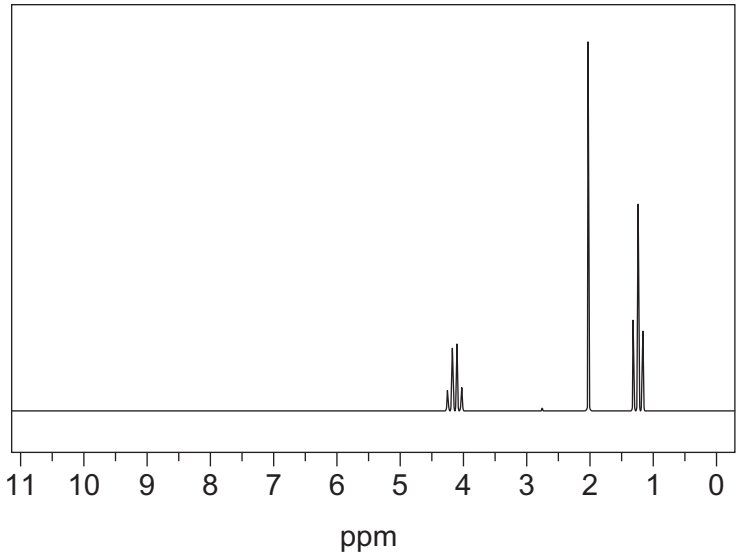


Ester 1



Ester 2

One of the two esters produced this spectrum.



Deduce which of the two esters produced the spectrum shown. In your answer, explain the position and splitting of the quartet peak at $\delta = 4.1$ ppm in the spectrum.

Predict the δ value of the quartet peak in the spectrum of the other ester.

Use **Table B** on the Data Sheet.

[4 marks]

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7 (b) Cetrimide is used as an antiseptic.

$$[CH_3(CH_2)_{15}N(CH_3)_3]^+ Br^-$$

cetrimide

Name this type of compound.

Give the reagent that must be added to $CH_3(CH_2)_{15}NH_2$ to make cetrimide and state the reaction conditions.

Name the type of mechanism involved in this reaction.

[4 marks]

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7 (c) Give a reagent that could be used in a test-tube reaction to distinguish between benzene and cyclohexene.
Describe what you would see when the reagent is added to each compound and the test tube is shaken.

[3 marks]

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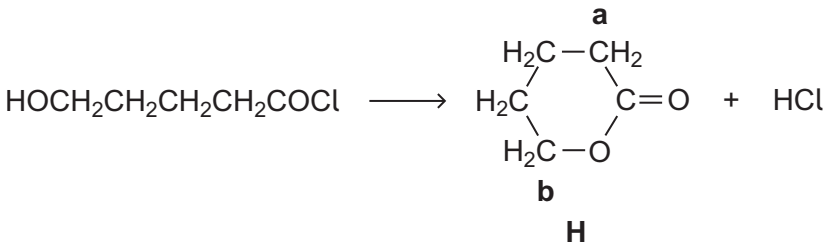
Turn over ▶

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8 This question is about some isomers of $C_5H_8O_2$

8 (a) Compound **H** is a cyclic ester that can be prepared as shown.

On the structure of **H**, two of the carbon atoms are labelled.



8 (a) (i) Name and outline a mechanism for this reaction.

Use **Table C** on the Data Sheet to give the ^{13}C n.m.r. δ value for the carbon atom labelled **a** and the δ value for the carbon atom labelled **b**.

[7 marks]

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Do not write outside the box

8 (a) (ii) $HOCH_2CH_2CH_2CH_2COCl$ can also react to form a polyester in a mechanism similar to that in Question **8 (a) (i)**.

Draw the repeating unit of the polyester and name the type of polymerisation involved.

[2 marks]

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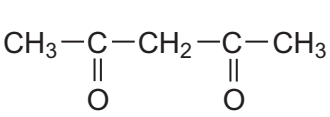
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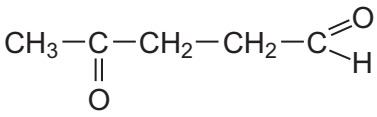
8 (b) State how you could distinguish between compounds **J** and **K** by a simple test-tube reaction.

State how you could distinguish between **J** and **K** by giving the number of peaks in the ^1H n.m.r. spectrum of each compound.

[5 marks]



J



K

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Question 8 continues on the next page

Do not write outside the box

8 (c) Draw the structure of each of the following isomers of $C_5H_8O_2$
Label each structure you draw with the correct letter **L**, **M**, **N**, **P** or **Q**.

L is methyl 2-methylpropenoate.

M is an ester that shows E-Z stereoisomerism.

N is a carboxylic acid with a branched carbon chain and does **not** show stereoisomerism.

P is an optically active carboxylic acid.

Q is a cyclic compound that contains a ketone group and has only two peaks in its ^1H n.m.r. spectrum.

[5 marks]

19

END OF QUESTIONS

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AQA Qualifications

A-LEVEL
CHEMISTRY

CHEM4 Kinetics, Equilibria and Organic Chemistry
Mark scheme

2420
June 2014

Version: 1.1 Final

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Mark schemes are prepared by the Lead Assessment Writer and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all associates participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the students' responses to questions and that every associate understands and applies it in the same correct way. As preparation for standardisation each associate analyses a number of students' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, associates encounter unusual answers which have not been raised they are required to refer these to the Lead Assessment Writer.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of students' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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Question		Marking Guidance	Mark	Comments
1(a)		Mol of **E** 1.6(00) Mol of **F** 0.2(00)	1 1	Ignore extra zeros.
1(b)		$K_c = \frac{[G]^2}{[E][F]^2}$ $mol^{-1}\ dm^3$	1 1	Penalise expression containing V. Penalise missing brackets or ( ). If K_c wrong, allow units consequential to their K_c, but no marks in (c) unless correct K_c used in (c).
1(c)		$K_c = \frac{(0.85/1.5)^2}{(2.50/1.5)(1.20/1.5)^2}$ = 0.3(01) Allow 0.299–0.304	1 1	Vol missed or used wrongly – no marks. If K_c correct in (b) but squared term missed here, no further marks. Ignore units.
1(d)	M1	Decrease	1	If M1 is incorrect CE=0 for the clip. If M1 is blank, mark on and seek to credit the correct information in the explanation.
	M2	More moles on LHS / reactants or fewer / less moles on RHS / products (allow correct ratio 3:2)	1	M2 not just a generic statement 'shifts to more moles'. M3 depends on a correct statement for M2
	M3	(Equilibrium) <u>shifts / moves</u> either to oppose reduction in pressure / or to increase the pressure	1	Not 'favours'. Allow 'to oppose change' only if reduction in pressure noted.

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1(e)	M1	T_1	1 1	If M1 is incorrect, CE=0 for the clip. If M1 is blank, mark on and seek to credit the correct information in the explanation.
	M2	(Forward*) reaction is <u>exothermic</u> **OR** <u>Backward</u> reaction is <u>endothermic</u>	1	*Assume answer refers to forward reaction unless otherwise stated.
	M3	(at T_2 or lower temperature) (Equilibrium) <u>shifted / moved</u> to oppose reduction in temp **OR** at T_1 or higher temp, (Equilibrium) <u>shifted / moved</u> to oppose (increase in temp)		M3 depends on a correct statement for M2 Allow "to oppose change" only if change in temperature is stated. Not 'favours'.

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Question	Marking Guidance		Mark	Comments
2(a)	(only) slightly or partially dissociated / ionised		1	Ignore 'not fully dissociated'. Allow low tendency to dissociate or to lose / donate a proton. Allow shown equilibrium well to the left. otherwise ignore equations
2(b)	$2CH_3CH_2COOH + Na_2CO_3 \rightarrow 2CH_3CH_2COONa + H_2O + CO_2$ **OR** $2CH_3CH_2COOH + CO_3^{2-} \longrightarrow 2CH_3CH_2COO^- + H_2O + CO_2$ **OR** $CH_3CH_2COOH + Na_2CO_3 \longrightarrow CH_3CH_2COONa + NaHCO_3$ **OR** $CH_3CH_2COOH + CO_3^{2-} \longrightarrow CH_3CH_2COO^- + HCO_3^-$		1	Must be propanoic acid, allow C_2H_5COOH not molecular formulae Allow multiples. Ignore reversible sign. Not H_2CO_3
2(c)	$[OH^-] = 2 \times 0.0120 = 0.0240$ $[H^+] = \frac{1 \times 10^{-14}}{0.0240} = 4.166 \times 10^{-13}$ ***OR*** pOH = 1.62 pH = 12.38	M1 M2 M3	1 1 1	Correct answer for pH with or without working scores 3 If × 2 missed or used wrongly can only score M3 for correct calculation of pH from their $[H^+]$ Lose M3 if not 2 decimal places: 12.4 scores 2 12.08 scores 1 (missing × 2) ; 12.1 scores 0 11.78 scores 1 (dividing by 2) 11.8 scores 0

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2(d)(i)		$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$	1	Ignore ( ) here but brackets must be present. Must be correct acid and salt. If wrong, mark (d)(ii) independently.
2(d)(ii)	M1	$K_a = \frac{[H^+]^2}{[C_6H_5COOH]}$ **OR** with numbers	1	Correct answer for pH with or without working scores 3 Allow HX, HA and ignore ( ) here. May score M1 in (d)(i).
	M2	$[H^+] = \sqrt{(6.31 \times 10^{-5} \times 0.0120)}$ or $\sqrt{(K_a \times [C_6H_5COOH])}$ $(= \sqrt{(7.572 \times 10^{-7}} = 8.70 \times 10^{-4})$	1	pH = 6.12 may score 2 if correct working shown and they show the square root but fail to take it. but if no working shown or wrong $K_a = \frac{[H^+]}{[C_6H_5COOH]}$ used
	M3	pH = 3.<u>06</u>	1	which also leads to 6.12, then zero scored. Must be 2 decimal places ie 3.1 loses M3

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2(d)(iii)	M1	$[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$	1	Correct answer for mass with or without working scores 5 Allow 1×10^{-4}
	M2	$[X^-] = \frac{Ka \times [HX]}{[H^+]}$	1	Ignore ( ) here. If $[HX]/[X^-]$ upside down, can score M1 plus M4 for 5.26×10^{-7}
	M3	$= \frac{6.31 \times 10^{-5} \times 0.0120}{1.00 \times 10^{-4}}$	1	And M5 for 7.57×10^{-5} g
	M4	$= 7.572 \times 10^{-3}$	1	
	M5	Mass (C_6H_5COONa) $= 7.572 \times 10^{-3} \times 144 = 1.09$ g or 1.1 g	1	Wrong method, eg using $[H^+]^2$ may only score M1 and M5 for correct multiplication of their M4 by 144 (provided not of obviously wrong substance)

2(e)	M1	CO_2	1	Allow NO_x and SO_2
	M2	pH (It) falls/decreases	1	If M1 wrong, no further marks.
	M3	mark M2 & M3 independently acidic (gas) **OR** reacts with alkali(ne solution)/ OH^- **OR** $CO_2 + 2OH^- \longrightarrow CO_3^{2-} + H_2O$ **OR** $CO_2 + OH^- \longrightarrow HCO_3^-$	1	Not forms H_2CO_3 H_2SO_3 H_2SO_4 etc OR H^+ ions.

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Question	Marking Guidance	Mark	Comments
3(a)(i)	2	1	
3(a)(ii)	0	1	
3(b)(i)	$k = \dfrac{6.64 \times 10^{-5}}{(4.55 \times 10^{-2}) \times (1.70 \times 10^{-2})^2}$ = 5.05 (range allowed 5.03–5.07) $\underline{mol^{-2}\, dm^{+6}\, s^{-1}}$	1 1 1	Correct answer for *k* with or without working scores 2 First mark is for insertion of numbers into a correctly rearranged rate equ , *k* = etc. AE (-1) for copying numbers wrongly or swapping two numbers. Mark units separately, ie only these units but can be in any order.
3(b)(ii)	8.3×10^{-6} (mol $dm^{-3}\, s^{-1}$) **OR** if not 8.3×10^{-6}, look at their *k* in 3(b)(i) and if not 5.05 Allow ecf for their (incorrect) $k \times (1.64 \times 10^{-6})$	1	Allow 0.83×10^{-5} Ignore units

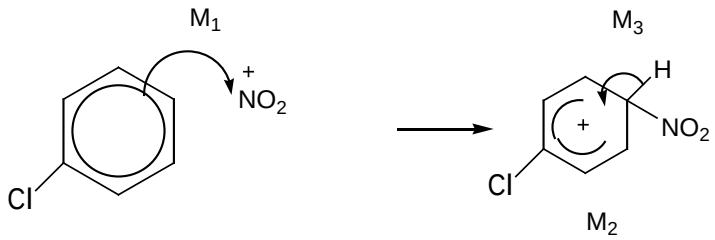
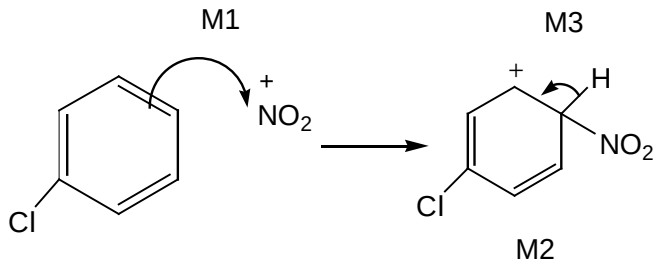
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Question	Marking Guidance	Mark	Comments
4(a)	Hydrogen bond(ing)	1	Allow H bonding. Penalise mention of any other type of bond.
4(b)(i)	Ammonia is a nucleophile Benzene repels nucleophiles	1 1	Allow ammonia has a lone pair. Allow (benzene) attracts/reacts with electrophiles. **OR** benzene repels electron rich species or lone pairs **OR** C–Cl bond is short / strong / weakly polar
4(b)(ii)	H_2/Ni **OR** H_2/Pt **OR** Sn/HCl **OR** Fe/HCl	1	Ignore dil/conc of HCl Ignore the term 'catalyst'. Allow H_2SO_4 with Sn and Fe but not conc. Ignore NaOH following correct answer. Not $NaBH_4$ nor $LiAlH_4$

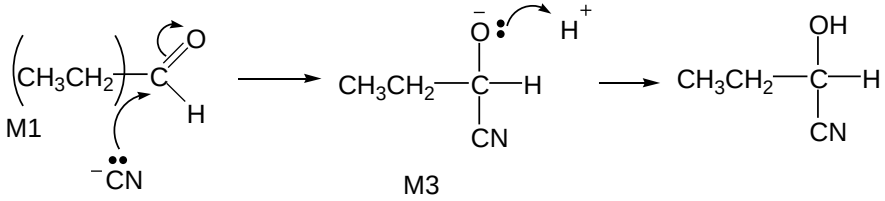
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4(b)(iii)	<u>conc HNO_3</u> <u>conc H_2SO_4</u> $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ **OR** using two equations $HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$ $H_2NO_3^+ \longrightarrow H_2O + NO_2^+$	1 1 1	If either or both conc missed can score 1 for both acids Allow 1:1 equation $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2O + HSO_4^-$

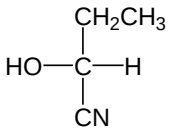
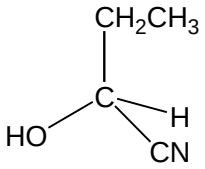
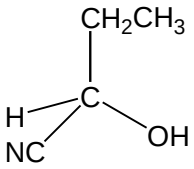
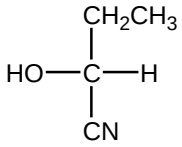
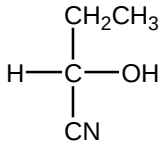
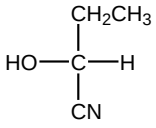
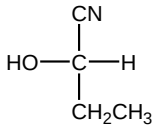
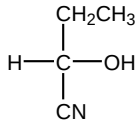
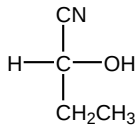
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4(b)(iv)	<u>Electrophilic substitution</u>  **OR**  	1 3	• Ignore position or absence of Cl in M1 but must be in correct position for M2 • M1 arrow from within hexagon to N or <u>+ on N</u> • Allow NO_2^+ in mechanism. • Bond to NO_2 must be to N for structure mark M2 • Gap in horseshoe must be centered around correct carbon (C1). • + in intermediate not too close to C1 (allow on or "below" a line from C2 to C6). • M3 arrow into hexagon unless Kekule. • Allow M3 arrow independent of M2 structure. • Ignore base removing H in M3 • + on H in intermediate loses M2 not M3

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Question	Marking Guidance	Mark	Comments
5(a)	<u>Nucleophilic addition</u> M4 for lp, arrow and H+ M2  Allow C_2H_5– for CH_3CH_2–	1 4	• M1 and M4 include lone pair and curly arrow. • Allow :CN^- but arrow must start at lone pair on C • M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • Penalise incorrect partial charges. • M3 is for correct structure including minus sign but lone pair is part of M4 • Penalise extra curly arrows in M4

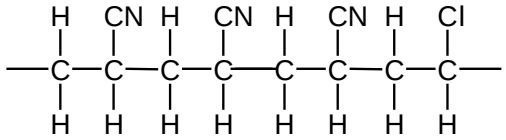
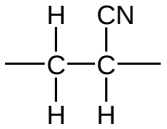
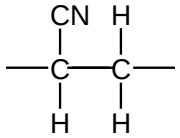
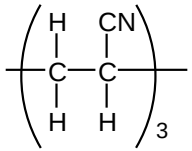
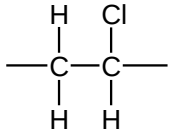
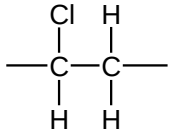
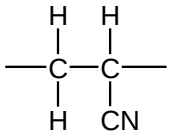
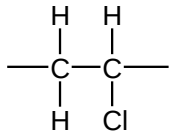
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5(b)(i)	M1 M2	   Students must <u>show</u> an attempt at mirror images, eg allow   ie vertical groups same and horizontal swapped as if there was a mirror between them No mirror need be shown Do not penalize wedge bond when wedge comes into contact with both C & N	1 1	M1 for correct structure of product of 5(a) Allow C_2H_{5-} for CH_3CH_2– Penalise wrongly bonded, OH or CN or CH_2CH_3 once only in clip. M2 cannot be gained by simply swapping two or more groups with no attempt to show a mirror image., e.g. do not allow M2 for   because these do not <u>show</u> the enantiomers as mirror images. However these two could score M2 if placed as below as if with a “mirror” horizontally between them  

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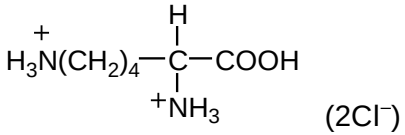
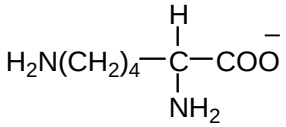
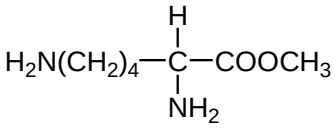
5(b)(ii)	M1 M2	(Plane) <u>polarized light</u> <u>Rotated</u> in <u>opposite</u> directions (equally) (only allow if M1 correct or close)	1 1	M2 only scores following correct M1 Not just in different directions but allow one rotates light to the left and one to the right. Not molecules rotate.
5(c)	<u>2-hydroxybutane(-1-)nitrile</u>		1	
5(d)	Weak acid / (acid) only slightly / partially dissociated/ionised $[CN^-]$ very low		1 1	Ignore rate of dissociation. Allow (very) few cyanide ions. Mark independently.
5(e)(i)	$H_2C{=}CH{-}CH_3 + NH_3 + \frac{3}{2}O_2 \longrightarrow H_2C{=}CH{-}CN + 3H_2O$ **OR** $H_2C{=}CH{-}CH_3 + NH_3 + 3O_2 \longrightarrow H_2C{=}CH{-}CN + 3H_2O_2$		1	OR doubled. Allow C_3H_6 and CH_2CHCN or C_3H_3N on this occasion only.

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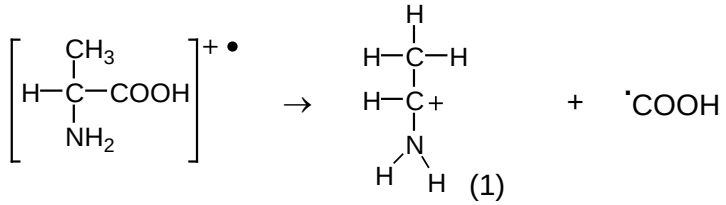
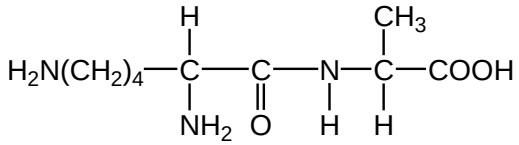
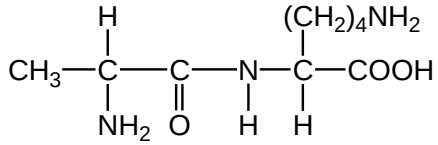
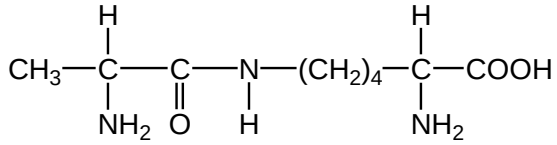
5(e)(ii)	 Must contain, in any order, 3 of  or 3 of  or  and one of  or 	1	Ignore n Must show trailing bonds. Do not penalise C—NC bond here on this occasion. allow  or  etc allow –$CH_2CH(CN)CH_2CHCl$– etc

5(e)(iii)	Addition (polymerization)	1	Allow self-addition. Do not allow additional.

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Question	Marking Guidance	Mark	Comments
6(a)	2,6-diaminohexanoic acid	1	Ignore additional , or – or spaces.
6(b)(i)	 $(2Cl^-)$	1	NB both N must be protonated. Allow $-NH_3^+$ allow CO_2H Allow $-^+H_3N$ Penalise – C_4H_8 – here.
6(b)(ii)	 (Na^+)	1	Allow CO_2^- Allow $–H_2N$ Allow –COONa but penalise O—Na bond shown.
6(b)(iii)		1	Allow CO_2CH_3 Allow $–NH_3^+$ or $–H_2N$

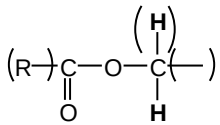
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6(c)	 (1)	2	1 for <u>displayed formula</u> of fragment ion. 1 for molecular ion of alanine AND radical. Allow molecular ion without brackets and fragment ion in brackets with outside + Allow dot anywhere on radical. Allow $[C_3H_7NO_2]^{+\bullet}$ for molecular ion.
6(d)	 **OR**  **OR** 	1	Dipeptide, not repeating unit/ Allow CO_2H Allow $-H_2N$ Allow –CONH–

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6(e)	M1 M2	In acid lysine has double positive or more positive charge (Lysine ion) has greater affinity / greater attraction / adheres better / sticks better to polar / stationary phase	1 1	 M2 only scores after a correct M1 Ignore greater retention time.

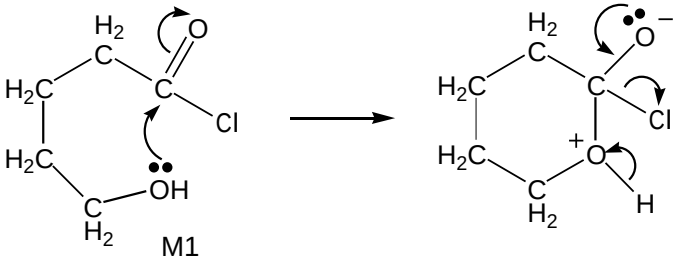
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Question		Marking Guidance	Mark	Comments
7(a)	M1	Ester **1**	1	If Ester 2, can score M3 only.
	M2	peak at δ = 4.1 due to 	1	When marking M2 and M3, check any annotation of structures in the stem at the top of the page.
	M3	(δ = 4.1 peak is) quartet as <u>adjacent/next to/attached to CH_3</u>	1	
	M4	Other spectrum quartet at δ = 2.1-2.6 (or value in this range)	1	
7(b)	M1	<u>Quaternary</u> (alkyl) <u>ammonium salt / bromide</u>	1	
	M2	CH_3Br or bromomethane	1	Penalise contradictory formula and name.
	M3	Excess (CH_3Br or bromomethane)	1	Mention of acid eg H_2SO_4 OR alkali eg NaOH loses both M2 and M3
	M4	Nucleophilic substitution	1	Can only score M3 if reagent correct. Ignore alcohol or ethanol (conditions) or Temp.

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7(c)		Bromine (penalise Br but mark on)	Acidified $KMnO_4$ (Penalise missing acid but mark on)	1	Wrong reagent = no marks. If bromine colour stated it must be red, yellow, orange, brown or any combination, penalise wrong starting colour. Ignore 'clear', 'nothing'. Allow colour fades slowly. Allow 'nvc' for no visible change.
	Benzene	no reaction / colour remains / no (visible) change	no reaction / colour remains / no (visible) change	1	
	cyclohexene	(Bromine) decolourised	(Acidified $KMnO_4$) decolourised	1	

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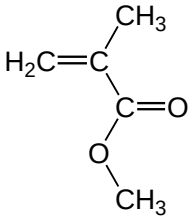
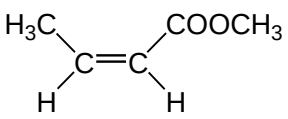
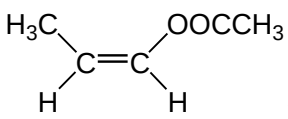
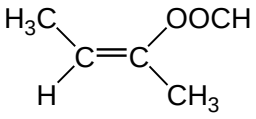
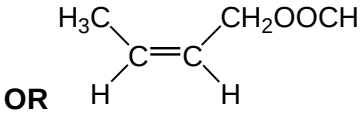
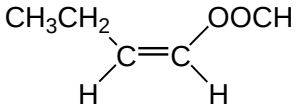
Question	Marking Guidance	Mark	Comments
8(a)(i)	(nucleophilic) <u>addition-elimination</u>	1	Not electrophilic addition-elimination Ignore esterification
	M2  M1 M4 for 3 arrows and lp M3 for structure	4	• If wrong nucleophile used or O–H broken in first step, can only score M2 • M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • If Cl lost with C=O breaking lose M2 • M3 for correct structure <u>with charges</u> but lone pair on O is part of M4 • Only allow M4 after correct / very close M3 • Ignore HCl shown as a product
	a 20-50 (ppm) or single value or range entirely within this range	1	If values not specified as a or b then assume first is a
	b 50-90 (ppm) or single value or range entirely within this range	1	

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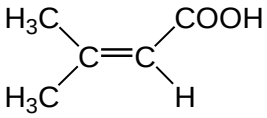
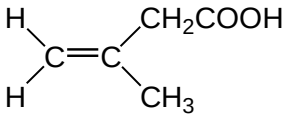
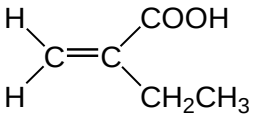
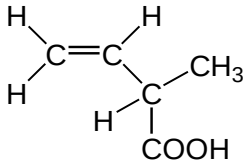
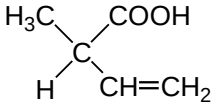
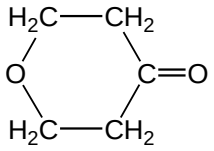
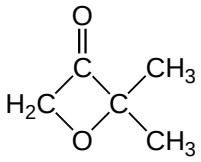
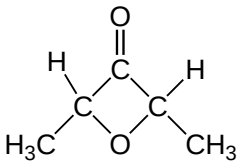
8(a)(ii)	—O—$CH_2CH_2CH_2CH_2$—C(=O)— **OR** —$CH_2CH_2CH_2CH_2$—C(=O)—O—	1	Must have trailing bonds, but ignore *n* Allow —O—$(CH_2)_4$—C(=O)—
	OR –$OCH_2CH_2CH_2CH_2CO$– **OR** –$CH_2CH_2CH_2CH_2COO$– one unit only		
	Condensation	1	but not - C_4H_{8-}

8(b)		Tollens'	Fehling's / Benedicts	Acidified potassium dichromate	1	Penalise wrong formula for Tollens or missing acid with potassium dichromate but mark on. Ignore 'clear', 'nothing'. Penalise wrong starting colour for dichromate.
	J	No reaction / no (visible) change / no silver mirror	No reaction / no (visible) change / stays blue / no red ppt	No reaction / no (visible) change / stays orange/ does not turn green	1	
	K	Silver <u>mirror</u> / grey <u>ppt</u>	Red <u>ppt</u> (allow brick red or red-orange)	(orange) turns green	1	
	J	Two (peaks)			1	Allow trough, peak, spike. Ignore details of splitting. If values not specified as J or K then assume first is J
	K	Four (peaks)			1	

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<table>
<tr><td rowspan="3">8(c)</td><td></td><td colspan="3">If all the structures are unlabelled, assume that the first drawn ester is L, the second ester is M; the first drawn acid is N, the second P. The cyclic compound should be obvious.</td></tr>
<tr><td>L
ester</td><td> 
OR $H_2C=C(CH_3)COOCH_3$</td><td>1</td><td>All $C_5H_8O_2$ L to P must have C=C
Allow CH_3–
Allow $-CO_2CH_3$ etc
Allow $CH_2C(CH_3)COOCH_3$</td></tr>
<tr><td>M
ester</td><td>  OR  OR 
$CH_3CH=CHCOOCH_3$ $CH_3CH=CHOOCCH_3$ $CH_3CH=C(CH_3)OOCH$
  OR 
OR
$CH_3CH=CHCH_2OOCH$ $CH_3CH_2CH=CHOOCH$</td><td>1</td><td>Allow either E–Z isomer.
Allow CH_3– or C_2H_5- but not CH_2CH_3–
Allow $CH_3CHCHCOOCH_3$ etc.</td></tr>
</table>

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	N acid	 **OR**  **OR**  $(CH_3)_2C=CHCOOH$ $H_2C=C(CH3)CH_2COOH$ $H_2C=C(COOH)CH_2CH_3$	1 1	Allow CH_3– or C_2H_5- but not CH_2CH_3– Allow -CO_2H Not cyclic isomers. Not the optically active isomer  which is P anyway Allow $(CH_3)_2CCHCOOH$ etc.
	P acid	 $CH_3CH(COOH)CH=CH_2$	1	Allow -CO_2H Allow $CH_3CH(CO_2H)CHCH_2$ or $CH_3CH(CO_2H)C_2H_3$
	Q	 **OR**  **OR** 		Not cyclic esters

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General principles applied to marking CHEM4 papers by CMI+ (June 2014)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are <u>required information</u> to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a student gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

NB Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. <u>Spelling</u>

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

NB Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are <u>generally</u> ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the student to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a student provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

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F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

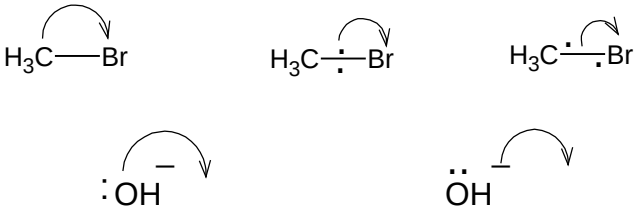
G. Marking calculations

In general

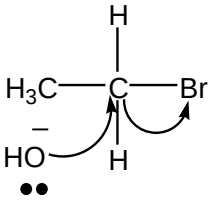
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



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When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

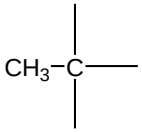
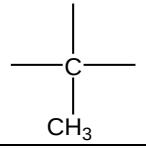
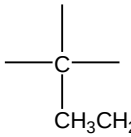
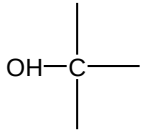
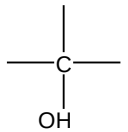
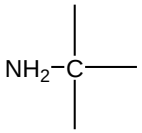
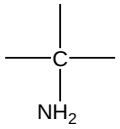
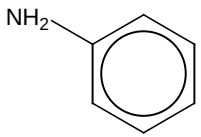
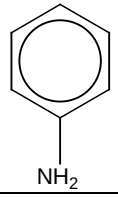
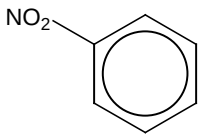
I. Organic structures

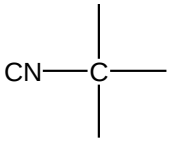
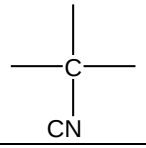
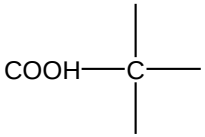
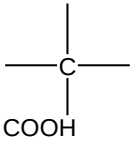
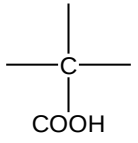
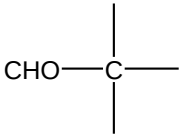
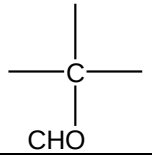
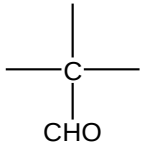
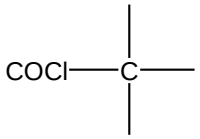
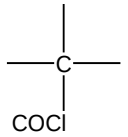
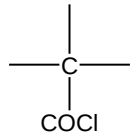
In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if students show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.

  By way of illustration, the following would apply.

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allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

					
not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of “sticks” to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.

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- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

NB Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
ethan-1,2-diol	should be **ethane-1,2-diol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
3	
4	
5	
6	
7	
8	
9	
TOTAL	

General Certificate of Education
Advanced Level Examination
June 2013

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 12 June 2013 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 75 minutes on **Section A** and about 30 minutes on **Section B**.

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Section A

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

1 This question involves the use of kinetic data to calculate the order of a reaction and also a value for a rate constant.

1 (a) The data in this table were obtained in a series of experiments on the rate of the reaction between compounds **E** and **F** at a constant temperature.

Experiment	Initial concentration of **E** / mol dm^{-3}	Initial concentration of **F** / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.15	0.24	0.42×10^{-3}
2	0.45	0.24	3.78×10^{-3}
3	0.90	0.12	7.56×10^{-3}

1 (a) (i) Deduce the order of reaction with respect to **E**.

.....

(1 mark)

(*Space for working*) .....

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1 (a) (ii) Deduce the order of reaction with respect to **F**.

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(1 mark)

(*Space for working*) .....

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Do not write outside the box

1 (b) The data in the following table were obtained in two experiments on the rate of the reaction between compounds **G** and **H** at a constant temperature.

Experiment	Initial concentration of **G** / mol dm^{-3}	Initial concentration of **H** / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
4	3.8×10^{-2}	2.6×10^{-2}	8.6×10^{-4}
5	6.3×10^{-2}	7.5×10^{-2}	To be calculated

The rate equation for this reaction is

$$rate = k[\mathbf{G}]^2[\mathbf{H}]$$

1 (b) (i) Use the data from Experiment **4** to calculate a value for the rate constant k at this temperature. Deduce the units of k.

Calculation .....

.....

.....

.....

Units .....

.....

(3 marks)

1 (b) (ii) Calculate a value for the initial rate of reaction in Experiment **5**.

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.....

(1 mark)

6

Turn over ▶

Do not write outside the box

2 When heated above 100 °C, nitrosyl chloride (NOCl) partly decomposes to form nitrogen monoxide and chlorine as shown in the equation.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

2 (a) A 2.50 mol sample of NOCl was heated in a sealed container and equilibrium was established at a given temperature. The equilibrium mixture formed contained 0.80 mol of NO

Calculate the amount, in moles, of Cl_2 and of NOCl in this equilibrium mixture.

Moles of Cl_2 .....

Moles of NOCl .....

(2 marks)

2 (b) A different mixture of NOCl, NO and Cl_2 reached equilibrium in a sealed container of volume 15.0 dm^3. The equilibrium mixture formed contained 1.90 mol of NOCl and 0.86 mol of NO at temperature *T*.

The value of K_c for the equilibrium at temperature *T* was 7.4×10^{-3} mol dm^{-3}.

2 (b) (i) Write an expression for the equilibrium constant K_c

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(1 mark)

2 (b) (ii) Calculate the amount, in moles, of Cl_2 in this equilibrium mixture.

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(4 marks)

(Extra space) .....

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Do not write outside the box

2 (b) (iii) Consider this alternative equation for the equilibrium at temperature *T*.

$$NOCl(g) \rightleftharpoons NO(g) + \tfrac{1}{2}Cl_2(g)$$

Calculate a value for the different equilibrium constant K_c for the equilibrium as shown in this alternative equation. Deduce the units of this K_c

Calculation .....

.....

.....

.....

Units .....

.....

(2 marks)

9

Turn over for the next question

Do not write outside the box

3 This question is about Brønsted–Lowry acids of different strengths.

3 (a) State the meaning of the term *Brønsted–Lowry acid*.

.....

(1 mark)

3 (b) (i) Write an expression for the acid dissociation constant K_a for ethanoic acid.

.....

.....

(1 mark)

3 (b) (ii) The value of K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 25 ºC.

Calculate the concentration of ethanoic acid in a solution of the acid that has a pH of 2.69

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(4 marks)

3 (c) The value of K_a for chloroethanoic acid ($ClCH_2COOH$) is 1.38×10^{-3} mol dm^{-3} at 25 ºC.

3 (c) (i) Write an equation for the dissociation of chloroethanoic acid in aqueous solution.

.....

(1 mark)

3 (c) (ii) Suggest why chloroethanoic acid is a stronger acid than ethanoic acid.

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(2 marks)

Do not write outside the box

3 (d) **P** and **Q** are acids. **X** and **Y** are bases. The table shows the strength of each acid and base.

Acids		Bases	
strong	weak	strong	weak
P	**Q**	**X**	**Y**

The two acids were titrated separately with the two bases using methyl orange as indicator.
The titrations were then repeated using phenolphthalein as indicator.
The pH range for methyl orange is 3.1–4.4
The pH range for phenolphthalein is 8.3–10.0

For each of the following titrations, select the letter, **A**, **B**, **C**, or **D**, for the correct statement about the indicator(s) that would give a precise end-point.
Write your answer in the box provided.

A Both indicators give a precise end-point.

B **Only** methyl orange gives a precise end-point.

C **Only** phenolphthalein gives a precise end-point.

D Neither indicator gives a precise end-point.

3 (d) (i) Acid **P** with base **X** ☐

(1 mark)

3 (d) (ii) Acid **Q** with base **X** ☐

(1 mark)

3 (d) (iii) Acid **Q** with base **Y** ☐

(1 mark)

Question 3 continues on the next page

Do not write outside the box

3 (e) Using a burette, 26.40 cm^3 of 0.550 mol dm^{-3} sulfuric acid were added to a conical flask containing 19.60 cm^3 of 0.720 mol dm^{-3} aqueous sodium hydroxide.
Assume that the sulfuric acid is fully dissociated.

Calculate the pH of the solution formed.

Give your answer to 2 decimal places.

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(6 marks)

(Extra space) .....

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18

Do not write outside the box

4 This question is about acylium ions, $[RCO]^+$

4 (a) The acylium ion $H_3C-\overset{+}{C}=O$ is formed in a mass spectrometer by fragmentation of the molecular ion of methyl ethanoate.

Write an equation for this fragmentation.

Include in your answer a displayed formula for the radical formed.

.....

(2 marks)

4 (b) The acylium ion $H_3C-\overset{+}{C}=O$ can also be formed from ethanoyl chloride. The ion reacts with benzene to form $C_6H_5COCH_3$

4 (b) (i) Write an equation to show the formation of this acylium ion by the reaction of ethanoyl chloride with **one** other substance.

.....

(2 marks)

4 (b) (ii) Name and outline a mechanism for the reaction of benzene with this acylium ion.

Name of mechanism .....

Mechanism

(4 marks)

4 (b) (iii) Ethanoic anhydride also reacts with benzene to form $C_6H_5COCH_3$

Write an equation for this reaction.

.....

(1 mark)

9

Do not write outside the box

5 Lactic acid, $CH_3CH(OH)COOH$, is formed in the human body during metabolism and exercise. This acid is also formed by the fermentation of carbohydrates such as sucrose, $C_{12}H_{22}O_{11}$

5 (a) (i) Give the IUPAC name for lactic acid.

.....

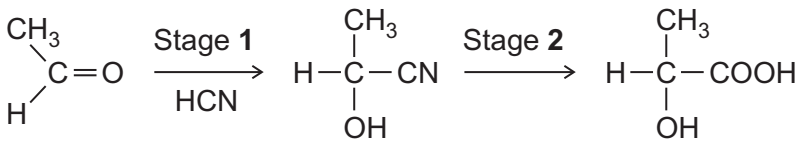
(1 mark)

5 (a) (ii) Write an equation for the formation of lactic acid from sucrose and water.

.....

(1 mark)

5 (b) A molecule of lactic acid contains an asymmetric carbon atom.
The lactic acid in the body occurs as a single enantiomer.
A racemic mixture (racemate) of lactic acid can be formed in the following two-stage synthesis.



5 (b) (i) Name and outline a mechanism for Stage **1**.

Name of mechanism .....

Mechanism

(5 marks)

Do not write outside the box

5 (b) (ii) Give the meaning of the term *racemic mixture (racemate)*.

.....

.....

.....

(1 mark)

5 (b) (iii) Explain how you could distinguish between a racemic mixture (racemate) of lactic acid and one of the enantiomers of lactic acid.

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(2 marks)

5 (c) A mixture of lactic acid and its salt sodium lactate is used as an acidity regulator in some foods. An acidity regulator makes sure that there is little variation in the pH of food.

5 (c) (i) Write an equation for the reaction of lactic acid with sodium hydroxide.

.....

(1 mark)

5 (c) (ii) The acid dissociation constant K_a for lactic acid has the value 1.38×10^{-4} mol dm^{-3} at 298 K.

Calculate the pH of an equimolar solution of lactic acid and sodium lactate.

.....

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.....

(2 marks)

Question 5 continues on the next page

Turn over ▶

Do not write outside the box

5 (c) (iii) Suggest an alternative name for the term *acidity regulator*.
Explain how a mixture of lactic acid and sodium lactate can act as a regulator when natural processes increase the acidity in some foods.

Name .....

Explanation .....

.....

.....

.....

(3 marks)

(Extra space) .....

.....

5 (d) The cup shown is made from PLA, poly(lactic acid).
PLA is the condensation polymer formed from lactic acid.



The polymer is described as 100% biodegradable and 100% compostable.

Compostable material breaks down slowly in contact with the moist air in a garden bin. This produces compost that can be used to improve soil.

The manufacturers stress that PLA cups differ from traditional plastic cups that are neither biodegradable nor compostable.

5 (d) (i) Draw a section of PLA that shows **two** repeating units.

(2 marks)

Do not write outside the box

5 (d) (ii) Name the type of condensation polymer in PLA.

.....

(1 mark)

5 (d) (iii) An intermediate in the production of PLA is a cyclic compound ($C_6H_8O_4$) that is formed from two PLA molecules.

Draw the structure of this cyclic compound.

(1 mark)

5 (d) (iv) Traditional non-biodegradable plastic cups can be made from poly(phenylethene), commonly known as *polystyrene*.

Draw the repeating unit of poly(phenylethene).

(1 mark)

5 (d) (v) The manufacturers of PLA claim that the material will break down to compost in just 12 weeks.

Suggest **one** reason why PLA in landfill may take longer than 12 weeks to break down.

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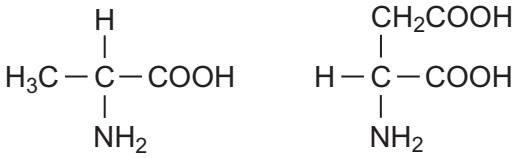
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(1 mark)

22

Do not write outside the box

6 Alanine and aspartic acid are naturally occurring amino acids.



alanine

aspartic acid

6 (a) Draw the structure of the zwitterion formed by alanine.

(1 mark)

6 (b) Draw the structure of the compound formed when alanine reacts with methanol in the presence of a small amount of concentrated sulfuric acid.

(1 mark)

6 (c) Draw the structure of the species formed by aspartic acid at high pH.

(1 mark)

6 (d) Draw the structure of a dipeptide formed by two aspartic acid molecules.

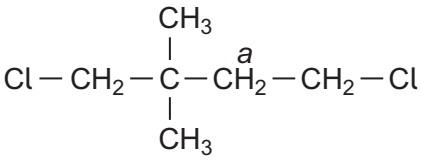
(1 mark)

4

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7 N.m.r. spectroscopy can be used to study the structures of organic compounds.

7 (a) Compound **J** was studied using ^{1}H n.m.r. spectroscopy.



J

7 (a) (i) Identify a solvent in which **J** can be dissolved before obtaining its ^{1}H n.m.r. spectrum.

.....

(1 mark)

7 (a) (ii) Give the number of peaks in the ^{1}H n.m.r. spectrum of **J**.

.....

(1 mark)

7 (a) (iii) Give the splitting pattern of the protons labelled *a*.

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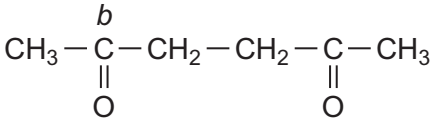
(1 mark)

7 (a) (iv) Give the IUPAC name of **J**.

.....

(1 mark)

7 (b) Compound **K** was studied using ^{13}C n.m.r. spectroscopy.



K

7 (b) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of **K**.

.....

(1 mark)

7 (b) (ii) Use **Table 3** on the Data Sheet to suggest a δ value of the peak for the carbon labelled *b*.

.....

(1 mark)

7 (b) (iii) Give the IUPAC name of **K**.

.....

(1 mark)

7

Turn over ▶

Do not write outside the box

Section B

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

8 This question is about the primary amine $CH_3CH_2CH_2NH_2$

8 (a) The amine $CH_3CH_2CH_2NH_2$ reacts with CH_3COCl

Name and outline a mechanism for this reaction.

Give the IUPAC name of the organic product.

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(6 marks)

Do not write outside the box

8 (b) Isomers of $CH_3CH_2CH_2NH_2$ include another primary amine, a secondary amine and a tertiary amine.

8 (b) (i) Draw the structures of these **three** isomers.
Label each structure as primary, secondary or tertiary.

(3 marks)

8 (b) (ii) Use **Table 1** on the Data Sheet to explain how you could use infrared spectra in the range outside the fingerprint region to distinguish between the secondary amine and the tertiary amine.

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(2 marks)

Question 8 continues on the next page

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8 (c) The amine $CH_3CH_2CH_2NH_2$ can be prepared by two different routes.

Route **A** is a two-stage process and starts from CH_3CH_2Br

Route **B** is a one-stage process and starts from $CH_3CH_2CH_2Br$

8 (c) (i) Identify the intermediate compound in Route **A**.

Give the reagents and conditions for both stages in Route **A** and the single stage in Route **B**.

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(7 marks)

8 (c) (ii) Give **one** disadvantage of Route **A** and **one** disadvantage of Route **B**.

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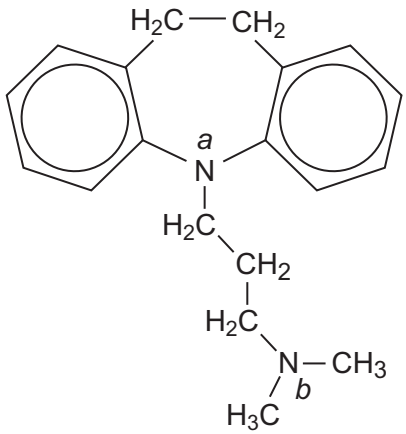
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(2 marks)

20

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9 Imipramine has been prescribed as an antidepressant. The structure of imipramine is shown below.



9 (a) The medicine is usually supplied as a salt. The salt is formed when one mole of imipramine reacts with one mole of hydrochloric acid.

Suggest why the nitrogen atom labelled *b* is more likely to be protonated than the nitrogen atom labelled *a* when the salt is formed.

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(3 marks)

9 (b) Deduce the molecular formula of imipramine and give the number of peaks in its ^{13}C n.m.r. spectrum.

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(2 marks)

END OF QUESTIONS

5

There are no questions printed on this page

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Version 1.0

General Certificate of Education (A-level)
June 2013

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for standardisation each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

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Question	Marking Guidance	Mark	Comments
1(a)(i)	2 or two or second or $[E]^2$	1	
1(a)(ii)	1 or one or first or $[F]^1$ or [F]	1	
1(b)(i)	$k = \frac{8.6 \times 10^{-4}}{(3.8 \times 10^{-2})^2 \times (2.6 \times 10^{-2})}$	1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc. AE (-1) for copying numbers wrongly or swapping two numbers.
	= 22.9 (Allow 22.9 – 24 after correct rounding)	1	
	$\underline{mol^{-2}\,dm^{+6}\,s^{-1}}$	1	Any order.
1(b)(ii)	$6.8(2) \times 10^{-3}$ (mol $dm^{-3}s^{-1}$) ***OR*** if their k is wrong, award the mark consequentially a quick check can be achieved by using $\frac{\text{their answer}}{\text{their k}}$ = 2.9768×10^{-4} Allow $2.9 – 3.1 \times 10^{-4}$ for the mark	1	Allow 6.8×10^{-3} to 6.9×10^{-3} Ignore units.

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Question		Marking Guidance	Mark	Comments
2(a)		Cl_2 0.4	1	
		NOCl 1.7	1	
2(b)(i)		$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$	1	Penalise expression containing V Allow ( ) here, but must have all brackets. If K_c expression wrong, max 2 in (b)(ii) for M1 for correct rearrangement of their K_c and M4 for multiplying by 15
2(b)(ii)	M1	$[Cl_2] = K_c \times \frac{[NOCl]^2}{[NO]^2}$	1	Mark is for rearrangement of correct K_c expression. If K_c rearrangement wrong, can only score max 2 for: M3 and M4
	M2	$[Cl_2] = \frac{(7.4\times10^{-3})\times(1.90/15)^2}{(0.86/15)^2}$ $(= \frac{(7.4\times10^{-3})\times(0.127)^2}{(0.0573)^2})$	1	Rounding 1.90/15 wrongly to 0.126 is AE
	M3	$[Cl_2]$ = 0.0361 to 0.0365 (min 2 sfs)	1	Mark for correct calculation of $[Cl_2]$
	M4	mol Cl_2 = 0.54 to 0.55	1	**Correct answer scores 4 ignore working** Mark is for <u>answer</u> of (M3 × 15)

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2(b)(iii)	($\sqrt{(7.4 \times 10^{-3})}$ =) 0.086 Allow 0.085 to 0.086)	1	Mark for answer ***OR*** conseq on their Cl_2 $K_c = \sqrt{\frac{M4}{15}} \times \frac{0.86}{1.90} = \sqrt{M4} \times 0.117$ Or $\sqrt{M3} \times 0.453$
	$\underline{mol^{½}\ dm^{-3/2}}$ ***OR*** $\underline{mol^{0.5}\ dm^{-1.5}}$	1	NOT $\sqrt{moldm^{-3}}$ nor $(mol\ dm^{-3})^{1/2}$

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Question		Marking Guidance	Mark	Comments
3(a)		Proton donor or H^+ donor	1	
3(b)(i)		$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$ or $\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$	1	If K_a wrong, can only score M1 below. Must be ethanoic acid not HA Must have square brackets (penalise here only) but mark on in (b)(ii).
3(b)(ii)	M1	$[H^+] = 10^{-2.69}$ ***OR*** 2.042×10^{-3} (mol dm^{-3})	1	
	M2	$[CH_3COOH] = \frac{[H^+]^2}{K_a}$	1	Ignore ( ) Mark for correctly rearranged expression incl $[H^+]^2$
	M3	$= \frac{(2.042 \times 10^{-3})^2}{1.75 \times 10^{-5}}$	1	If M2 wrong no further marks.
	M4	$= 0.238$ (mol dm^{-3}) Allow 0.229 – 0.24	1	
3(c)(i)		$ClCH_2COOH \rightleftharpoons ClCH_2COO^- + H^+$ ***OR*** $ClCH_2COOH + H_2O \rightleftharpoons ClCH_2COO^- + H_3O^+$	1	Allow $\rightarrow$ Allow $ClCH_2CO_2H$ and $ClCH_2CO_2^-$
3(c)(ii)	M1	Cl is (more electronegative so) withdraws electrons **OR** negative inductive effect of Cl	1	Ignore electronegativity. Ignore chloroethanoic acid has a lower K_a value. Allow Cl reduces +ve inductive effect of methyl group.
	M2	Weakens O—H bond ***OR*** O—H bond is more polar ***OR*** reduces negative charge on COO^- ***OR*** stabilizes COO^- (more)	1	M1 & M2 are independent marks. Ignore H^+ lost more easily.

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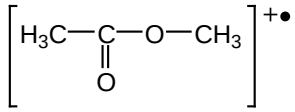
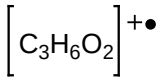
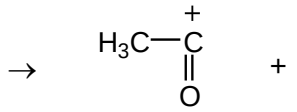
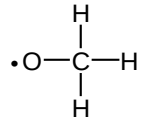
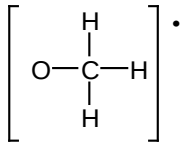
3(d)(i)	**A**		1	

3(d)(ii)	**C**		1	

3(d)(iii)	**D**		1	

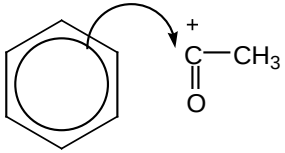
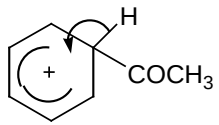
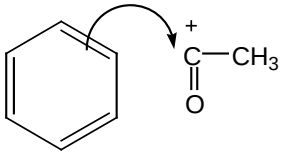
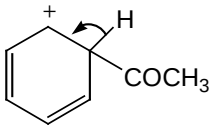
3(e)	M1	Mol NaOH = mol OH^- = $(19.6 \times 10^{-3}) \times 0.720 = 1.41(1) \times 10^{-2}$	1	Mark for answer.
	M2	Mol H_2SO_4 = $(26.4 \times 10^{-3}) \times 0.550 = 1.45(2) \times 10^{-2}$	1	Mark for answer.
	M3	Mol H^+ added = **2 ×** $(1.452 \times 10^{-2}) = 2.90(4) \times 10^{-2}$ ***OR*** XS mol H_2SO_4 = $7.46(4) \times 10^{-3}$	1	If factor × 2 missed completely (pH = 2.05) or used wrongly later, can score max 4 for M1, M2, M5 & M6
	M4	XS mol H^+ = 0.0149(3)	1	
	M5	For dividing by volume $[H^+] = 0.0149(3) \times (1000 / 46.0) = 0.324 – 0.325$ mol dm^{-3}	1	If no use or wrong use of volume lose M5 and M6 ie can score 4 for pH = 1.83 (no use of vol) Treat missing 1000 as AE (-1) & score 5 for pH = 3.49
	M6	pH = 0.49	1	**2dp** (penalise more or less).
				If × 2 missed & vol not used, pH=3.39 scores M1 & M2 only.

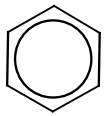
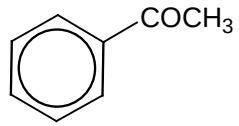
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Question	Marking Guidance	Mark	Comments
4(a)	  ***OR***	1	NOT penalise missing brackets. If wrong ester, no further mark.
	 Must be displayed formula  (1) Radical dot must be on O Ignore lone pair(s) on O in addition to single electron	1	Allow radical with brackets as  Ignore errors in acylium ion.

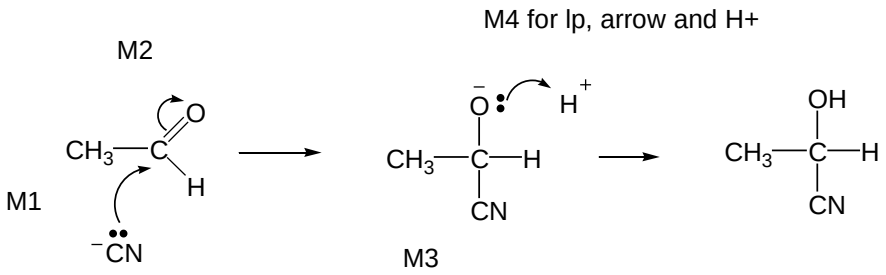
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4(b)(i)	$AlCl_3$ or $FeCl_3$	1	If wrong no further marks.
	$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$	1	Correct equation scores 2 - contrast with 4(b)(iii) Allow + on C or O in equation.

4(b)(ii)	Electrophilic substitution	1	Ignore Friedel crafts.
	M1  M3  M2 ***OR*** M1  M3  M2	3	• + must be on C of RCO here • M1 arrow from within hexagon to C or to + on C • Gap in horseshoe must approximately be centred around C1 and not extend towards C1 beyond C2 and C6 • + not too close to C1 • M3 arrow into hexagon unless Kekule • allow M3 arrow independent of M2 structure, i.e. + on H in intermediate loses M2 not M3 • ignore base removing H for M3

4(b)(iii)	$(CH_3CO)_2O + C_6H_6 \rightarrow C_6H_5COCH_3 + CH_3COOH$ ***OR*** $(CH_3CO)_2O) +$   $+ CH_3COOH$	1	Correct equation scores 1 – contrast with 4(b)(i) Not allow molecular formula for ethanoic anhydride or ethanoic acid.

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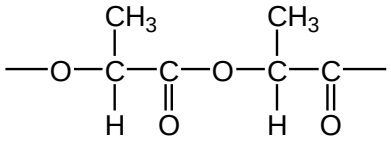
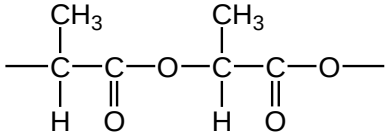
Question	Marking Guidance	Mark	Comments
5(a)(i)	2-hydroxypropanoic acid ***OR*** 2-hydroxypropan(-1-)oic acid	1	Do not penalise different or missing punctuation or extra spaces. Spelling must be exact and order of letters and numbers as here. Can ignore -1- before –oic, but penalise any other numbers here.
5(a)(ii)	$C_{12}H_{22}O_{11} + H_2O \rightarrow 4CH_3CH(OH)COOH$ ***OR*** $C_{12}H_{22}O_{11} + H_2O \rightarrow 2CH_3CH(OH)COOH + C_6H_{12}O_6$	1	Allow $4C_3H_6O_3$ Allow $2C_3H_6O_3$
5(b)(i)	Nucleophilic addition	1	
		4	• M1 lp and minus must be on C • M1 and M4 include lone pair and curly arrow. • M2 not allowed independent of M1, but allow following some attempt at attack on carbonyl C • allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • M3 is for correct structure including minus sign but lone pair is part of M4 • Allow arrow in M4 to H of H-CN with arrow forming cyanide ion.
5(b)(ii)	Equal mixture of enantiomers / (optical) isomers	1	
5(b)(iii)	(Plane) polarized light	1	If missing no further mark.
	(Polarised light) rotated by single enantiomer but unaffected by racemate	1	Both needed; not allow bend, twist etc.

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5(c)(i)	$CH_3CH(OH)COOH + NaOH \rightarrow CH_3CH(OH)COONa + H_2O$ ***OR*** $CH_3CH(OH)COOH + OH^- \rightarrow CH_3CH(OH)COO^- + H_2O$	1	Not ambiguous mol formulae for product - must show COONa or CO_2Na or COO^- or CO_2^-

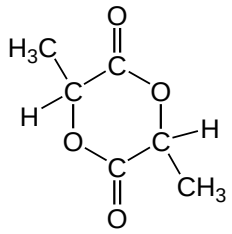
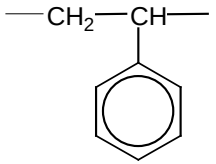
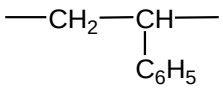
5(c)(ii)	$[H^+] = K_a$ ***OR*** $pH = pK_a$	1	
	pH = 3.86	1	Allow more than 2 decimal places but not fewer.

5(c)(iii)	M1	buffer	1	Ignore acidic but penalise alkaline or basic.
	Any two out of the three marks M2 , M3 & M4			
	M2	Large lactate concentration in buffer ***OR*** sodium lactate completely ionised	Max 2	
	M3	added acid reacts with/is removed by lactate ion or A^- or sodium lactate or salt ***OR*** equation $H^+ + A^- \rightarrow HA$		Ignore reaction of H^+ with OH^- Ignore reference to equilibrium unless it is shown.
	M4	ratio $[HA]/[A^-]$ stays almost constant		Ignore H^+ or pH remains constant.

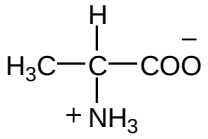
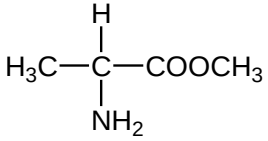
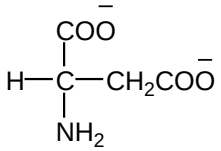
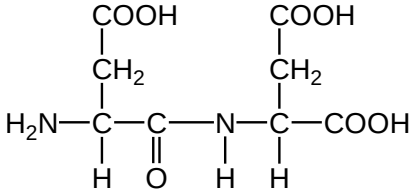
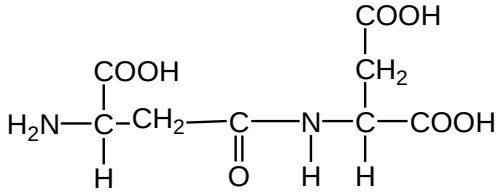
5(d)(i)	 ***OR*** 	No marks if ester link missing Correct ester link allow —COO— All rest correct with trailing bonds	1 1	**NB Correct answer scores 2** Ignore *n* here (compare with 5(d)(iv). Ignore brackets. If OH or COOH on either or both ends, lose one, ie dimer scores 1 If more than two repeating units, lose 1

5(d)(ii)	(Poly)ester ie allow ester	1	Not terylene. Ignore spaces and brackets in answer.

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5(d)(iii)		1	Allow any cyclic $C_6H_8O_4$
5(d)(iv)	 ***OR*** 	1	Penalise *n* here (compare with 5(d)(i) Ignore brackets. Not allow Ph for phenyl.
5(d)(v)	In landfill, no air or UV, to assist decay ***OR*** not enough water or moisture (to hydrolyse polyester)	1	Allow landfill has/contains: no or few bacteria / micro-organisms / enzymes compared with compost heap ***OR*** less oxygen ***OR*** lower temperature.

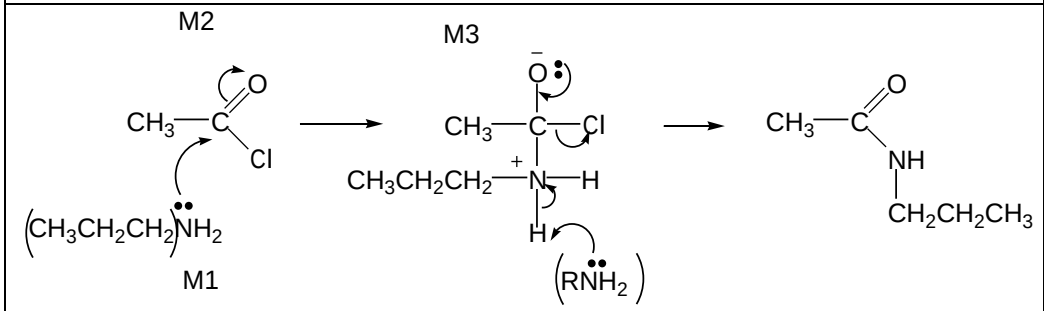
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Question	Marking Guidance	Mark	Comments
6(a)		1	Allow $-NH_3^+$ and $^+NH_3-$
6(b)		1	Allow protonated form, i.e. $-NH_3^+$ or $^+NH_3-$
6(c)		1	Allow $-CO_2^-$
6(d)		1	Allow zwitterion with any COO^- Allow use of "wrong" COOH 

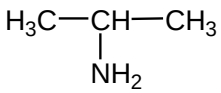
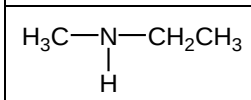
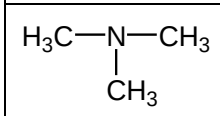
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Question	Marking Guidance	Mark	Comments
7(a)(i)	$CDCl_3$ or CD_2Cl_2 or C_6D_6 or CCl_4	1	Not D_2O Allow CD_3Cl
7(a)(ii)	4 or four	1	
7(a)(iii)	Triplet or 3 or three	1	
7(a)(iv)	1,4-dichloro-2,2-dimethylbutane	1	Do not penalise different or missing punctuation or extra spaces. Spelling must be exact and order of letters and numbers as here.
7(b)(i)	3 or three	1	
7(b)(ii)	190-220 (cm^{-1})	1	Allow a single number within the range. ***OR*** a smaller range entirely within this range.
7(b)(iii)	hexan**e**-2,5-dione	1	Do not penalise different or missing punctuation or extra spaces. Spelling must be exact and order of letters and numbers as here. NB so must have middle e

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Question	Marking Guidance	Mark	Comments
8(a)	(nucleophilic) addition-elimination	1	
	 M4 for 3 arrows and lp Allow wrong amine in M1 but penalise in M3 Allow C_3H_7 in M3 Minus sign on NH_3 loses M1 (but not M4 if NH_3 also shown here)	4	• Allow attack by **:**$NH_2CH_2CH_2CH_3$ • M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • If Cl lost with C=O breaking, max1 for M1 • M3 for correct structure <u>with charges</u> but lone pair on O is part of M4 • 3 arrows in M4 can be shown in two separate steps. • If M3 drawn twice, mark first answer eg ignore missing + if missed off second structure • Only allow M4 after correct / very close M3 • For M4, ignore RNH_2 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism, • but ignore HCl shown as a product.
	<u>N-propylethanamide</u> must be this name even if wrong amine used	1	NOT N-propylethaneamide

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8(b)(i)	 Primary	Not allow ambiguous $C_3H_7NH_2$ BEWARE No mark for the original amine $CH_3CH_2CH_2NH_2$	1	Label and structure must both be correct for each type to score the mark. Penalize wrong number of carbons but otherwise correct, first time only.
	 secondary	Allow C_2H_5	1	
	 tertiary		1	

8(b)(ii)	Absorption at <u>3300-3500</u> (cm^{-1}) in spectrum	1	Allow trough, peak, spike. Ignore absorption at 750 – 1100 for C—C bond in secondary - this is within fingerprint region. Allow any number in this range. If range missing, no further marks. If range linked to tertiary, no further marks.
	N—H (bond) (only) present in secondary amine or not present in tertiary amine ***OR*** This peak or N—H absorption (only) present in spectrum of secondary amine or not present in spectrum of tertiary amine	1	

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8(c)(i)	M1	Route **A** : stage 1	KCN		1	Apply list principle for extra reagents or catalysts NOT HCN NOT KCN/acid Not KCN/HCN
	M2		Aqueous or ethanolic		1	M2 only scores after correct M1 ignore warm; acid here loses M1 & M2
	M3	Route **A** Intermediate	CH_3CH_2CN or propanenitrile Name alone must be exactly correct to gain M1 but mark on if name close correct formula gains M1 (ignore name if close) contradiction of name and formula loses mark		1	If M3 intermediate wrong, max 2 for M1 & M2 ie no mark for stage 2 But if M3 intermediate close, eg "nitrile" or wrong nitrile, can award marks in stage 2 If stage 1 correct and intermediate is missing, can award marks in stage 2 stage 1 wrong & intermediate missing, no marks.
	M4	Route **A** : stage 2	H_2 H loses M4 but mark on	$LiAlH_4$	1	Apply list principle for extra reagents or catalysts. M5 only scores after correct M4 Not $NaBH_4$ not Sn or Fe / HCl Allow (dil) acid after but not with $LiAlH_4$ Penalise conc acid.
	M5		Ni or Pt or Pd	ether	1	
	M6	Route **B**	NH_3		1	With acid loses M6 & M7 Apply list principle for extra reagents or catalysts.
	M7		Excess NH_3		1	Ignore conc, ignore high P, ignore solvent.

8(c)(ii)	Route **A** disadv	Toxic /poisonous KCN or cyanide or CN^- or HCN	Expensive $LiAlH_4$ Ignore acidified	1	Allow H_2 flammable/explosive etc. Not just dangerous. Ignore time reasons.
		OR lower <u>yield</u> because 2 steps			
	Route **B** disadv	Further reaction/substitution likely		1	Allow impure product.

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Question		Marking Guidance	Mark	Comments
9(a)	M1	Lone pair on N labelled b more available / more able to be donated than lone pair on N labelled *a*	1	Ignore N(b) more readily accepts protons. Ignore N(b) is stronger base.
	M2	lp or electrons or electron density on N labelled *a:* delocalized into (benzene) ring	1	QoL
	M3	lp or electrons or electron density on N labelled *b:* methyl/alkyl groups electron releasing or donating or (positive) inductive effect or push electrons or electron density	1	QoL
9(b)		$C_{19}H_{24}N_2$	1	Any order.
		11	1	

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General principles applied to marking CHEM4 papers by CMI+ (June 2013)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

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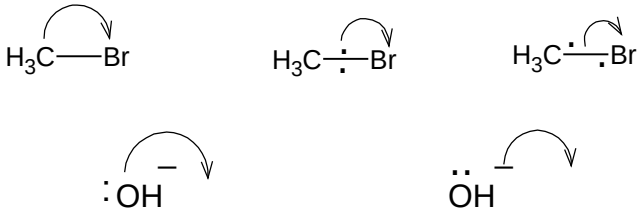
G. Marking calculations

In general

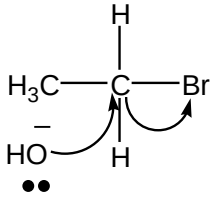
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

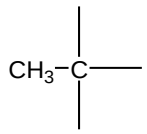
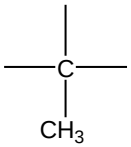
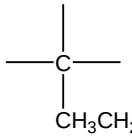
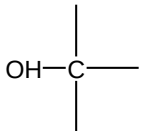
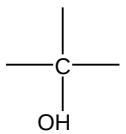
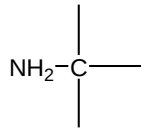
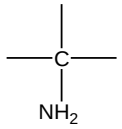
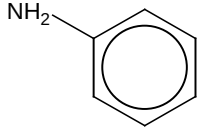
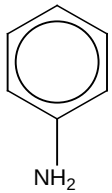
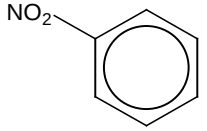
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In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

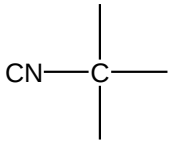
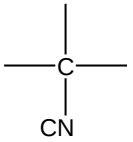
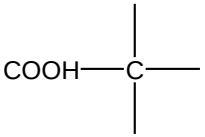
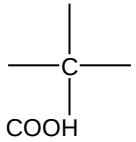
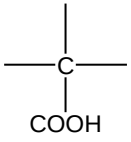
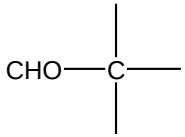
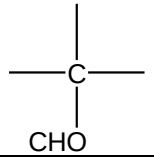
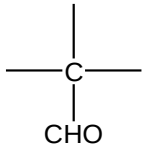
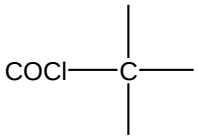
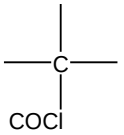
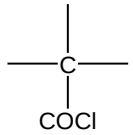
I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g. nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

				
allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

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not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
ethan-1,2-diol	should be **ethane-1,2-diol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
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TOTAL	

General Certificate of Education
Advanced Level Examination
January 2013

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Monday 14 January 2013 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use scientific terminology accurately.

Advice
- You are advised to spend about 75 minutes on **Section A** and about 30 minutes on **Section B**.

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Section A

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

1 (a) The data in the following table were obtained in two experiments about the rate of the reaction between substances **B** and **C** at a constant temperature.

Experiment	Initial concentration of **B** / mol dm^{-3}	Initial concentration of **C** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	4.2×10^{-2}	2.6×10^{-2}	8.4×10^{-5}
2	6.3×10^{-2}	7.8×10^{-2}	To be calculated

The rate equation for this reaction is known to be

$$\text{rate} = k[\mathbf{B}]^2[\mathbf{C}]$$

1 (a) (i) Use the data from Experiment **1** to calculate a value for the rate constant k at this temperature and deduce its units.

Calculation .....

.....

.....

.....

.....

Units .....

.....

(3 marks)

(Extra space) .....

.....

1 (a) (ii) Calculate a value for the initial rate in Experiment **2**.

.....

.....

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(1 mark)

Do not write outside the box

1 (b) The data in the following table were obtained in a series of experiments about the rate of the reaction between substances **D** and **E** at a constant temperature.

Experiment	Initial concentration of **D** / mol dm^{-3}	Initial concentration of **E** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
3	0.13	0.23	0.26×10^{-3}
4	0.39	0.23	2.34×10^{-3}
5	0.78	0.46	9.36×10^{-3}

1 (b) (i) Deduce the order of reaction with respect to **D**.

.....

.....

.....

(1 mark)

1 (b) (ii) Deduce the order of reaction with respect to **E**.

.....

.....

.....

(1 mark)

Question 1 continues on the next page

Do not write outside the box

1 (c) The compound $(CH_3)_3CBr$ reacts with aqueous sodium hydroxide as shown in the following equation.

$$(CH_3)_3CBr + OH^- \longrightarrow (CH_3)_3COH + Br^-$$

This reaction was found to be first order with respect to $(CH_3)_3CBr$ but zero order with respect to hydroxide ions.

The following two-step process was suggested.

Step **1** $(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-$

Step **2** $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3COH$

1 (c) (i) Deduce the rate-determining step in this two-step process.

.....

(1 mark)

1 (c) (ii) Outline a mechanism for this step using a curly arrow.

(1 mark)

8

Do not write outside the box

2 In this question, give all values of pH to 2 decimal places.

2 (a) The ionic product of water has the symbol K_w

2 (a) (i) Write an expression for the ionic product of water.

.....

(1 mark)

2 (a) (ii) At 42 °C, the value of K_w is 3.46×10^{-14} mol^2 dm^{-6}.

Calculate the pH of pure water at this temperature.

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(2 marks)

2 (a) (iii) At 75 °C, a 0.0470 mol dm^{-3} solution of sodium hydroxide has a pH of 11.36

Calculate a value for K_w at this temperature.

.....

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(2 marks)

Question 2 continues on the next page

Do not write outside the box

2 (b) Methanoic acid (HCOOH) dissociates slightly in aqueous solution.

2 (b) (i) Write an equation for this dissociation.

.....

(1 mark)

2 (b) (ii) Write an expression for the acid dissociation constant K_a for methanoic acid.

.....

.....

(1 mark)

2 (b) (iii) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.

Calculate the pH of a 0.0560 mol dm^{-3} solution of methanoic acid.

.....

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(3 marks)

2 (b) (iv) The dissociation of methanoic acid in aqueous solution is endothermic.

Deduce whether the pH of a solution of methanoic acid will increase, decrease or stay the same if the solution is heated. Explain your answer.

Effect on pH .....

Explanation .....

.....

.....

.....

(3 marks)

(Extra space) .....

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Do not write outside the box

2 (c) The value of K_a for methanoic acid is 1.78×10^{-4} mol dm^{-3} at 25 °C.
A buffer solution is prepared containing 2.35×10^{-2} mol of methanoic acid and 1.84×10^{-2} mol of sodium methanoate in 1.00 dm^3 of solution.

2 (c) (i) Calculate the pH of this buffer solution at 25 °C.

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(3 marks)

(Extra space) .....

.....

2 (c) (ii) A 5.00 cm^3 sample of 0.100 mol dm^{-3} hydrochloric acid is added to the buffer solution in part **(c) (i)**.

Calculate the pH of the buffer solution after this addition.

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(4 marks)

(Extra space) .....

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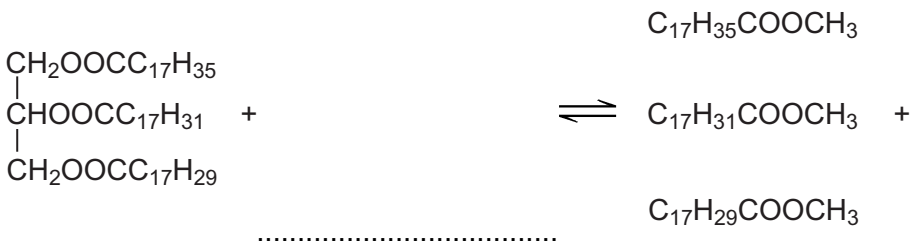
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3 Esters are produced by the reaction of alcohols with other esters and by the reaction of alcohols with carboxylic acids.

3 (a) The esters which make up biodiesel are produced industrially from the esters in vegetable oils.

3 (a) (i) Complete the equation for this formation of biodiesel.



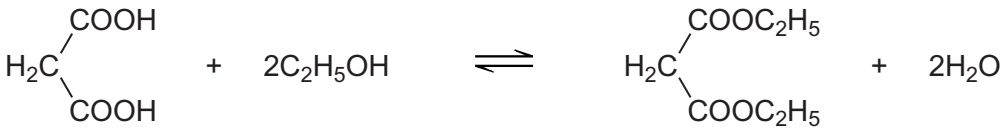
(2 marks)

3 (a) (ii) Write an equation for the complete combustion of $C_{17}H_{35}COOCH_3$

.....

(2 marks)

3 (b) The ester commonly known as diethyl malonate (**DEM**) occurs in strawberries and grapes. It can be prepared from acid **A** according to the following equilibrium.



A **DEM**

3 (b) (i) A mixture of 2.50 mol of **A** and 10.0 mol of ethanol was left to reach equilibrium in an inert solvent in the presence of a small amount of concentrated sulfuric acid. The equilibrium mixture formed contained 1.80 mol of **DEM** in a total volume, V dm^3, of solution.

Calculate the amount (in moles) of **A**, of ethanol and of water in this equilibrium mixture.

Moles of **A** .....

Moles of ethanol .....

Moles of water.....

(3 marks)

Do not write outside the box

3 (b) (ii) The total volume of the mixture in part **(b) (i)** was doubled by the addition of more of the inert solvent.

State and explain the effect of this addition on the equilibrium yield of **DEM**.

Effect .....

Explanation .....

.....

(2 marks)

3 (b) (iii) Using **A** to represent the acid and **DEM** to represent the ester, write an expression for the equilibrium constant K_c for the reaction.

.....

.....

(1 mark)

3 (b) (iv) In a second experiment, the equilibrium mixture was found to contain 0.85 mol of **A**, 7.2 mol of ethanol, 2.1 mol of **DEM** and 3.4 mol of water.

Calculate a value of K_c for the reaction and deduce its units.

Calculation.....

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Units.....

.....

(3 marks)

13

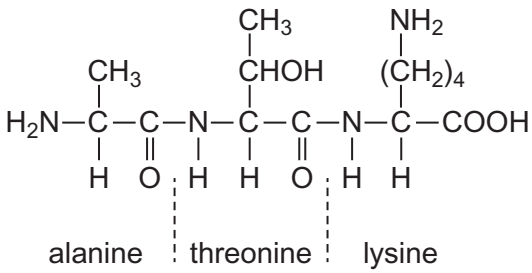
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ANSWER IN THE SPACES PROVIDED

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4 (a) The tripeptide shown is formed from the amino acids alanine, threonine and lysine.



4 (a) (i) Draw a separate circle around **each** of the asymmetric carbon atoms in the tripeptide.

(1 mark)

4 (a) (ii) Draw the zwitterion of alanine.

(1 mark)

4 (a) (iii) Give the IUPAC name of threonine.

.....

(1 mark)

4 (a) (iv) Draw the species formed by lysine at low pH.

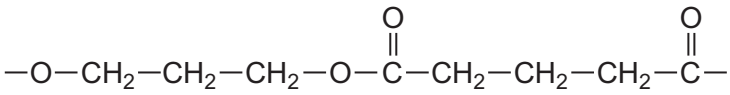
(1 mark)

Question 4 continues on the next page

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4 (b) The repeating unit shown represents a polyester.



4 (b) (i) Name this type of polymer.

.....

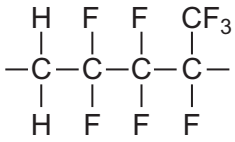
(1 mark)

4 (b) (ii) Give the IUPAC name for the alcohol used to prepare this polyester.

.....

(1 mark)

4 (c) The repeating unit shown represents a polyalkene co-polymer. This co-polymer is made from two different alkene monomers.



4 (c) (i) Name the type of polymerisation occurring in the formation of this co-polymer.

.....

(1 mark)

4 (c) (ii) Draw the structure of each alkene monomer.

Alkene monomer 1 Alkene monomer 2

(2 marks)

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4 (d) One of the three compounds shown in parts **(a)**, **(b)** and **(c)** **cannot** be broken down by hydrolysis.

Write the letter **(a)**, **(b)** or **(c)** to identify this compound and explain why hydrolysis of this compound does **not** occur.

Compound .....

Explanation .....

.....

.....

(2 marks)

11

Turn over for the next question

Do not write outside the box

5 This question concerns isomers of $C_6H_{12}O_2$ and how they can be distinguished using n.m.r. spectroscopy.

5 (a) The non-toxic, inert substance TMS is used as a standard in recording both ^1H and ^{13}C n.m.r. spectra.

5 (a) (i) Give **two** other reasons why TMS is used as a standard in recording n.m.r. spectra.

Reason 1 .....

.....

Reason 2 .....

.....

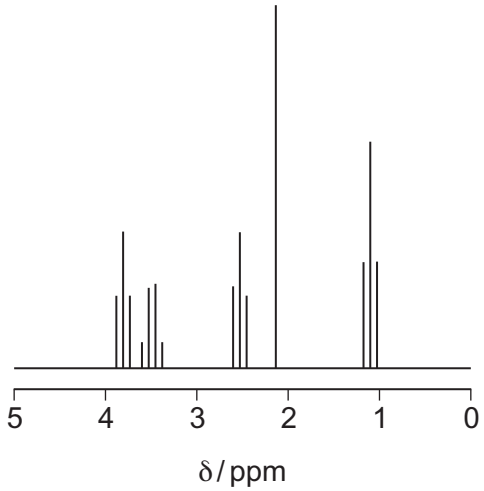
(2 marks)

5 (a) (ii) Give the structural formula of TMS.

(1 mark)

5 (b) The proton n.m.r. spectrum of compound **P** ($C_6H_{12}O_2$) is represented in **Figure 1**.

Figure 1



The integration trace gave information about the five peaks as shown in **Figure 2**.

Figure 2

δ / ppm	3.8	3.5	2.6	2.2	1.2
Integration ratio	2	2	2	3	3

Do not write outside the box

5 (b) (i) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peak at δ 2.2

(1 mark)

5 (b) (ii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.5 and 1.2

(1 mark)

5 (b) (iii) Use **Table 2** on the Data Sheet, **Figure 1** and **Figure 2** to deduce the structural fragment that leads to the peaks at δ 3.8 and 2.6

(1 mark)

5 (b) (iv) Deduce the structure of **P**.

(1 mark)

Question 5 continues on the next page

Do not write outside the box

5 (c) These questions are about different isomers of **P** ($C_6H_{12}O_2$).

5 (c) (i) Draw the structures of the two esters that both have only two peaks in their proton n.m.r. spectra. These peaks both have an integration ratio of 3:1

Ester 1

Ester 2

(2 marks)

5 (c) (ii) Draw the structure of an optically active carboxylic acid with five peaks in its ^{13}C n.m.r. spectrum.

(1 mark)

5 (c) (iii) Draw the structure of a cyclic compound that has only two peaks in its ^{13}C n.m.r. spectrum and has no absorption for C = O in its infrared spectrum.

(1 mark)

11

Turn over for the next question

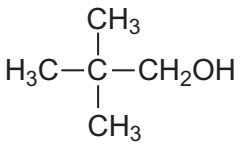
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ANSWER IN THE SPACES PROVIDED

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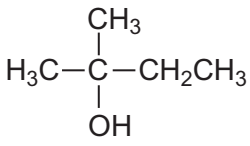
6 Describe how you could distinguish between the compounds in the following pairs using **one** simple test-tube reaction in each case.

For each pair, identify a reagent and state what you would observe when both compounds are tested separately with this reagent.

6 (a)



R



S

Reagent .....

Observation with **R** .....

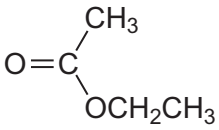
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Observation with **S** .....

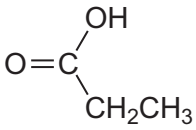
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(3 marks)

6 (b)



T



U

Reagent .....

Observation with **T** .....

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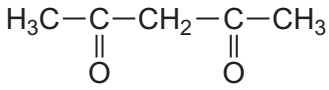
Observation with **U** .....

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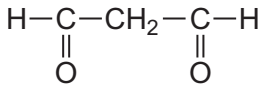
(3 marks)

Do not write outside the box

6 (c)



V



W

Reagent .....

Observation with **V** .....

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Observation with **W** .....

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(3 marks)

9

Turn over for the next question

Do not write outside the box

Section B

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

7 Each of the following conversions involves reduction of the starting material.

7 (a) Consider the following conversion.



Identify a reducing agent for this conversion.

Write a balanced equation for the reaction using molecular formulae for the nitrogen-containing compounds and [H] for the reducing agent.

Draw the repeating unit of the polymer formed by the product of this reaction with benzene-1,4-dicarboxylic acid.

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(5 marks)

(Extra space) .....

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7 (b) Consider the following conversion.



Identify a reducing agent for this conversion.

State the empirical formula of the product.

State the bond angle between the carbon atoms in the starting material and the bond angle between the carbon atoms in the product.

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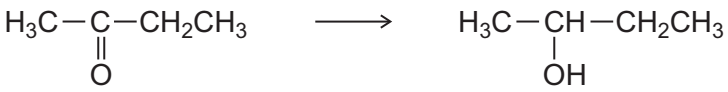
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(4 marks)

Question 7 continues on the next page

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7 (c) The reducing agent in the following conversion is $NaBH_4$



7 (c) (i) Name and outline a mechanism for the reaction.

Name of mechanism .....

Mechanism

(5 marks)

7 (c) (ii) By considering the mechanism of this reaction, explain why the product formed is optically inactive.

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(3 marks)

17

Do not write outside the box

8 Acyl chlorides such as CH_3COCl are useful compounds in synthesis.

8 (a) The acyl chloride CH_3COCl reacts with benzene.

8 (a) (i) Write an equation for this reaction and name the organic product.

Identify a catalyst for the reaction.

Write an equation to show how this catalyst reacts with CH_3COCl to produce a reactive intermediate.

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(4 marks)

8 (a) (ii) Name and outline a mechanism for the reaction of benzene with the reactive intermediate in part **(a) (i)**.

Name of mechanism .....

Mechanism

(4 marks)

Question 8 continues on the next page

Turn over ▶

Do not write outside the box

8 (b) Nucleophiles such as alcohols can react with CH_3COCl
The ion CH_3COO^- can act as a nucleophile in a similar way.

State the meaning of the term *nucleophile*.

Draw the structure of the organic product formed by the reaction of CH_3COO^- with CH_3COCl

Name the functional group produced in this reaction.

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(3 marks)

11

END OF QUESTIONS

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Version 1.4



General Certificate of Education (A-level)
January 2013

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the students' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for standardisation each examiner analyses a number of students' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of students' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

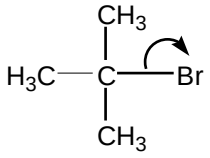
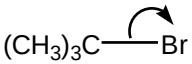
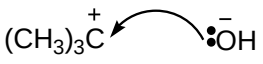
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Question	Marking Guidance	Mark	Comments
1(a)(i)	$k = \frac{8.4\times10^{-5}}{(4.2\times10^{-2})^2 \times 2.6\times10^{-2}}$ ***OR*** $\frac{8.4\times10^{-5}}{(1.76\times10^{-3})\times 2.6\times10^{-2}}$ = 1.8(3) $mol^{-2}\,dm^{+6}\,s^{-1}$	1 1 1	Mark is for insertion of numbers into a correctly rearranged rate equ , k = etc. If upside down, score only units mark from their k AE (-1) for copying numbers wrongly or swapping two numbers Any order If *k* calculation wrong, allow units consequential to their *k* = expression
1(a)(ii)	5.67×10^{-4} (mol $dm^{-3}s^{-1}$) ***OR*** their $k \times 3.1 \times 10^{-4}$	1	Allow 5.57×10^{-4} to 5.7×10^{-4}
1(b)(i)	2 or second or $[D]^2$	1	
1(b)(ii)	0 or zero or $[E]^0$	1	
1(c)(i)	Step 1 or equation as shown	1	Penalise Step 2 but mark on
1(c)(ii)	 or  Ignore correct partial charges, penalise full / incorrect partial charges	1	If Step 2 given above, can score the mark here for  allow :OH^- (must show lp) If S_N2 mechanism shown then no mark (penalise involvement of :OH^- in step 1) Ignore anything after correct step 1

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Question		Marking Guidance	Mark	Comments
2(a)(i)		$[H^+][OH^-]$ ***OR*** $[H_3O^+][OH^-]$ Ignore (aq)	1	Must have [ ] not ( )
2(a)(ii)		$\sqrt{3.46 \times 10^{-14}}$ (= 1.86×10^{-7}) pH = 6.73	1 1	If no square root, CE=0 **Must be 2dp**
2(a)(iii)		$[H^+] = 10^{-11.36}$ (= 4.365×10^{-12} OR 4.37×10^{-12}) $K_w = [4.365 \times 10^{-12}$ ***OR*** $4.37 \times 10^{-12} \times 0.047] = 2.05 \times 10^{-13}$ Allow 2.05×10^{-13} - 2.1×10^{-13}	1 1	Mark for working Mark for answer Ignore units
2(b)(i)		$HCOOH \rightleftharpoons HCOO^- + H^+$ ***OR*** $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$	1	Must have $\rightleftharpoons$ but ignore brackets. Allow HCO_2^- or $CHOO^-$ ie minus must be on oxygen, so penalise $COOH^-$
2(b)(ii)		$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$ ***OR*** $\frac{[H_3O^+][HCOO^-]}{[HCOOH]}$	1	Must have all brackets but allow ( ) Must be HCOOH etc. Allow ecf in formulae from 2(b)(i)
2(b)(iii)	M1	$K_a = \frac{[H^+]^2}{[HCOOH]}$ ($[H^+]^2 = 1.78 \times 10^{-4} \times 0.056 = 9.97 \times 10^{-6}$)	1	Allow HA or HX etc. Allow $[H^+] = \sqrt{(Ka \times [HA])}$ for M1
	M2	$[H^+] = 3.16 \times 10^{-3}$	1	Mark for answer
	M3	pH = 2.50 allow more than 2 dp but not fewer	1	**Allow correct pH from their wrong $[H^+]$ here only** If square root shown but not taken, pH = 5.00 can score max 2 for M1 and M3

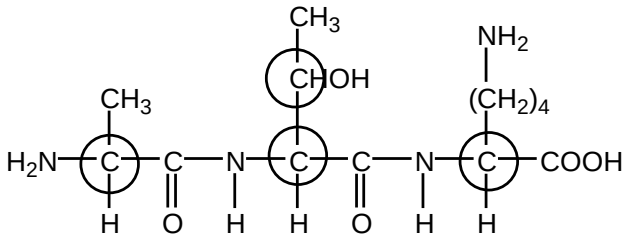
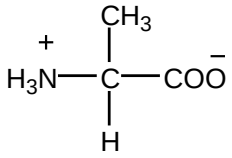
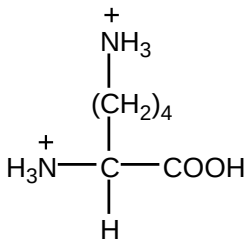
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2(b)(iv)	M1	Decrease **Mark M1 independently**	1	
	M2	Equm shifts/moves to RHS ***OR*** more H^+ ***OR*** K_a increases ***OR*** more dissociation	1	
	M3	To reduce temperature or oppose increase/change in temperature	1	**Only award M3 following correct M2**
2(c)(i)	M1	$[H^+] = \frac{Ka \times [HX]}{[X^-]}$ ***OR*** $pH = pK_a - \log \frac{[HX]}{[X^-]}$	1	If [HX]/[X^-] upside down, no marks
	M2	$\frac{1.78\times10^{-4} \times 2.35\times10^{-2}}{1.84\times10^{-2}}$ ***OR*** $pH = 3.75 - \log \frac{2.35\times10^{-2}}{1.84\times10^{-2}}$ (= 2.27×10^{-4})	1	
	M3	pH = 3.64 allow more than 2 dp but not fewer	1	**pH calc NOT allowed from their wrong [H^+] here**
2(c)(ii)	M1	Mol H^+ added = 5.00×10^{-4}	1	Mark on from AE in moles of HCl (eg 5×10^{-3} gives pH = 3.42 scores 3)
	M2	Mol $HCOOH = 2.40 \times 10^{-2}$ **and** Mol $HCOO^- = 1.79 \times 10^{-2}$	1	If either wrong no further marks except AE (-1) OR if ECF in mol acid and/or mol salt from (c)(i), can score all 4
	M3	$[H^+] (= \frac{Ka \times [HX]}{[X^-]}) = \frac{1.78\times10^{-4} \times 2.40\times10^{-2}}{1.79\times10^{-2}}$ ($= 2.39 \times 10^{-4}$) ***OR*** $pH = 3.75 - \log \frac{2.40\times10^{-2}}{1.79\times10^{-2}}$	1	If [HX]/[X^-] upside down here after correct expression in (c)(i), no further marks If [HX]/[X^-] upside down here and is repeat error from (c)(i), max 3 (pH = 3.88 after 3.86 in 2(c)(i))
	M4	pH = 3.62 allow more than 2 dp but not fewer	1	**pH calc NOT allowed from their wrong [H^+] here**

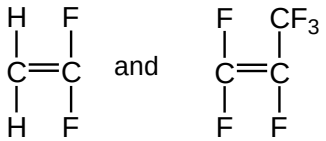
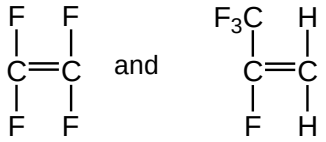
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Question	Marking Guidance	Mark	Comments
3(a)(i)	$\underline{3}CH_3OH$ $HOCH_2CH(OH)CH_2OH$	1 1	Not molecular formula
3(a)(ii)	$\rightarrow$ $19CO_2$ + $19H_2O$ $C_{17}H_{35}COOCH_3$ + 27½ or 55/2 O_2	1 1	Or doubled Consequential on correct right-hand side
3(b)(i)	A 0.7 Ethanol 6.4 Water 3.6	1 1 1	
3(b)(ii)	No effect Equal moles on each side of equation ***OR*** V cancels	1 1	If wrong, CE= 0 Ignore moles of gas
3(b)(iii)	M1 $K_c = \frac{[DEM][H_2O]^2}{[A][C_2H_5OH]^2}$	1	Must have all brackets but allow ( )
3(b)(iv)	M2 $\frac{2.1 \times (3.4)^2}{0.85 \times (7.2)^2}$ M3 0.55 (min 2dp) M4 No units	1 1 1	If K_c wrong can only score M4 for units consequential to their K_c working in (b)(iv)

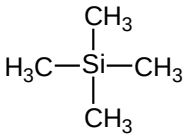
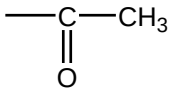
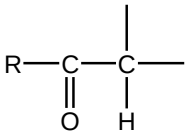
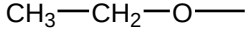
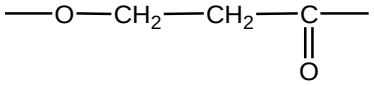
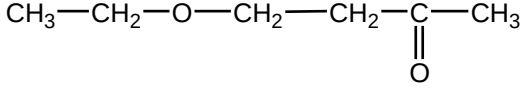
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Question	Marking Guidance	Mark	Comments
4(a)(i)		1	These four only
4(a)(ii)		1	Allow $-NH_3^+$ and $^+NH_3-$
4(a)(iii)	<u>2-amino-3-hydroxybutanoic acid</u> Do not penalise commas or missing hyphens	1	Ignore 1 in butan-1-oic acid Penalise other numbers
4(a)(iv)		1	Allow $-NH_3^+$ and $^+NH_3-$

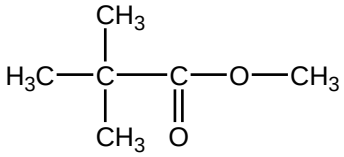
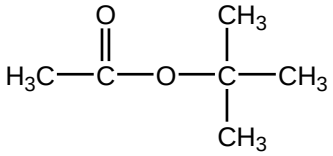
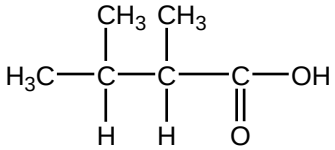
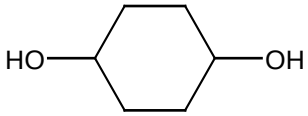
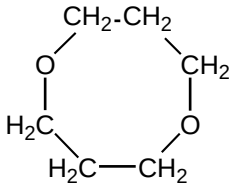
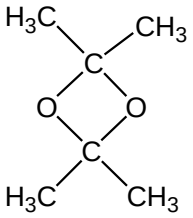
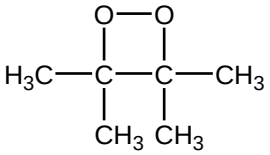
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4(b)(i)	Condensation	1	Allow polyester
4(b)(ii)	propan**e**-1,3-diol	1	Must have e Allow 1,3-propan**e**diol
4(c)(i)	Addition	1	Not additional
4(c)(ii)	 and ***OR***  and	1 for each structure within each pair	Allow monomers drawn either way round Allow bond to F in CF_3
4(d)	c C-C or C-F bonds too strong	1 1	If wrong, CE = 0

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Question	Marking Guidance	Mark	Comments
5(a)(i)	Single/one (intense) peak/signal ***OR*** all H or all C in same environment ***OR*** 12 equiv H or 4 equiv C ***OR*** Upfield / to the right of (all) other peaks ***OR*** well away from others ***OR*** doesn't interfere with other peaks ***OR*** Low bp ***OR*** volatile ***OR*** can easily be removed	2	**Do not allow non-toxic or inert (both given in Q)** Any 2 from three Ignore peak at zero Ignore cheap Ignore non-polar Ignore mention of solubility
5(a)(ii)		1	Allow $Si(CH_3)_4$
5(b)(i)	 or with sticks or 	1	Ignore any group joined on other side of CO Ignore missing trailing bond Ignore charges
5(b)(ii)	 or with sticks	1	Ignore any group joined on other side of –O– Ignore missing trailing bond Ignore charges as if MS fragment
5(b)(iii)	 or with sticks	1	Ignore missing trailing bond Ignore charges as if MS fragment
5(b)(iv)		1	

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5(c)(i)	Check structure has 6 carbons  	1 1	Allow $(CH_3)_3CCOOCH_3$ or $(CH_3)_3CCO_2CH_3$ Allow $CH_3COOC(CH_3)_3$ or $CH_3CO_2C(CH_3)_3$
5(c)(ii)	Check structure has 6 carbons 	1	Allow $(CH_3)_2CHCH(CH_3)COOH$ or $(CH_3)_2CHCH(CH_3)CO_2H$ Penalise C_3H_7
5(c)(iii)	Check structure has 6 carbons  ***OR*** 	1	Allow  OR 

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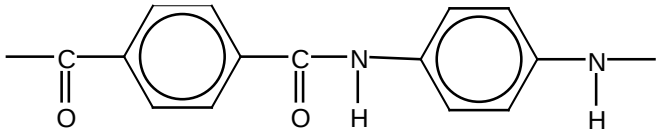
Question	Marking Guidance	Mark	Comments
6	In each section • If wrong or no reagent given, no marks for any observations; • Penalise incomplete reagent or incorrect formula – but mark observations • Mark each observation independently • Allow *no reaction* for no change / no observable reaction in all three parts, but not *none* or *nothing* • Q says **one test.** If two tests are given, score zero		

6(a)		$K_2Cr_2O_7$ / H^+	$KMnO_4$ / H^+	Lucas test ($ZnCl_2$ / HCl)	1	Allow acidified potassium manganate and acidified potassium dichromate without oxidation numbers			
	R Primary alcohol	(Orange) goes green Penalise wrong starting colour	(purple) goes colourless / decolourises allow goes brown	No cloudiness	1				
	S Tertiary alcohol	no change / no observable reaction	no change / no observable reaction	Rapid cloudiness	1				
6(b)		Na_2CO_3 / $NaHCO_3$ named carbonate	metal eg Mg	named indicator	1	PCl_5 PCl_3 $SOCl_2$	Named alcohol + HCl / H_2SO_4		
	T ester	no change / no observable reaction	no change / no observable reaction	no effect	1	no change / no observable reaction	no change / no observable reaction		
	U Acid	Effervescence or (CO_2) gas formed	Effervescence or (H_2) gas formed	acid colour	1	Fumes / (HCl) gas formed	Sweet smell		

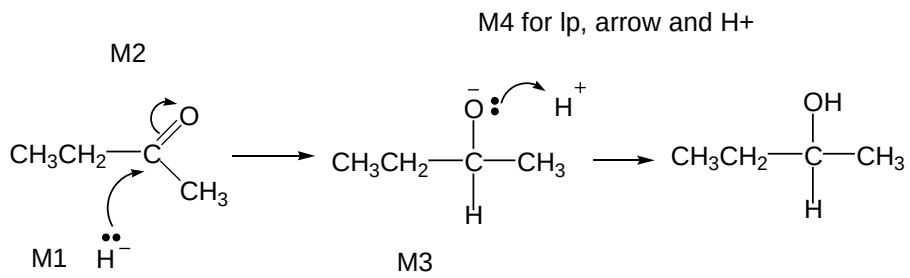
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Question	Marking Guidance				Mark	Comments		
	In each section • If wrong or no reagent given, no marks for any observations; • Penalise incomplete reagent or incorrect formula – but mark observations • Mark each observation independently • Allow *no reaction* for no change / no observable reaction in all three parts, but not *none* or *nothing* • Q says **one test.** If two tests are given, score zero							
6(c)		Fehling's / Benedict's	Tollens' / $[Ag(NH_3)_2]^+$	$K_2Cr_2O_7$ / H^+	1	I_2 / NaOH		
	V Ketone	no change / no observable reaction	no change / no observable reaction	no change / no observable reaction	1	Yellow ppt		
	W aldehyde	Red ppt	Silver mirror	(Orange) goes green Penalise wrong starting colour	1	no change / no observable reaction		

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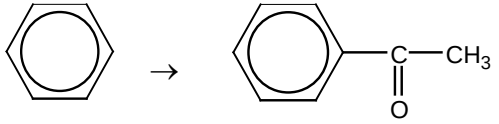
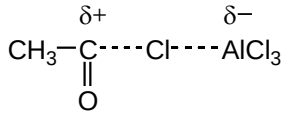
Question	Marking Guidance	Mark	Comments
7(a)	Sn / HCl ***OR*** Fe / HCl not conc H_2SO_4 nor any HNO_3 Ignore subsequent use of NaOH	1	Ignore reference to Sn as a catalyst with the acid Allow H_2 (Ni / Pt) but penalise wrong metal But NOT $NaBH_4$ $LiAlH_4$ Na / C_2H_5OH
	Equation must use molecular formulae $C_6H_4N_2O_4 + 12\,[H]$	1	12[H] and $4H_2O$ without correct molecular formula scores 1 out of 2
	$\rightarrow C_6H_8N_2 + 4H_2O$	1	Allow ….. + $6H_2$ if H_2 / Ni used
		2	Allow –CONH— or —COHN— or —C_6H_4—
			Mark two halves separately : lose 1 each for • error in diamine part • error in diacid part • error in peptide link • missing trailing bonds at one or both ends • either or both of H or OH on ends
			Ignore *n*
7(b)	H_2 (Ni / Pt) but penalise wrong metal	1	NOT Sn / HCl, $NaBH_4$ etc.
	CH_2	1	
	In benzene 120°	1	
	In cyclohexane $109^o\,28'$ or $109½^o$	1	Allow 108° - 110°
	If only one angle stated without correct qualification, no mark awarded		

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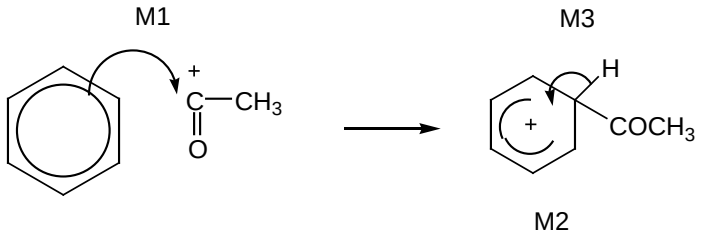
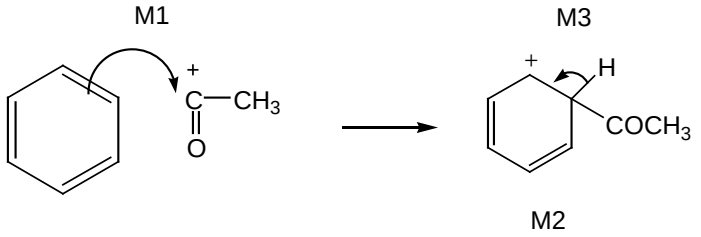
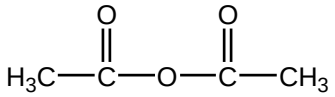
7(c)(i)	Nucleophilic addition  	1 4	• M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • M3 is for correct structure including minus sign but lone pair is part of M4 • Allow C_2H_5 • M1 and M4 include lp and curly arrow • Allow M4 arrow to <u>H</u> in H_2O (ignore further arrows)

7(c)(ii)	M1 Planar C=O (bond/group) M2 Attack (equally likely) from either side M3 (about product): Racemic mixture formed ***OR*** 50:50 mixture or each enantiomer equally likely	1 1 1	Not just planar molecule Not just planar bond without reference to carbonyl

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Question	Marking Guidance	Mark	Comments
8(a)(i)	$CH_3COCl + C_6H_6 \rightarrow C_6H_5COCH_3 + HCl$	1	Not molecular formulae Not allow $C_6H_5CH_3CO$
	OR		
	$CH_3COCl +$  $+ HCl$		
	phenylethanone	1	Ignore number 1 in name but penalise other numbers
	$AlCl_3$ can be scored in equation	1	
	$CH_3COCl + AlCl_3 \longrightarrow CH_3\overset{+}{C}O + AlCl_4^-$	1	Allow RHS as  Allow + on C or O in equation but + must be on C in mechanism below Ignore curly arrows in balanced equation even if wrong

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8(a)(ii)	Electrophilic substitution  ***OR***  	1 3	• M1 arrow from within hexagon to C or to + on C • + must be on C of CH_3CO in mechanism • + in intermediate not too close to C1 • Gap in horseshoe must be centred approximately around C1 • M3 arrow into hexagon unless Kekule • Allow M3 arrow independent of M2 structure, ie + on H in intermediate loses M2 not M3 • Ignore base removing H for M3
8(b)	Electron pair donor or lone pair donor  (acid) anhydride	1 1 1	Allow donator Allow lone pair used in description of (dative) bond formation Allow $(CH_3CO)_2O$ Allow ethanoic anhydride but not any other anhydride

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General principles applied to marking CHEM4 papers by CMI+ (January 2013)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a student gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the student to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a student provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

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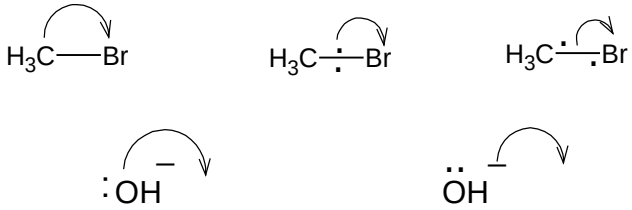
G. Marking calculations

In general

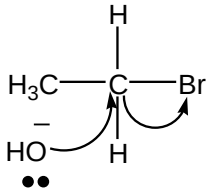
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

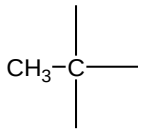
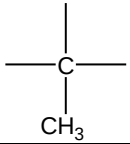
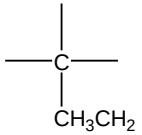
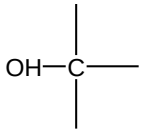
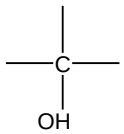
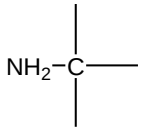
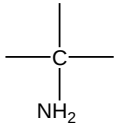
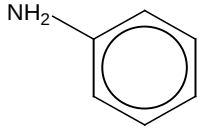
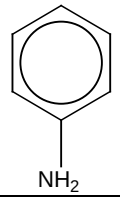
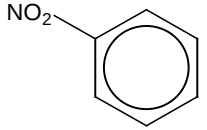
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

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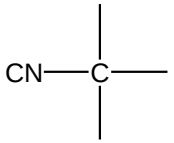
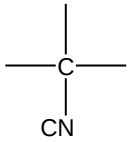
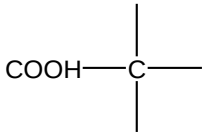
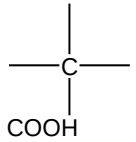
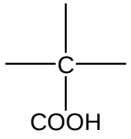
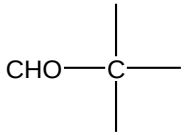
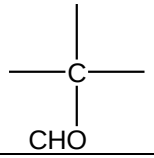
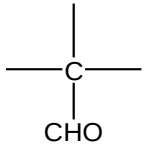
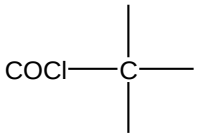
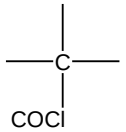
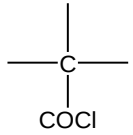
I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if students show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

				
allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

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not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions may be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
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TOTAL	



General Certificate of Education
Advanced Level Examination
June 2012

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 13 June 2012 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- You are expected to use a calculator, where appropriate.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.



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Section A

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

1 (a) A mixture of 1.50 mol of hydrogen and 1.20 mol of gaseous iodine was sealed in a container of volume V dm^3. The mixture was left to reach equilibrium as shown by the following equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At a given temperature, the equilibrium mixture contained 2.06 mol of hydrogen iodide.

1 (a) (i) Calculate the amounts, in moles, of hydrogen and of iodine in the equilibrium mixture.

Moles of hydrogen .....

Moles of iodine .....

(2 marks)

1 (a) (ii) Write an expression for the equilibrium constant (K_c) for this equilibrium.

.....

.....

(1 mark)

1 (a) (iii) K_c for this equilibrium has no units.
State why the units cancel in the expression for K_c

.....

.....

(1 mark)

1 (a) (iv) A different mixture of hydrogen, iodine and hydrogen iodide was left to reach equilibrium at the same temperature in a container of the same volume.
This second equilibrium mixture contained 0.38 mol of hydrogen, 0.19 mol of iodine and 1.94 mol of hydrogen iodide.

Calculate a value for K_c for this equilibrium at this temperature.

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(2 marks)

(Extra space) .....

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1 (b) This question concerns changes made to the four equilibria shown in parts **(b) (i)** to **(b) (iv)**.
In each case, use the information in the table to help you choose from the letters **A** to **E** the best description of what happens as a result of the change described. Write your answer in the box.

Each letter may be used once, more than once or not at all.

	Position of equilibrium	Value of equilibrium constant, K_c
A	remains the same	same
B	moves to the right	same
C	moves to the left	same
D	moves to the right	different
E	moves to the left	different

1 (b) (i) Change: increase the temperature of the equilibrium mixture at constant pressure.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad \Delta H^{\ominus} = +52\ kJ\ mol^{-1}$

(1 mark)

1 (b) (ii) Change: increase the total pressure of the equilibrium mixture at constant temperature.

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$ $\quad \Delta H^{\ominus} = -92\ kJ\ mol^{-1}$

(1 mark)

1 (b) (iii) Change: add a catalyst to the equilibrium mixture at constant temperature.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\quad \Delta H^{\ominus} = -41\ kJ\ mol^{-1}$

(1 mark)

1 (b) (iv) Change: add chlorine to the equilibrium mixture at constant temperature.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\quad \Delta H^{\ominus} = +93\ kJ\ mol^{-1}$

(1 mark)

10

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2 Gases **P** and **Q** react as shown in the following equation.

$$2P(g) + 2Q(g) \longrightarrow R(g) + S(g)$$

The initial rate of the reaction was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

2 (a) Complete the table of data for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	2.5×10^{-2}	1.8×10^{-2}	5.0×10^{-5}
2	7.5×10^{-2}	1.8×10^{-2}	
3	5.0×10^{-2}		5.0×10^{-5}
4		5.4×10^{-2}	4.5×10^{-4}

(3 marks)

(Space for working) .....

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2 (b) Use the data from Experiment **1** to calculate a value for the rate constant (k) at this temperature. Deduce the units of k.

Calculation .....

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Units .....

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(3 marks)

6

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3 This question is about several Brønsted–Lowry acids and bases.

3 (a) Define the term *Brønsted–Lowry* acid.

.....

.....

(1 mark)

3 (b) Three equilibria are shown below. For each reaction, indicate whether the substance immediately **above** the box is acting as a Brønsted–Lowry acid (**A**) or a Brønsted–Lowry base (**B**) by writing **A** or **B** in each of the six boxes.

3 (b) (i) CH_3COOH + H_2O $\rightleftharpoons$ CH_3COO^- + H_3O^+

(1 mark)

3 (b) (ii) CH_3NH_2 + H_2O $\rightleftharpoons$ $CH_3NH_3^+$ + OH^-

(1 mark)

3 (b) (iii) HNO_3 + H_2SO_4 $\rightleftharpoons$ $H_2NO_3^+$ + HSO_4^-

(1 mark)

3 (c) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker. Distilled water was added until the pH of the solution was 1.25

Calculate the total volume of the solution formed. State the units.

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(3 marks)

(*Extra space*) .....

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Question 3 continues on the next page

Do not write outside the box

3 (d) At 298 K, the value of the acid dissociation constant (K_a) for the weak acid HX in aqueous solution is 3.01×10^{-5} mol dm^{-3}.

3 (d) (i) Calculate the value of pK_a for HX at this temperature.
Give your answer to 2 decimal places.

.....

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(1 mark)

3 (d) (ii) Write an expression for the acid dissociation constant (K_a) for the weak acid HX.

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(1 mark)

3 (d) (iii) Calculate the pH of a 0.174 mol dm^{-3} solution of HX at this temperature.
Give your answer to 2 decimal places.

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(3 marks)

(Extra space) .....

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Do not write outside the box

3 (e) An acidic buffer solution is formed when 10.0 cm^3 of 0.125 mol dm^{-3} aqueous sodium hydroxide are added to 15.0 cm^3 of 0.174 mol dm^{-3} aqueous HX.
The value of K_a for the weak acid HX is 3.01×10^{-5} mol dm^{-3}.

Calculate the pH of this buffer solution at 298 K.
Give your answer to 2 decimal places.

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(6 marks)

(Extra space) .....

18

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Do not write outside the box

4 Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

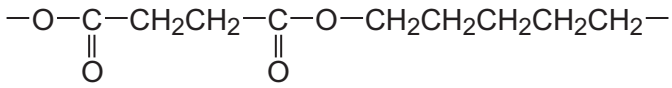
4 (a) Outline a mechanism for the reaction of CH_3CH_2COCl with CH_3OH and name the organic product formed.

Mechanism

Name of organic product .....

(5 marks)

4 (b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



4 (b) (i) Name the diol used.

.....

(1 mark)

4 (b) (ii) Draw the displayed formula of the diacyl chloride used.

(1 mark)

Do not write outside the box

4 (b) (iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

Type of reaction .....

Explanation .....

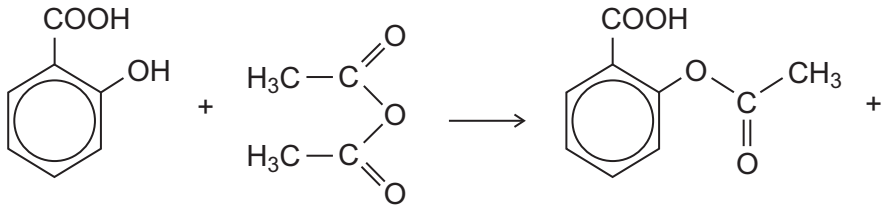
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(3 marks)

4 (c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



.....

aspirin

(1 mark)

4 (c) (ii) Suggest a name for the mechanism for the reaction in part **(c) (i)**.

.....

(1 mark)

4 (c) (iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1 .....

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Advantage 2 .....

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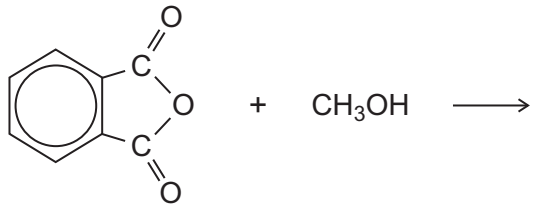
(2 marks)

Question 4 continues on the next page

Turn over ▶

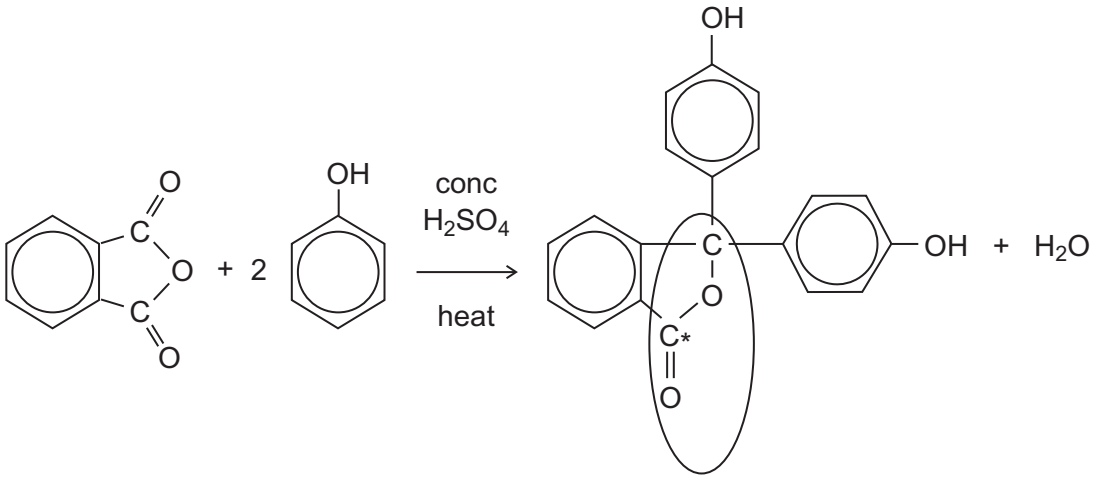
Do not write outside the box

4 (d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product.



(1 mark)

4 (e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



phenol phenolphthalein

4 (e) (i) Name the functional group ringed in the structure of phenolphthalein.

.....

(1 mark)

4 (e) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1 mark)

4 (e) (iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).
Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

.....

(1 mark)

Do not write outside the box

4 (f) Phenolphthalein can be used as an indicator in some acid–alkali titrations.
The pH range for phenolphthalein is 8.3 – 10.0

4 (f) (i) For **each** acid–alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	Alkali	Tick box (✓)
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2 marks)

4 (f) (ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator.
Give the colour **change** at the end-point.

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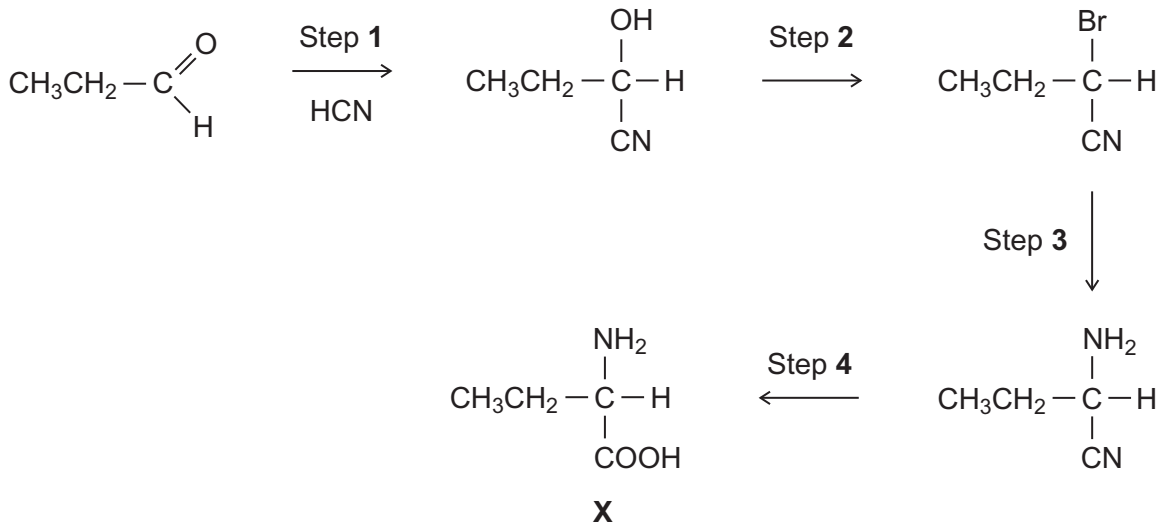
(1 mark)

21

Turn over for the next question

Do not write outside the box

5 A possible synthesis of the amino acid **X** is shown below.



X

5 (a) Name and outline a mechanism for Step **1**.

Name of mechanism .....

Mechanism

(5 marks)

5 (b) Give the IUPAC name of the product of Step **2**.

.....

(1 mark)

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5 (c) For Step **3**, give the reagent, give a necessary condition and name the mechanism.

Reagent .....

Condition .....

Name of mechanism .....

(3 marks)

5 (d) At room temperature, the amino acid **X** exists as a solid.

5 (d) (i) Draw the structure of the species present in the solid amino acid.

(1 mark)

5 (d) (ii) With reference to your answer to part **(d) (i)**, explain why the melting point of the amino acid **X** is higher than the melting point of $CH_3CH_2CH(OH)COOH$

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(2 marks)

(Extra space) .....

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Question 5 continues on the next page

Do not write outside the box

5 (e) There are many structural isomers of **X**, $CH_3CH_2CH(NH_2)COOH$

5 (e) (i) Draw a structural isomer of **X** that is an ethyl ester.

(1 mark)

5 (e) (ii) Draw a structural isomer of **X** that is an amide and also a tertiary alcohol.

(1 mark)

5 (e) (iii) Draw a structural isomer of **X** that has an unbranched carbon chain and can be polymerised to form a polyamide.

(1 mark)

5 (f) Draw the structure of the tertiary amine formed when **X** reacts with bromomethane.

(1 mark)

16

Turn over for the next question

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

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Section B

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

6 Benzene reacts with ethanoyl chloride in a substitution reaction to form $C_6H_5COCH_3$
This reaction is catalysed by aluminium chloride.

6 (a) Write equations to show the role of aluminium chloride as a catalyst in this reaction.

Outline a mechanism for the reaction of benzene.

Name the product, $C_6H_5COCH_3$

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(6 marks)

Do not write outside the box

6 (b) The product of the substitution reaction ($C_6H_5COCH_3$) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with $m/z = 105$
Draw the structure of this fragment ion.

(1 mark)

6 (c) When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene.
Suggest why the reaction of methylbenzene is faster.

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(2 marks)

9

Turn over for the next question

Do not write outside the box

7 (a) A chemist discovered four unlabelled bottles of liquid, each of which contained a different pure organic compound. The compounds were known to be propan-1-ol, propanal, propanoic acid and 1-chloropropane.

Describe four **different** test-tube reactions, one for each compound, that could be used to identify the four organic compounds.
Your answer should include the name of the organic compound, the reagent(s) used and the expected observation for each test.

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(8 marks)

(*Extra space*) .....

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7 (b) A fifth bottle was discovered labelled propan-2-ol. The chemist showed, using infrared spectroscopy, that the propan-2-ol was contaminated with propanone.

The chemist separated the two compounds using column chromatography. The column contained silica gel, a polar stationary phase.

The contaminated propan-2-ol was dissolved in hexane and poured into the column. Pure hexane was added slowly to the top of the column. Samples of the eluent (the solution leaving the bottom of the column) were collected.

- Suggest the chemical process that would cause a sample of propan-2-ol to become contaminated with propanone.
- State how the infrared spectrum showed the presence of propanone.
- Suggest why propanone was present in samples of the eluent collected first (those with shorter retention times), whereas samples containing propan-2-ol were collected later.

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(4 marks)

(*Extra space*) .....

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12

Turn over for the next question

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8 When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts **(a)** to **(d)**.

8 (a) Compounds **F** and **G** have the molecular formula $C_6H_4N_2O_4$ and both are dinitrobenzenes.
F has two peaks in its ^{13}C n.m.r. spectrum.
G has three peaks in its ^{13}C n.m.r. spectrum.

F **G**

(2 marks)

(Space for working)

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8 (b) Compounds **H** and **J** have the molecular formula C_6H_{12}
Both have only one peak in their ^1H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H **J**

(2 marks)

(Space for working)

Question 8 continues on the next page

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8 (c) **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K **L**

(2 marks)

(Space for working)

Do not write outside the box

8 (d) Compounds **M** and **N** have the molecular formula $C_6H_{15}N$
M is a tertiary amine with only two peaks in its ^1H n.m.r. spectrum.
N is a secondary amine with only three peaks in its ^1H n.m.r. spectrum.

M **N**

(2 marks)

(Space for working)

8

END OF QUESTIONS

There are no questions printed on this page

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Version 1.2



General Certificate of Education (A-level)
June 2012

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

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Question	Marking Guidance		Mark	Additional Guidance
1(a)(i)	mol H_2 = 0.47 mol I_2 = 0.17		1 1	If answers reversed, ie mol H_2 = 0.17 mol I_2 = 0.47 then allow one mark (for second answer).
1(a)(ii)	$\frac{[HI]^2}{[H_2][I_2]}$	Penalise expression containing V But mark on in (a)(iv)	1	**Penalise missing square brackets** in this part (and not elsewhere in paper) but mark on in (a)(iv)
1(a)(iii)	equal number of <u>moles</u> (on each side of equation) ***OR*** equal <u>moles</u> (top and bottom of *K*c expression)		1	
1(a)(iv)	$\frac{[1.94]^2}{[0.38][0.19]}$ = 52(.1)	Ignore V	1 1	If *K*c wrong in (a)(ii) (wrong powers or upside down etc) no marks here
1(b)(i)	**D**		1	
1(b)(ii)	**B**		1	
1(b)(iii)	**A**		1	
1(b)(iv)	**C**		1	

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Question	Marking Guidance	Mark	Additional Guidance
2(a)	Exp 2 4.5×10^{-4} Exp 3 4.5×10^{-3} Exp 4 0.043 OR 4.3×10^{-2} OR 0.044 OR 4.4×10^{-2}	1 1 1	Min 2sf If three wrong answers, check their value of *k* in 2(b). They can score all 3 if they have used their (incorrect) value of *k*. see below. Exp 2 rate = $k \times (1.0125 \times 10^{-4})$ Exp 3 [**Q**] = $0.02/k$ Exp 4 [**P**] = $0.0913/\sqrt{k}$
2(b)	$k = \frac{5.0 \times 10^{-5}}{(2.5 \times 10^{-2})^2 \times (1.8 \times 10^{-2})}$ = 4.4(4) (allow 40/9) $mol^{-2}dm^{+6}s^{-1}$	1 1 1	Mark is for insertion of numbers into a correctly rearranged rate equ , *k* = etc If upside down, score only units mark from their *k* AE (-1) for copying numbers wrongly or swapping two numbers Any order If *k* calculation wrong, allow units conseq to their *k* expression

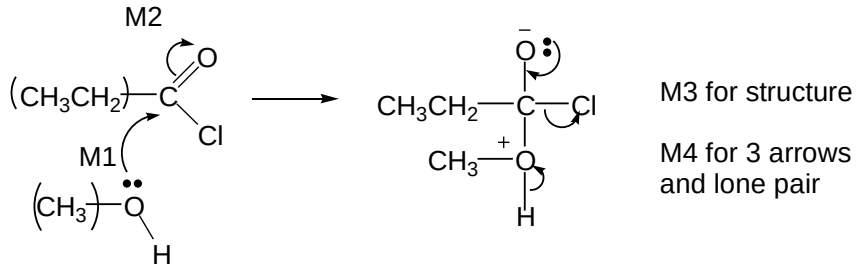
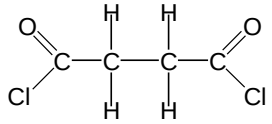
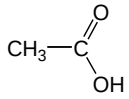
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Question	Marking Guidance	Mark	Additional Guidance
3(a)	Proton donor or H^+ donor	1	Allow donator
3(b)(i)	B B	1	Both need to be correct to score the mark
3(b)(ii)	A A	1	Both need to be correct to score the mark
3(b)(iii)	B A	1	Both need to be correct to score the mark
3(c)	M1 $[H^+] = 10^{-1.25}$ OR 0.05623	1	
	M2 mol HCl = $(25 \times 10^{-3}) \times 0.0850$ (= 2.125×10^{-3})	1	Mark for Working
	M3 vol (= $\frac{2.125 \times 10^{-3}}{0.05623}$) = 0.0378 dm^3 or 37.8 cm^3		Units and answer tied
			Lose M3 if total given as (25+ 37.8) = 62.8 cm^3
	allow 0.0375 – 0.038 dm^3 or 37.5 –38 cm^3	1	Ignore "vol added = 12.8cm^3" after correct answer
3(d)(i)	4.52	1	Must be 2dp
3(d)(ii)	$K_a = \frac{[H^+][X^-]}{[HX]}$ ignore = $\frac{[H^+]^2}{[HX]}$ but this may score M1 in d(iii)	1	Must have all brackets but allow ( ) Allow HA etc **NO** mark for 10^{-pKa}
3(d)(iii)	M1 $K_a = \frac{[H^+]^2}{[HX]}$ or with numbers	1	Allow $[H^+] = \sqrt{(Ka \times [HA])}$ for M1
	M2 $[H^+] = (\sqrt{(3.01 \times 10^{-5} \times 0.174)} = \sqrt{(5.24 \times 10^{-6})})$	1	Mark for <u>answer</u>
	$= 2.29 \times 10^{-3} - 2.3 \times 10^{-3}$		**Allow 1 for correct pH from their wrong $[H^+]$**
	M3 pH = 2.64 (allow more than 2dp but not fewer)	1	If square root forgotten, pH = 5.28 scores 2 for M1 and M3

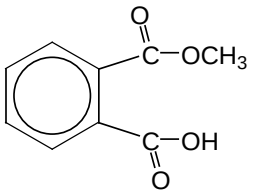
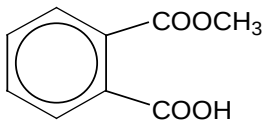
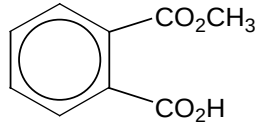
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3(e)	M1	mol OH^- = $(10.0 \times 10^{-3}) \times 0.125 = 1.25 \times 10^{-3}$	1	Mark for answer
	M2	orig mol HX = $(15.0 \times 10^{-3}) \times 0.174 = 2.61 \times 10^{-3}$	1	Mark for answer
	M3	mol HX in buffer = orig mol HX – mol OH^- = $2.61 \times 10^{-3} - 1.25 \times 10^{-3} = 1.36 \times 10^{-3}$ ($[HX] = 1.36 \times 10^{-3}/25 \times 10^{-3} = 0.0544$)	1	Mark for answer Allow conseq on their (M2 – M1) If no subtraction, max 3 for M1, M2 & M4 (pH = 4.20) If $[H^+] = [X^-]$ & √ used, max 3 for M1, M2 & M3 (pH = 2.89)
	M4	mol X^- in buffer = mol OH^- = 1.25×10^{-3} ($[X^-] = 1.25 \times 10^{-3}/25 \times 10^{-3} = 0.05$)	1	May be scored in M5 expression
	M5	$[H^+]$ $\left(= \frac{Ka \times [HX]}{[X^-]}\right)$ $= \frac{3.01\times10^{-5} \times 1.36\times10^{-3}}{1.25\times10^{-3}}$ OR $\frac{3.01\times10^{-5} \times 0.0544}{0.05}$ $(= 3.27 \times 10^{-5})$	1	If use $K_a = \frac{[H^+]^2}{[HX]}$ no further marks If either value of HX or X^- used wrongly or expression upside down, no further marks
	M6	pH = 4.48 or 4.49 (allow more than 2dp but not fewer)	1	Do **not** allow M6 for correct calculation of pH using their $[H^+]$ - this only applies in 3d(iii) - apart from earlier AE

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Question	Marking Guidance	Mark	Additional Guidance
4(a)	 methyl propanoate (**NO** mark for name of mechanism)	4 1	• M2 not allowed independent of M1, but allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • If Cl lost with C=O breaking, max1 for M1 • M3 for correct structure <u>with charges</u> but lp on O is part of M4 • only allow M4 after correct/very close M3 • ignore Cl^- removing H^+
4(b)(i)	pentan<u>e</u>-<u>1,5</u>-diol	1	Second 'e' and numbers needed Allow <u>1,5</u>-pentan<u>e</u>diol but this is not IUPAC name
4(b)(ii)		1	Must show ALL bonds
4(b)(iii)	All three marks are independent M1 (base or alkaline) Hydrolysis (allow close spelling) M2 <u>δ+ C</u> in polyester M3 reacts with OH^- or hydroxide ion	 1 1 1	 Allow (nucleophilic) addition-elimination or saponification Not reacts with NaOH
4(c)(i)		1	Allow CH_3COOH or CH_3CO_2H

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4(c)(ii)	(nucleophilic) addition-elimination OR (nucleophilic) addition followed by elimination	1	Both addition and elimination needed and in that order Do **not** allow electrophilic addition-elimination / esterification Ignore acylation
4(c)(iii)	any **two** from: ethanoic anhydride is • less corrosive • less vulnerable to hydrolysis • less dangerous to use, • less violent/exothermic/vigorous reaction OR more controllable rxn • does not produce toxic/corrosive/harmful fumes (of HCl) OR does not produce HCl • less volatile	2 max	**NOT** COST List principle beyond two answers
4(d)		1	Allow  or 
4(e)(i)	ester	1	Do **not** allow ether Ignore functional group/linkage/bond
4(e)(ii)	12 or twelve (peaks)	1	

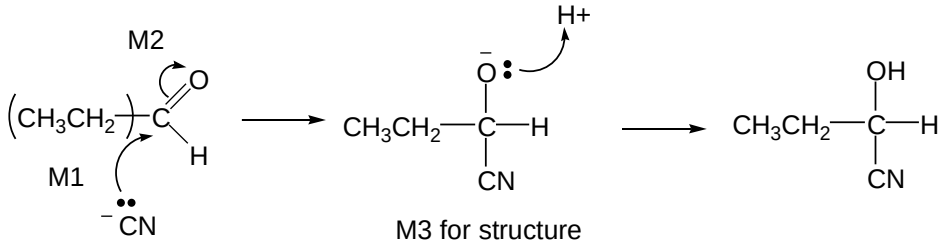
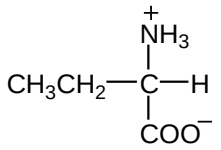
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4(e)(iii)	160 – 185			1	Allow a number or range within these limits Penalize extra ranges given Ignore units

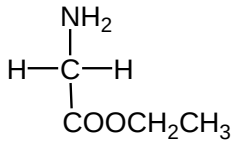
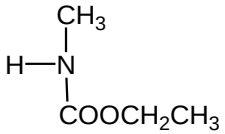
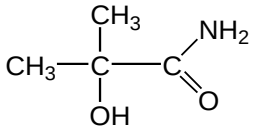
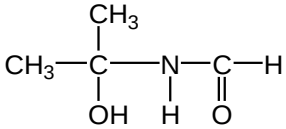
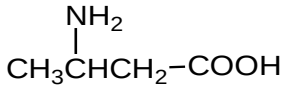
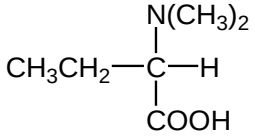
4(f)(i)	sulfuric acid	sodium hydroxide	√	2	4 correct scores 2 3 correct scores 1 2 or 1 correct scores 0
	hydrochloric acid	ammonia	X or blank		
	ethanoic acid	potassium hydroxide	√		
	nitric acid	methylamine	X or blank		

4(f)(ii)	<u>Pink to colourless</u>	1	Allow 'red' OR 'purple' OR 'magenta' instead of 'pink' Do **not** allow 'clear' instead of 'colourless'

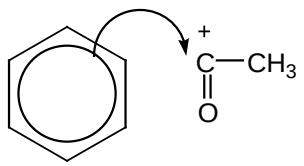
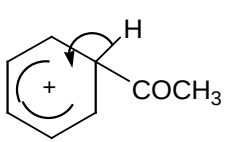
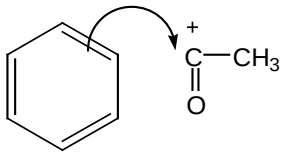
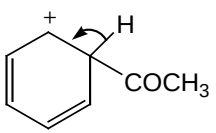
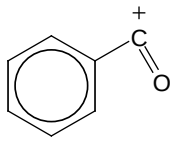
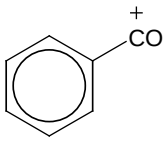
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Question	Marking Guidance	Mark	Additional Guidance
5(a)	nucleophilic addition M4 for lp and arrow to H^+  M3 for structure	1 4	• allow **:**CN^- • M2 not allowed independent of M1, but • allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • M3 is for correct structure including minus sign but lone pair is part of M4 • Allow C_2H_5 • M1 and M4 for lp and curly arrow
5(b)	2-bromobutanenitrile	1	Allow 2-bromobutane-1-nitrile
5(c)	**M1** ammonia or NH_3 **M2** excess (ammonia) **M3** nucleophilic substitution excess tied to NH_3 and may score in M1 unless contradicted	1 1 1	Ignore temp or pressure Ignore concentrated or sealed container, Acid loses conditions mark Allow close spelling
5(d)(i)	 	1	Allow C_2H_5 Allow $-CO_2^-$ Allow $^+NH_3-$ Don't penalize position of + on NH_3
5(d)(ii)	**M1** electrostatic forces between ions in **X** **QOL** Marks independent **M2** (stronger than) hydrogen bonding between $CH_3CH_2CH(OH)COOH$	1 1	Allow ionic bonding. **CE** mention of molecules of **X** or inter molecular forces between **X** loses both marks

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5(e)(i)	 OR 	1	Isomer of $C_4H_9NO_2$ Allow NH_2–
5(e)(ii)		1	Isomer of $C_4H_9NO_2$ allow NH_2– Allow 
5(e)(iii)	$H_2N—CH_2CH_2CH_2—COOH$ or $H_2N—(CH_2)_3—COOH$ OR 	1	Isomer of $C_4H_9NO_2$ allow NH_2– Do **not** allow $–C_3H_6-$ Beware – do not credit **X** itself
5(f)		1	Answer has 6 carbons so **NOT** isomer of **X** Allow C_2H_5 Must have bond from C to N not to methyl group

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Question	Marking Guidance	Mark	Additional Guidance
6(a)	$CH_3COCl + AlCl_3 \longrightarrow CH_3CO^+ + AlCl_4^-$	1	Allow RHS as $CH_3-C(=O)\cdots Cl\cdots AlCl_3$ with $\delta+$ on C and $\delta-$ on $AlCl_3$ Allow + on C or O in equation but + must be on C in mechanism below Ignore curly arrows in equation even if wrong.
	$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$	1	
	M1  M3  M2 OR M1  M3  M2	3	• M1 arrow from within hexagon to C or to + on C • + must be on C of RCO in mechanism • + in intermediate not too close to C1 • gap in horseshoe must be centred approximately around C1 • M3 arrow into hexagon unless Kekule • allow M3 arrow independent of M2 structure • ignore base removing H for M3 • **NO** mark for name of mechanism
	Phenylethanone ignore 1 in name, penalise other numbers	1	Note: this is the sixth marking point in 6a
6(b)	 or 	1	+ must be on C But allow $[C_6H_5CO]^+$

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6(c)	M1 about electrons	methyl group has (positive) inductive effect OR increases electron density on benzene ring OR pushes electrons OR is electron releasing	1	Ignore reference to delocalisation
	M2 about attraction	electrophile attracted more or benzene ring better nucleophile	1	Allow intermediate ion stabilised **M2 only awarded after correct or close M1**

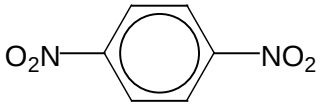
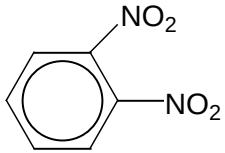
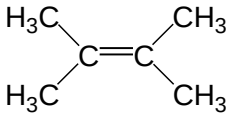
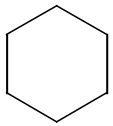
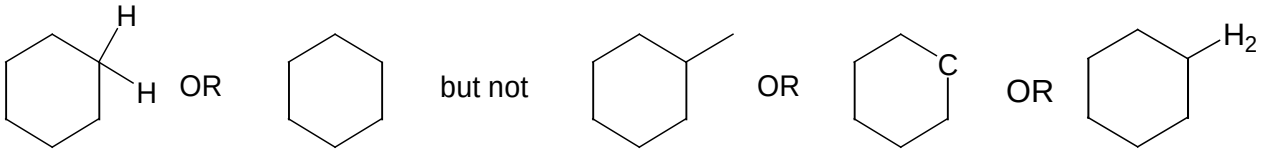
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Question	Marking Guidance							Mark	Additional Guidance
7(a)	**If 2 stage test for one compound, award no marks for that compound, eg no mark for ROH or RX to alkene then Br_2 test. If reagent is wrong or missing, no mark for that test; if wrong but close/incomplete, lose reagent mark but can award for correct observation. In each test, penalise each example of wrong chemistry, eg $AgCl_2$**								
	propan-1-ol	M1	acidified potassium dichromate	sodium	Named acid + conc H_2SO_4	named acyl chloride	PCl_5	1	
		M2	(orange) turns green	effervescence	Sweet smell	Sweet smell /misty fumes	Misty fumes	1	
	propanal	M3	add Tollens or Fehlings / Benedicts	acidified potassium dichromate	Bradys or 2,4-dnph			1	if dichromate used for alcohol cannot be used for aldehyde
		M4	Tollens: silver mirror or Fehlings/ Benedicts: red ppt	(orange) turns green	Yellow or orange ppt			1	
	propanoic acid	M5	Named carbonate/ hydrogencarbonate	water and UI (paper)	Named alcohol + conc H_2SO_4	sodium or magnesium	PCl_5	1	if sodium used for alcohol cannot be used for acid
		M6	effervescence	orange/red	Sweet smell	effervescence	Misty fumes	1	if PCl_5 used for alcohol cannot be used for acid
	1-chloro propane	M7	NaOH then acidified $AgNO_3$	$AgNO_3$				1	If acidification missed after NaOH, no mark here but allow mark for observation
		M8	white ppt	white ppt				1	

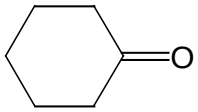
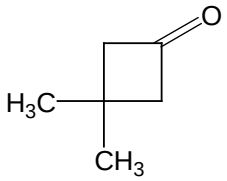
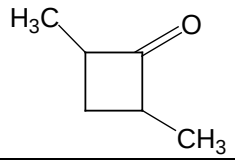
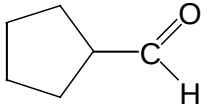
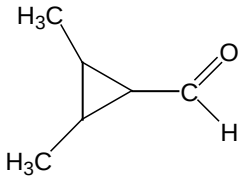
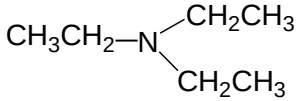
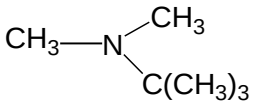
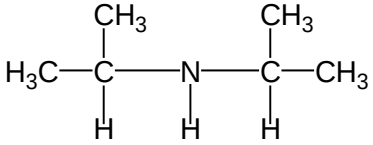
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7(b)	M1 oxidation (of alcohol by oxygen in air) M2 absorption at <u>1680 -1750</u> (due to C=O) M3 – comparison of polarity of molecules or correct imf statement: propanone is less polar OR propan-2-ol is more polar OR propanone has dipole-dipole forces OR propan-2-ol has hydrogen bonding M4 - about attraction to stationary phase or solubility in moving phase Propan-2-ol has greater affinity for stationary phase or vice versa OR propanone is more soluble in solvent/moving phase or vice versa I	1 1 1 1 	Must refer to the spectrum

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Question	Marking Guidance		Mark	Additional Guidance
8(a)	**F**	**G**		
			1, 1	Penalize $-O_2N$ once Penalise missing circle once Don't penalise attempt at bonding in NO_2
8(b)	**H**	**J**		
			1, 1	If **both H** and **J** correct but reversed, award one mark
	A carbon in saturated ring structures should be shown as 			

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Question	Marking Guidance		Mark	Additional Guidance
8(c)	**K**	**L**		
	 OR  OR 	 OR 	1, 1	
8(d)	**M**	**N**		Allow C_2H_5 but NOT allow C_4H_9 or C_3H_7
	 OR 		1, 1	

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General principles applied to marking CHEM4 papers by CMI+ (June 2012)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

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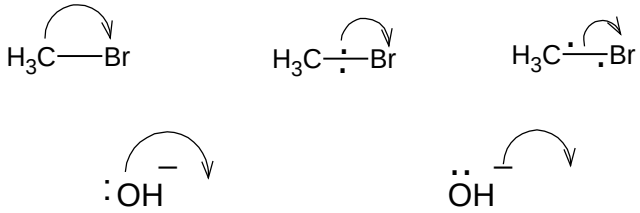
G. Marking calculations

In general

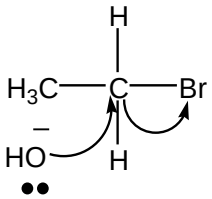
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

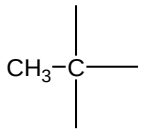
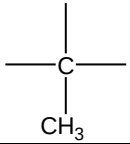
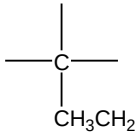
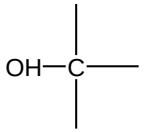
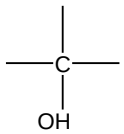
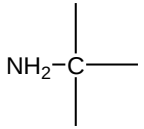
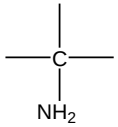
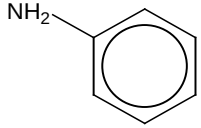
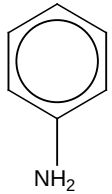
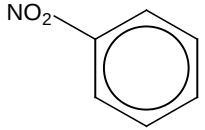
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

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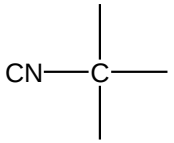
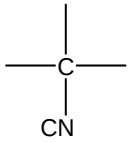
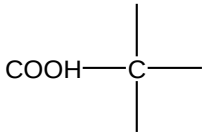
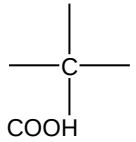
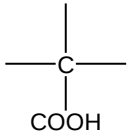
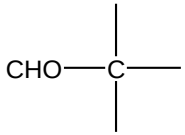
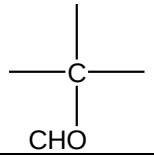
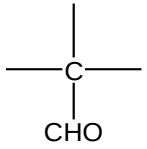
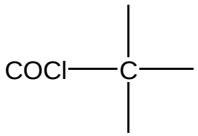
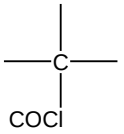
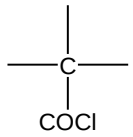
I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

				
allowed	**allowed**	not allowed	not allowed	not allowed
				
allowed	**allowed**	**allowed**	**allowed**	not allowed

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not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
ethan-1,2-diol	should be **ethane-1,2-diol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
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11	
TOTAL	



General Certificate of Education
Advanced Level Examination
January 2012

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Thursday 26 January 2012 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 80 minutes on **Section A** and about 25 minutes on **Section B**.



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Do not write outside the box

Section A

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

1 The initial rate of the reaction between two gases **P** and **Q** was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

1 (a) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	1.8×10^{-3}
2	0.40	0.60	
3	0.60		5.4×10^{-3}
4		0.90	12.2×10^{-3}

(3 marks)

(*Space for working*) .....

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1 (b) Use the data from Experiment **1** to calculate a value for the rate constant *k* and deduce its units.

Calculation .....

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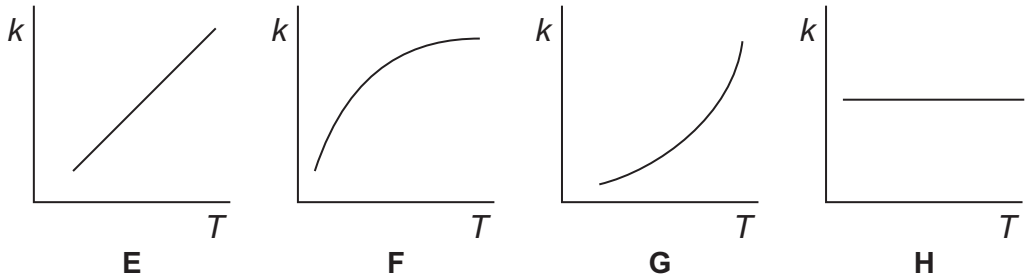
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Units .....

.....

(3 marks)

1 (c) Consider the graphs **E**, **F**, **G** and **H** below.



E **F** **G** **H**

Write in the box below the letter of the graph that shows how the rate constant *k* varies with temperature.

(1 mark)

7

Turn over ▶

Do not write outside the box

2 At high temperatures and in the presence of a catalyst, sulfur trioxide decomposes according to the following equation.

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad \Delta H^{\ominus} = +196\,kJ\,mol^{-1}$$

2 (a) In an experiment, 8.0 mol of sulfur trioxide were placed in a container of volume 12.0 dm^3 and allowed to come to equilibrium.
At temperature T_1 there were 1.4 mol of oxygen in the equilibrium mixture.

2 (a) (i) Calculate the amount, in moles, of sulfur trioxide and of sulfur dioxide in the equilibrium mixture.

Amount of sulfur trioxide .....

Amount of sulfur dioxide .....

(2 marks)

2 (a) (ii) Write an expression for the equilibrium constant, K_c, for this equilibrium.

.....

.....

(1 mark)

2 (a) (iii) Deduce the units of K_c for this equilibrium.

.....

.....

(1 mark)

2 (a) (iv) Calculate a value of K_c for this equilibrium at temperature T_1

(If you were unable to complete the calculations in part **(a) (i)** you should assume that the amount of sulfur trioxide in the equilibrium mixture was 5.8 mol and the amount of sulfur dioxide was 2.1 mol. These are **not** the correct values.)

.....

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.....

.....

(3 marks)

(Extra space) .....

.....

Do not write outside the box

2 (b) The experiment was repeated at the same temperature using the same amount of sulfur trioxide but in a larger container.
State the effect, if any, of this change on:

2 (b) (i) the amount, in moles, of oxygen in the new equilibrium mixture

.....

(1 mark)

2 (b) (ii) the value of K_c

.....

(1 mark)

2 (c) The experiment was repeated in the original container but at temperature T_2
The value of K_c was smaller than the value at temperature T_1
State which is the higher temperature, T_1 or T_2
Explain your answer.

Higher temperature .....

Explanation .....

.....

.....

.....

.....

(3 marks)

(Extra space) .....

.....

12

Do not write outside the box

3 Ammonia and ethylamine are examples of weak Brønsted–Lowry bases.

3 (a) State the meaning of the term *Brønsted–Lowry base*.

.....

.....

(1 mark)

3 (b) (i) Write an equation for the reaction of ethylamine ($CH_3CH_2NH_2$) with water to form a weakly alkaline solution.

.....

.....

(1 mark)

3 (b) (ii) In terms of this reaction, state why the solution formed is **weakly** alkaline.

.....

.....

(1 mark)

3 (c) State which is the stronger base, ammonia or ethylamine. Explain your answer.

Stronger base .....

Explanation .....

.....

.....

.....

(3 marks)

(Extra space) .....

.....

Do not write outside the box

3 (d) Give the formula of an organic compound that forms an alkaline buffer solution when added to a solution of ethylamine.

.....

(1 mark)

3 (e) Explain qualitatively how the buffer solution in part **(d)** maintains an almost constant pH when a small amount of hydrochloric acid is added to it.

.....

.....

.....

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(2 marks)

(Extra space) .....

.....

9

Turn over for the next question

Do not write outside the box

4 This question involves calculations about two strong acids and one weak acid.
All measurements were carried out at 25 °C.

4 (a) A 25.0 cm^3 sample of 0.0850 mol dm^{-3} hydrochloric acid was placed in a beaker and 100 cm^3 of distilled water were added.
Calculate the pH of the new solution formed.
Give your answer to 2 decimal places.

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

4 (b) HX is a weak monobasic acid.

4 (b) (i) Write an expression for the acid dissociation constant, K_a, for HX.

.....

.....

(1 mark)

4 (b) (ii) The pH of a 0.0850 mol dm^{-3} solution of HX is 2.79
Calculate a value for the acid dissociation constant, K_a, of this acid.
Give your answer to 3 significant figures.

.....

.....

.....

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.....

.....

(3 marks)

(Extra space) .....

.....

.....

Do not write outside the box

4 (c) A 25.0 cm^3 sample of 0.620 mol dm^{-3} nitric acid was placed in a beaker and 38.2 cm^3 of 0.550 mol dm^{-3} aqueous sodium hydroxide were added.
Calculate the pH of the solution formed.
Give your answer to 2 decimal places.

The ionic product of water $K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C.

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(6 marks)

12

(Extra space) .....

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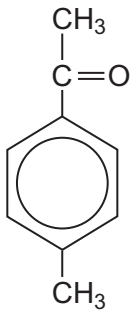
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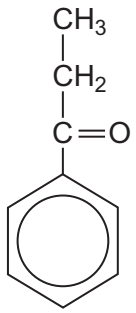
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5 Mass spectrometry is used by organic chemists to help distinguish between different compounds.

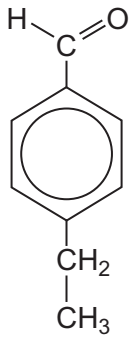
Four isomers of $C_9H_{10}O$, shown below, were analysed by mass spectrometry.



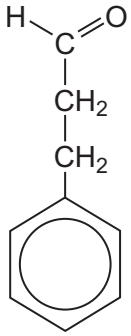
A



B



C



D

The mass spectra obtained from these four isomers were labelled in random order as I, II, III and IV.

Each spectrum contained a molecular ion peak at *m*/*z* = 134

The data in the table below show the *m*/*z* values greater than 100 for the **major** peaks in each spectrum due to fragmentation of the molecular ion. The table also shows where no major peaks occurred.

Spectrum	*m*/*z* values for major peaks	No major peak at *m*/*z*
I	119	133, 105
II	133, 119 and 105	
III	133, 105	119
IV	105	133, 119

5 (a) Two of the molecular ions fragmented to form an ion with *m*/*z* = 133 by losing a radical. Identify the radical that was lost.

.....

(1 mark)

5 (b) Two of the molecular ions fragmented to form an ion with *m*/*z* = 119 by losing a radical. Identify the radical that was lost.

.....

(1 mark)

Do not write outside the box

5 (c) Three of the molecular ions fragmented to form ions with m/z = 105 by losing a radical with M_r = 29

Identify **two** different radicals with M_r = 29 that could have been lost.

Radical 1 .....

Radical 2 .....

(2 marks)

5 (d) Consider the structures of the four isomers and the fragmentations indicated in parts **(a)** to **(c)**.
Write the letter **A**, **B**, **C** or **D**, in the appropriate box below, to identify the compound that produces each spectrum.

Spectrum I ☐

Spectrum II ☐

Spectrum III ☐

Spectrum IV ☐

(4 marks)

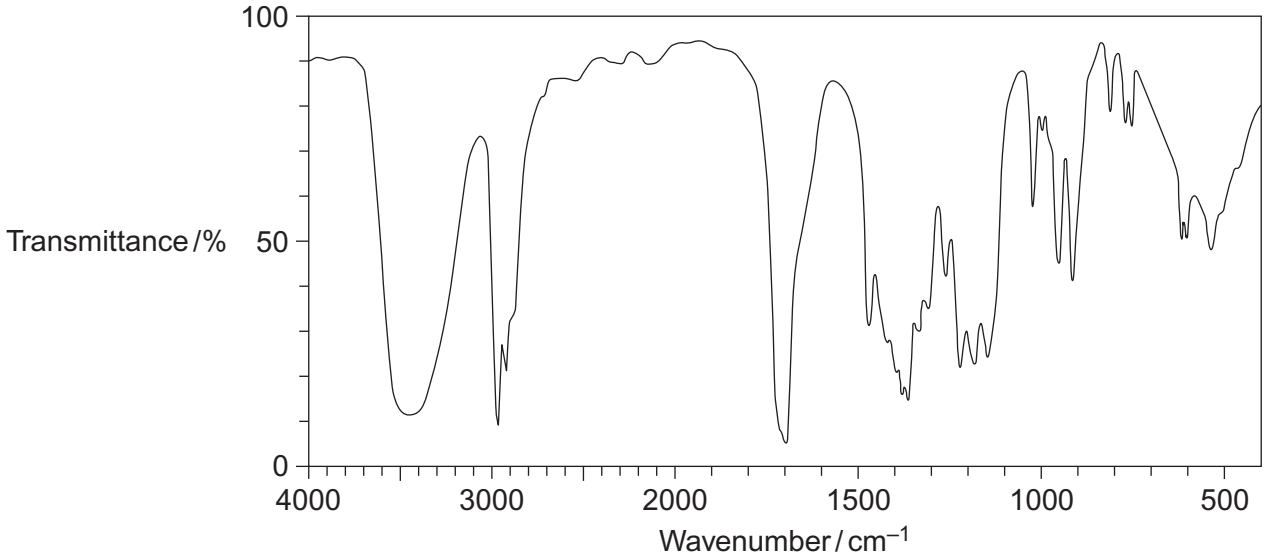
8

Turn over for the next question

Do not write outside the box

6 Compound **X** ($C_6H_{12}O_2$) was analysed by infrared spectroscopy and by proton nuclear magnetic resonance spectroscopy.

6 (a) The infrared spectrum of **X** is shown below.
Use **Table 1** on the Data Sheet to help you answer the question.



Identify the functional group that causes the absorption at 3450 cm^{-1} in the spectrum.

.....

(1 mark)

Do not write outside the box

6 (b) The proton n.m.r. spectrum of **X** consists of 4 singlet peaks.

The table below gives the chemical shift for each of these peaks, together with their integration values.

δ / ppm	1.2	2.2	2.6	3.8
Integration value	6	3	2	1

Use **Table 2** on the Data Sheet to help you answer the following questions.

Use the chemical shift and the integration data to show what can be deduced about the structure of **X** from the presence of the following in its proton n.m.r. spectrum.

6 (b) (i) The peak at δ = 2.6

.....

(1 mark)

6 (b) (ii) The peak at δ = 2.2

.....

(1 mark)

6 (b) (iii) The peak at δ = 1.2

.....

(1 mark)

6 (b) (iv) Deduce the structure of **X** ($C_6H_{12}O_2$)

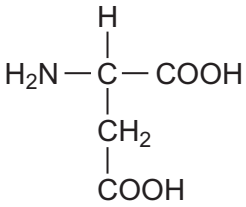
(1 mark)

5

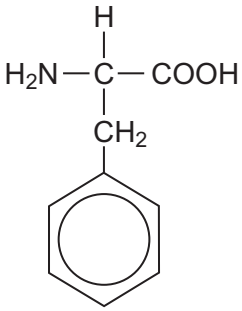
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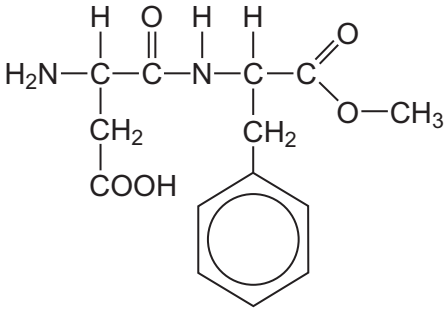
7 The amino acids aspartic acid and phenylalanine react together to form a dipeptide. This dipeptide can be converted into a methyl ester called aspartame.



aspartic acid



phenylalanine



aspartame

Aspartame has a sweet taste and is used in soft drinks and in sugar-free foods for people with diabetes.

Hydrolysis of aspartame forms methanol initially. After a longer time the peptide link breaks to form the free amino acids. Neither of these amino acids tastes sweet.

7 (a) Apart from the release of methanol, suggest why aspartame is **not** used to sweeten foods that are to be cooked.

.....

.....

(1 mark)

(Extra space) .....

.....

7 (b) Give the IUPAC name of aspartic acid.

.....

(1 mark)

7 (c) Draw the organic species formed by aspartic acid at high pH.

(1 mark)

Do not write outside the box

7 (d) Draw the zwitterion of phenylalanine.

(1 mark)

7 (e) Phenylalanine exists as a pair of stereoisomers.

7 (e) (i) State the meaning of the term *stereoisomers*.

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(2 marks)

7 (e) (ii) Explain how a pair of stereoisomers can be distinguished.

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(2 marks)

(Extra space) .....

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8

Do not write outside the box

8 Common substances used in everyday life often contain organic compounds.

8 (a) State an everyday use for each of the following compounds.

8 (a) (i) $CH_3(CH_2)_{17}COO^-Na^+$ .....

(1 mark)

8 (a) (ii) $CH_3(CH_2)_{19}COOCH_3$ .....

(1 mark)

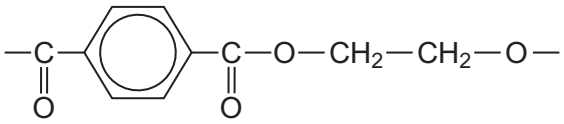
8 (a) (iii) $[C_{16}H_{33}N(CH_3)_3]^+ Br^-$ .....

(1 mark)

8 (b) The following structures are the repeating units of two different condensation polymers.

For each example, name the type of condensation polymer. Give a common name for a polymer of this type.

8 (b) (i)

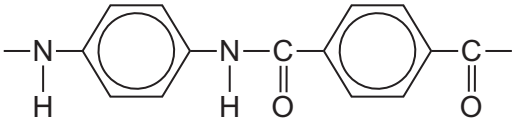


Type of condensation polymer .....

Common name .....

(2 marks)

8 (b) (ii)



Type of condensation polymer .....

Common name .....

(2 marks)

Do not write outside the box

8 (b) (iii) Explain why the polymer in part **(b) (ii)** has a higher melting point than the polymer in part **(b) (i)**.

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(2 marks)

(Extra space) .....

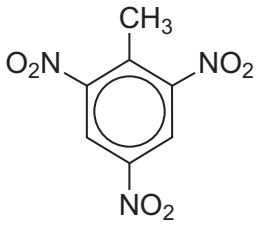
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9

Turn over for the next question

Do not write outside the box

9 Many aromatic nitro compounds are used as explosives. One of the most famous is 2-methyl-1,3,5-trinitrobenzene, originally called trinitrotoluene or TNT. This compound, shown below, can be prepared from methylbenzene by a sequence of nitration reactions.



9 (a) The mechanism of the nitration of methylbenzene is an electrophilic substitution.

9 (a) (i) Give the reagents used to produce the electrophile for this reaction.
Write an equation or equations to show the formation of this electrophile.

Reagents .....

.....

Equation .....

.....

(3 marks)

9 (a) (ii) Outline a mechanism for the reaction of this electrophile with methylbenzene to produce 4-methylnitrobenzene.

(3 marks)

Do not write outside the box

9 (b) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TNT.

.....

(1 mark)

9 (c) Deduce the number of peaks in the ^{1}H n.m.r. spectrum of TNT.

.....

(1 mark)

9 (d) Using the molecular formula ($C_7H_5N_3O_6$), write an equation for the decomposition reaction that occurs on the detonation of TNT. In this reaction equal numbers of moles of carbon and carbon monoxide are formed together with water and nitrogen.

.....

(1 mark)

9

Turn over for the next question

Do not write outside the box

Section B

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

10 The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of CH_3CH_2COCl and of $CH_3CH_2CH_2Cl$ with ammonia.

10 (a) For the reaction of CH_3CH_2COCl with ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

(Extra space) .....

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Do not write outside the box

10 (b) For the reaction of $CH_3CH_2CH_2Cl$ with an **excess** of ammonia, name and outline the mechanism and name the organic product.

(6 marks)

(Extra space) .....

Question 10 continues on the next page

Do not write outside the box

10 (c) Suggest **one** reason why chlorobenzene (C_6H_5Cl) does **not** react with ammonia under normal conditions.

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(1 mark)

(Extra space) .....

.....

13

Do not write outside the box

11 Chemists have to design synthetic routes to convert one organic compound into another.

Propanone can be converted into 2-bromopropane by a three-step synthesis.

Step 1: propanone is reduced to compound **L**.
Step 2: compound **L** is converted into compound **M**.
Step 3: compound **M** reacts to form 2-bromopropane.

Deduce the structure of compounds **L** and **M**.

For each of the three steps, suggest a reagent that could be used and name the mechanism.

Equations and curly arrow mechanisms are **not** required.

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(8 marks)

(Extra space) .....

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8

END OF QUESTIONS

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Version 1



General Certificate of Education (A-level)
January 2012

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

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Question	Marking Guidance	Mark	Comments
1(a)	Exp 2 $14.(4) \times 10^{-3}$ ***OR*** $1.4(4) \times 10^{-2}$ or 0.014 Exp 3 0.1(0) Exp 4 0.3(0)	1 1 1	Allow 2sf If three wrong answers, check their value of *k* in 1(b). They can score all 3 if they have used their (incorrect) value of *k*. see below. Exp 2 rate = $0.096 \times k$ Exp 3 [**Q**] = $0.015/k$ Exp 4 [**P**] = $0.116/\sqrt{k}$
1(b)	$k = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30}$ = 0.15 (min 2sfs) (allow $\frac{3}{20}$) $mol^{-2}\,dm^{+6}\,s^{-1}$	1 1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, score only units mark AE (-1) for copying numbers wrongly or swapping two numbers Any order If k calculation wrong, allow units conseq to their k
1(c)	G	1	

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Question	Marking Guidance			Mark	Comments	
2(a)(i)	Mol SO_3 = 5.2 Mol SO_2 = 2.8			1 1		
2(a)(ii)	$\frac{[SO_2]^2[O_2]}{[SO_3]^2}$	Penalise expression containing numbers or V Ignore subsequent <u>correct</u> working		1	Allow ( ) but must have all brackets. If brackets missing but otherwise correct, penalise here but mark on If Kc wrong (wrong powers or upside down etc) can only score M1 in 2(a)(iv)	
2(a)(iii)	mol dm^{-3}			1	Allow conseq to their wrong Kc	
					If Kc wrong in 2(a)(iv) (wrong powers or upside down etc) can only score M1	
2(a)(iv)	*Values from (a)(i)* $\frac{[2.8/12]^2[1.4/12]}{[5.2/12]^2}$ or $\frac{[0.233]^2[0.117]}{[0.433]^2}$	*Alternative values* $\frac{[2.1/12]^2[1.4/12]}{[5.8/12]^2}$	M1 M2	1 1	For dividing all three by volume - if volume missed or used wrongly, lose M1 & M2 but can score M3 conseq insertion of values (allow conseq use of their wrong values from 2a(i)) AE (-1) for copying numbers wrongly or swapping two numbers	
	= 0.0338 or 0.034 (allow 0.03376 to 0.035) Min 2 sfs Ignore units in (a)(iv)	0.0153 or 0.015 (allow 0.015 to 0.017) Min 2 sfs Ignore units in (a)(iv)	M3	1	If vol missed score only M3 *Values from (a)(i)* 0.406 - allow values between 0.40 (if correctly rounded) and 0.41	*from alternative values* allow 0.18 to 0.184

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2(b)(i)	Increase or more moles (of oxygen) or higher		1	
2(b)(ii)	No change or no effect or none or (remains) same		1	
2(c)	T_1	M1	1	If T_2 CE = 0
	(At Temp,T_2, when Kc is lower) Equm/reaction moves to left or towards reagent or towards SO_3 OR moles SO_3 increases	M2	1	
	This reverse reaction is exothermic,	M3	1	
	OR			
	(forward) reaction is endothermic	M3		
	if Temp is increased Equm/reaction moves to right or towards product or towards SO_2 OR moles SO_2 increases	M2		
	OR			
	(forward) reaction is endothermic	M3		
	if Temp is decreased Equm/reaction moves to left or towards reagent or towards SO_3 OR moles SO_3 increases	M2		

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Question	Marking Guidance		Mark	Comments
3(a)	Proton acceptor		1	
3(b)(i)	$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ + OH^-$		1	allow eq with or without $\rightleftharpoons$ allow $C_2H_5NH_2$ and $C_2H_5NH_3^+$ (plus can be on N or H or 3) allow RHS as $C_2H_5NH_3OH$
3(b)(ii)	Mark independently of 3b(i) reaction/equilibrium lies to left or low $[OH^-]$ ***OR*** little OH^- formed ***OR*** little ethylamine has reacted		1	Allow Ethylamine is only partly/slightly dissociated OR Ethylamine is only partly/slightly ionized Ignore "not fully dissociated" or "not fully ionized" Ignore reference to ionisation or dissociation of water
3(c)	Ethylamine alkyl group is electron releasing/donating ***OR*** alkyl group has (positive) inductive effect increases electron density on $N(H_2)$ ***OR*** increased availability of lp ***OR*** increases ability of lp (to accept H(+))	M1 M2 M3	1 1 1	If wrong no marks in 3c Mark M3 is independent of M2

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3(d)	$CH_3CH_2NH_3Cl$ allow name (ethylammonium chloride or ethylamine hydrochloride) or other halide for Cl	1	Or any amine hydrochloride or a strong **organic** acid **NOT** NH_4Cl

3(e)	Mark independently of 3(d) Extra H^+ reacts with ethylamine or OH^- ***OR*** $CH_3CH_2NH_2 + H^+ \rightarrow CH_3CH_2NH_3^+$ ***OR*** $H^+ + OH^- \rightarrow H_2O$ Equilibrium shifts to RHS ***OR*** ratio $[CH_3CH_2NH_3^+]/[CH_3CH_2NH_2]$ remains almost constant	 1 1	 Or makes reference to Equilibrium (in 3(b)(i)) with amine on LHS

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Question	Marking Guidance		Mark	Comments
4(a)	$[H^+]$ = 0.0170	M1	1	
	pH = 1.77	M2	1	2 dp **Allow M2 for correct pH calculation from their wrong $[H^+]$ for this pH calculation only**
4(b)(i)	$K_a = \frac{[H^+][X^-]}{[HX]}$ Ignore $K_a = \frac{[H^+]^2}{[HX]}$		1	Penalize missing [ ] here **and not elsewhere** Allow HA instead of HX
4(b)(ii)	$[H^+] = 10^{-2.79}$ OR $1.6218\ldots \times 10^{-3}$	M1	1	If $[H^+]$ wrong, can only score M2
	$K_a = \frac{[H^+]^2}{[HX]}$ OR $\frac{[1.62 \times 10^{-3}]^2}{[0.0850]}$	M2	1	Allow HA instead of HX
	$K_a = 3.09 \times 10^{-5}$ 3sfs min (allow 3.10×10^{-5} if 1.6218 rounded to 1.622) Ignore units	M3	1	If [HX] used as $(0.0850 - 1.62 \times 10^{-3})$ this gives $K_a = 3.15 \times 10^{-5}$ $(0.0016)^2/0.085 = 3.01 \times 10^{-5}$ scores 2 for AE

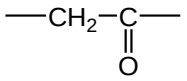
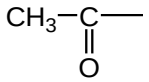
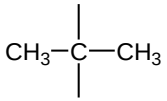
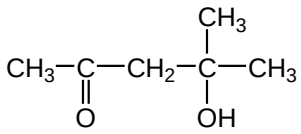
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4(c)	mol OH^- (= $(38.2 \times 10^{-3}) \times 0.550$) = $2.10(1) \times 10^{-2}$ or 0.0210(1) mol H^+ (= $(25.0 \times 10^{-3}) \times 0.620$) = 1.55×10^{-2} or 0.0155 excess mol OH^- = $5.5(1) \times 10^{-3}$	M1 M2 M3	1 1 1	Mark for answer Mark for answer Allow conseq for M1 – M2 **If wrong method** e.g. no subtraction or use of √ **can only score max of M1, M2, M3 and M4**.
	$[[OH^-] = 5.51 \times 10^{-3} \times \frac{10^3}{63.2}$ [= 0.08718 (0.0872)] ***OR*** $[OH^-] = 5.5 \times 10^{-3} \times \frac{10^3}{63.2}$ = 0.0870(2)	M4	1	(M1 – M2) / vol in dm^3 mark for dividing by volume (take use of 63.2 without 10^{-3} as AE so 9.94 scores 5) If no use or wrong use of vol lose M4 & M6 Can score M5 for showing (10^{-14}/their XS alkali)
	$[H^+] = \frac{10^{-14}}{0.08718} = 1.147 \times 10^{-13}$ ***OR*** $\frac{10^{-14}}{0.0870} = 1.149 \times 10^{-13}$ ***OR*** pOH = 1.06	M5	1	If no use or wrong use of K_w or pOH no further marks
	pH = 12.9(4) allow 3sf	M6	1	If vol missed score max 4 for 11.7(4)
				If acid- alkali reversed max 4 for pH = 1.06 Any excess acid - max 4

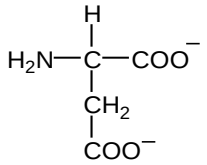
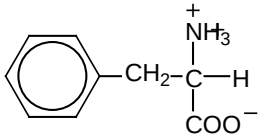
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Question	Marking Guidance	Mark	Comments
5(a)	H ***OR*** hydrogen ***OR*** $H^{\cdot}$	1	Ignore brackets ignore dot penalise + or – charge
5(b)	CH_3 ***OR*** methyl ***OR*** $CH_3^{\cdot}$ ***OR*** $^{\cdot}CH_3$	1	Ignore brackets ignore dot penalise + or – charge
5(c)	Either order C_2H_5 ***OR*** ethyl ***OR*** $CH_3CH_2^{\cdot}$ ***OR*** $C_2H_5^{\cdot}$ CHO ***OR*** HCO ***OR*** COH ***OR*** H—C=O	 1 1	 Ignore brackets ignore dot penalise + or – charge
5(d)	I A II C III D IV B	1 1 1 1	

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Question	Marking Guidance			Mark	Comments
6(a)	<u>OH alcohols</u>			1	
6(b)(i)	2.6		Ignore any group on RHS On LHS, penalise H or CH or CH_2 or CH_3	1	Must clearly indicate relevant **two** H on a C next to C=O Ignore missing trailing bonds or attached R groups
6(b)(ii)	2.2		Ignore all groups on RHS	1	Must clearly indicate relevant **three** H on C next to C=O Ignore missing trailing bonds or attached R group
6(b)(iii)	1.2		Or in words: two <u>equivalent</u> CH_3 groups Penalise attached H	1	Must clearly indicate two <u>equivalent</u> methyl groups. Ignore missing trailing bonds or attached R groups
6(b)(iv)				1	

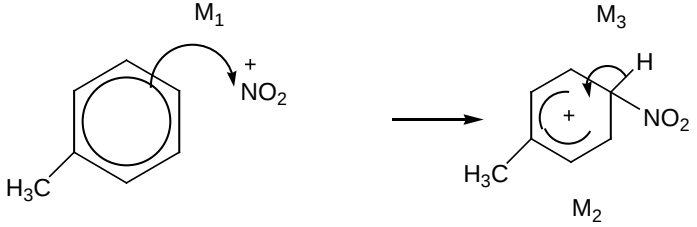
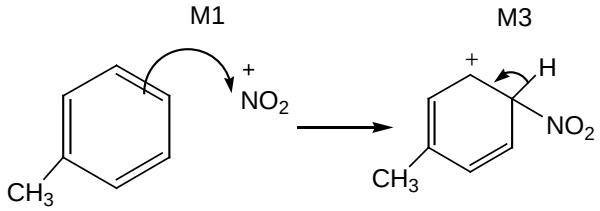
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Question	Marking Guidance		Mark	Comments
7(a)	Heating <u>speeds up</u> (hydrolysis / breaking of peptide bonds) ***OR*** forms non-sweet (amino acids)		1	
7(b)	(2-)aminobutan**e**dioic acid OR (2-)aminobutan**e**(-1,4-)dioic acid		1	2 not necessary but penalise other numbers at start 1,4 not necessary but penalise other numbers and 1,4 must be in correct place (QoL)
7(c)			1	allow $-CO_2^-$ allow NH_2-
7(d)			1	allow $-CO_2^-$ allow $^+NH_3-$ don't penalize position of + on NH_3
7(e)(i)	Compounds/molecules with same <u>structural formula</u> But with <u>bonds/atoms/groups</u> arranged differently <u>in space</u> or <u>in 3D</u>	M1 Independent marks M2	1 1	Not just structure Allow -with different <u>spatial</u> arrangement of <u>atom/bond/group</u>
7(e)(ii)	(Plane) polarised light <u>Rotated</u> in opposite directions		1 1	 Not bent or turned or twisted; not different directions (QoL)

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Question	Marking Guidance	Mark	Comments
8(a)(i)	(As a) soap	1	Allow washing, cleaning, degreasing, detergents
8(a)(ii)	(Bio)diesel or biofuel or fuel for cars/lorries	1	Allow <u>to make</u> soap
8(a)(iii)	(Cationic) surfactant /detergent /fabric softener /germicide / shampoos /(hair) conditioners /spermicidal jelly	1	Allow cleaning
8(b)(i)	(Poly)ester Terylene ***OR*** PET	1 1	 Allow polyester
8(b)(ii)	(Poly)amide Kevlar ***OR*** nylons	1 1	 Ignore numbers with nylons Allow polyamide(e)
8(b)(iii)	(Independent marks) Hydrogen bonding in b(ii) Imfs in (b)(ii) are stronger ***OR*** H bonding stronger than dipole-dipole/van der Waals/ dispersion/London forces in b(i)	 1 1	CE = 0

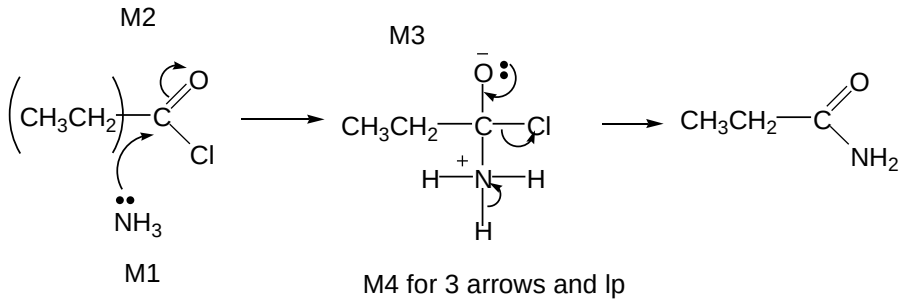
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Question	Marking Guidance	Mark	Comments
9(a)(i)	Conc HNO_3 Conc H_2SO_4 $2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$ **OR** $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + NO_2^+ + H_2O$ **OR** via two equations $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + H_2NO_3^+$ $H_2NO_3^+ \rightarrow\ NO_2^+ + H_2O$	1 1 1	If either or both conc missing, allow one; this one mark can be gained in equation` Allow + anywhere on NO_2^+
9(a)(ii)	M_1 M_3  M_2 **OR** M1 M3  M2	3	• ignore position or absence of methyl group in M1 but must be in correct position for M2 • M1 arrow from within hexagon to N or <u>+ on N</u> • Allow NO_2^+ in mechanism • Bond to NO_2 must be to N • horseshoe must not extend beyond C2 to C6 but can be smaller • + not too close to C1 • M3 arrow into hexagon unless Kekule • allow M3 arrow independent of M2 structure • ignore base removing H in M3 • + on H in intermediate loses M2 not M3
9(b)	5	1	

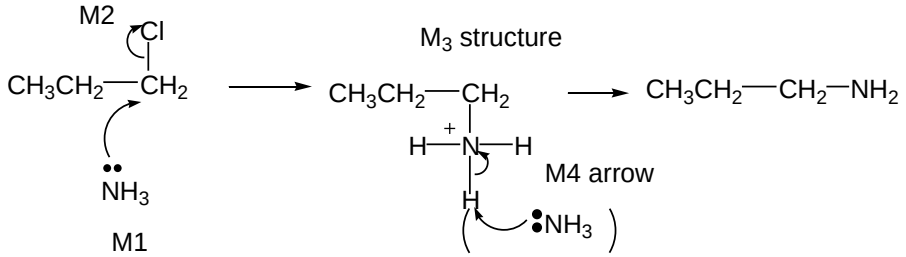
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9(c)	2	1	
9(d)	$2C_7H_5N_3O_6 \rightarrow 5H_2O + 3N_2 + 7C + 7CO$	1	Or halved

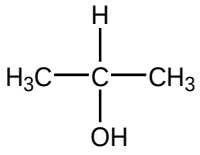
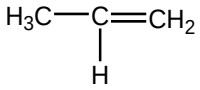
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Question	Marking Guidance	Mark	Comments
10(a)	(Nucleophilic) addition-elimination  M4 for 3 arrows and lp propanamide (Ignore -1-)	1 4 1	• Minus sign on NH_3 loses M1(but not M4 also) • M2 not allowed independent of M1, but • allow M1 for correct attack on C+ • + rather than δ+ on C=O loses M2 • **If Cl lost with C=O breaking, max1 for M1** • **M3** for correct structure <u>with charges</u> but lp on O is part of **M4** • only allow **M4** after correct/very close **M3** • For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism, • but ignore HCl shown as a product penalise other numbers penalise propaneamide and N-propanamide

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10(b)	Nucleophilic substitution  Propylamine (ignore number 1) or propan-1-amine or 1-aminopropane (number 1 needed)	1 4 1	• Minus sign on NH_3 loses M1 (not M4 also) • + rather than δ+ on C=O loses M2 • ALLOW SN1 so allow M2 for loss of Cl^- before attack of NH_3 on C+ for M1 • only allow M4 after correct/very close M3 • For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism, • but ignore HCl shown as a product penalise other numbers allow 1-propanamine
10(c)	electron rich ring or benzene or pi cloud repels nucleophile/ammonia	1 max	Allow • C–Cl bond is short/stronger than in haloalkane • C–Cl is less polar than in haloalkane • resonance stabilisation between ring and Cl

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Question	Marking Guidance		Mark	Comments
11	**L**		1	Allow name propan-2-ol Penalise contradiction of name and structure
		Allow $(CH_3)_2CHOH$ or $CH_3CH(OH)CH_3$		
	M		1	Allow name propene ignore -1- but penalise other numbers Penalise contradiction of name and structure
		Allow $CH_3CH=CH_2$		
	M1	Step 1 $NaBH_4$ or $LiAlH_4$	1	Ignore name if formula is correct ignore solvent ignore acid (for 2nd step) but penalise acidified $NaBH_4$ Apply list principle for extra reagents and catalysts.
		Zn/HCl or Sn/HCl or H_2/Ni or H_2/Pt		
	M2	(nucleophilic) addition	1	Penalise electrophilic Ignore reduction
		Addition (not nucleophilic)		
	M3	Step 2 <u>conc</u> H_2SO_4 or <u>conc</u> H_3PO_4 or Al_2O_3	1	Apply list principle for extra reagents and catalysts.
	M4	elimination	1	Independent from M3 penalise nucleophilic or electrophilic ignore dehydration
	M5	Step 3 HBr	1	Apply list principle for extra reagents and catalysts.
	M6	electrophilic addition	1	Independent from M5

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General principles applied to marking CHEM4 papers by CMI+ (January 2012)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

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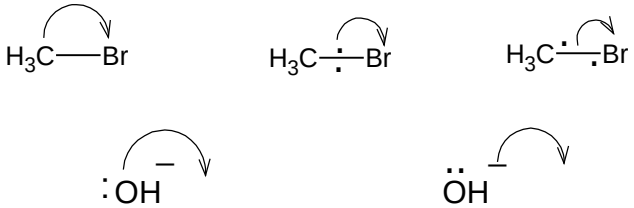
G. Marking calculations

In general

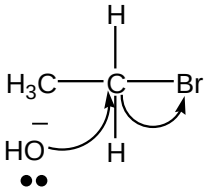
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

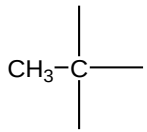
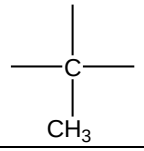
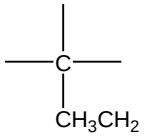
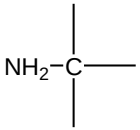
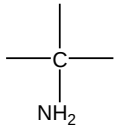
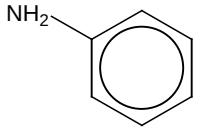
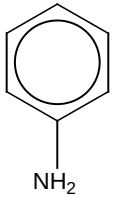
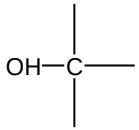
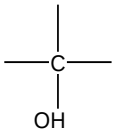
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

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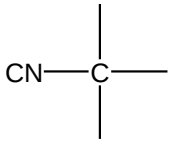
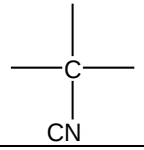
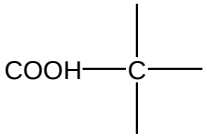
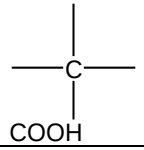
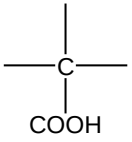
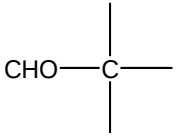
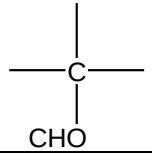
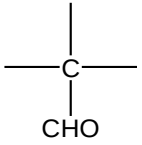
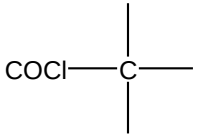
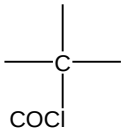
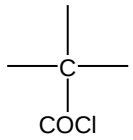
I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

					
allowed	**allowed**	not allowed			
					
allowed	**allowed**	**allowed**	**allowed**	not allowed	not allowed

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not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions <u>may</u> be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
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8	
TOTAL	



General Certificate of Education
Advanced Level Examination
June 2011

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 15 June 2011 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.



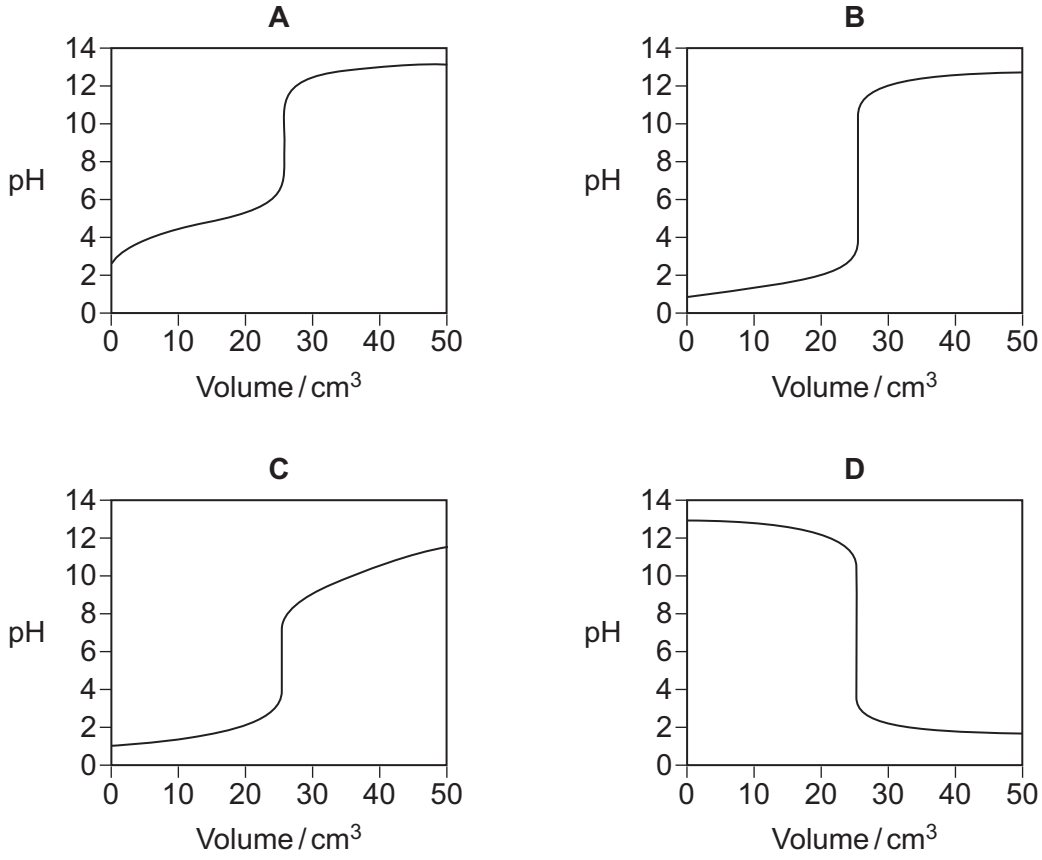
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Do not write outside the box

Section A

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

1 Titration curves labelled **A**, **B**, **C** and **D** for combinations of different aqueous solutions of acids and bases are shown below.
All solutions have a concentration of 0.1 mol dm^{-3}.



1 (a) In this part of the question write the appropriate letter in each box.

From the curves **A**, **B**, **C** and **D**, choose the curve produced by the addition of

ammonia to 25 cm^3 of hydrochloric acid ☐

sodium hydroxide to 25 cm^3 of ethanoic acid ☐

nitric acid to 25 cm^3 of potassium hydroxide ☐

(3 marks)

Do not write outside the box

1 (b) A table of acid–base indicators is shown below.
The pH ranges over which the indicators change colour and their colours in acid and alkali are also shown.

Indicator	pH range	Colour in acid	Colour in alkali
Trapaeolin	1.3 – 3.0	red	yellow
Bromocresol green	3.8 – 5.4	yellow	blue
Cresol purple	7.6 – 9.2	yellow	purple
Alizarin yellow	10.1 – 12.0	yellow	orange

1 (b) (i) Select from the table an indicator that could be used in the titration that produces curve **B** but **not** in the titration that produces curve **A**.

.....

(1 mark)

1 (b) (ii) Give the colour change at the end point of the titration that produces curve **D** when cresol purple is used as the indicator.

.....

(1 mark)

5

Turn over for the next question

Do not write outside the box

2 This question is about the pH of some solutions containing potassium hydroxide and ethanoic acid.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

.....

(1 mark)

2 (a) (ii) Write an expression for the ionic product of water, K_w

.....

(1 mark)

2 (a) (iii) At 10 °C, a 0.154 mol dm^{-3} solution of potassium hydroxide has a pH of 13.72
Calculate the value of K_w at 10 °C.

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

Do not write outside the box

2 (b) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (b) (i) Write an expression for K_a for ethanoic acid.

.....

.....

(1 mark)

2 (b) (ii) Calculate the pH of a 0.154 mol dm^{-3} solution of ethanoic acid at 25 °C.

.....

.....

.....

.....

.....

.....

(3 marks)

(Extra space) .....

.....

.....

Question 2 continues on the next page

Do not write outside the box

2 (c) At 25 °C, the acid dissociation constant K_a for ethanoic acid has the value 1.75×10^{-5} mol dm^{-3}.

2 (c) (i) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

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(4 marks)

(Extra space) .....

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Do not write outside the box

2 (c) (ii) Calculate the pH of the solution formed when 40.0 cm^3 of 0.154 mol dm^{-3} potassium hydroxide are added to 20.0 cm^3 of 0.154 mol dm^{-3} ethanoic acid at 25 °C.

At 25 °C, K_w has the value 1.00×10^{-14} mol^2 dm^{-6}.

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(4 marks)

(Extra space) .....

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.....

16

Turn over for the next question

Do not write outside the box

3 The following dynamic equilibrium was established at temperature T in a closed container.

$$P(g) + 2Q(g) \rightleftharpoons 2R(g) \qquad \Delta H^{\ominus} = -50\ kJ\ mol^{-1}$$

The value of K_c for the reaction was 68.0 mol^{-1} dm^3 when the equilibrium mixture contained 3.82 mol of **P** and 5.24 mol of **R**.

3 (a) Give the meaning of the term *dynamic equilibrium*.

.....

.....

.....

.....

(2 marks)

(Extra space) .....

.....

3 (b) Write an expression for K_c for this reaction.

.....

.....

(1 mark)

3 (c) The volume of the container was 10.0 dm^3.

Calculate the concentration, in mol dm^{-3}, of **Q** in the equilibrium mixture.

.....

.....

.....

.....

.....

.....

(4 marks)

(Extra space) .....

.....

Do not write outside the box

3 (d) State the effect, if any, on the equilibrium amount of **P** of increasing the temperature. All other factors are unchanged.

.....

(1 mark)

3 (e) State the effect, if any, on the equilibrium amount of **P** of using a container of larger volume. All other factors are unchanged.

.....

(1 mark)

3 (f) State the effect, if any, on the value of K_c of increasing the temperature. All other factors are unchanged.

.....

(1 mark)

3 (g) State the effect, if any, on the value of K_c of using a container of larger volume. All other factors are unchanged.

.....

(1 mark)

3 (h) Deduce the value of the equilibrium constant, at temperature *T*, for the reaction

$$2R(g) \rightleftharpoons P(g) + 2Q(g)$$

.....

.....

(1 mark)

12

Turn over for the next question

Do not write outside the box

4 The amide or peptide link is found in synthetic polyamides and also in naturally-occurring proteins.

4 (a) (i) Draw the repeating unit of the polyamide formed by the reaction of propanedioic acid with hexane-1,6-diamine.

(2 marks)

4 (a) (ii) In terms of the intermolecular forces between the polymer chains, explain why polyamides can be made into fibres suitable for use in sewing and weaving, whereas polyalkenes usually produce fibres that are too weak for this purpose.

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(3 marks)

(Extra space) .....

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Do not write outside the box

4 (b) (i) Name and outline a mechanism for the reaction of CH_3CH_2COCl with CH_3NH_2

Name of mechanism.....

Mechanism

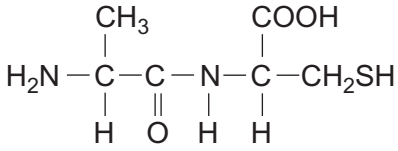
(5 marks)

4 (b) (ii) Give the name of the product containing an amide linkage that is formed in the reaction in part **4 (b) (i)**.

.....

(1 mark)

4 (c) The dipeptide shown below is formed from two different amino acids.



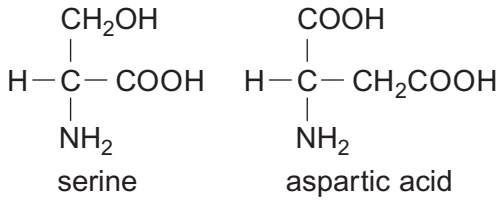
Draw the structure of the alternative dipeptide that could be formed by these two amino acids.

(1 mark)

Question 4 continues on the next page

Do not write outside the box

4 (d) The amino acids serine and aspartic acid are shown below.



4 (d) (i) Give the IUPAC name of serine.

.....

(1 mark)

4 (d) (ii) Draw the structure of the species formed when aspartic acid reacts with aqueous sodium hydroxide.

(1 mark)

4 (d) (iii) Draw the structure of the species formed when serine reacts with dilute hydrochloric acid.

(1 mark)

4 (d) (iv) Draw the structure of the species formed when serine reacts with an excess of bromomethane.

(1 mark)

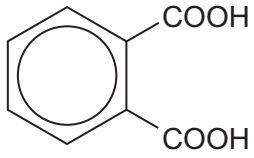
16

Do not write outside the box

5 Items softened with plasticisers have become an essential part of our modern society.

Compound **S**, shown below, is commonly known as phthalic acid.

Esters of phthalic acid are called phthalates and are used as plasticisers to soften polymers such as PVC, poly(chloroethene).



S

5 (a) Give the IUPAC name for phthalic acid.

.....

(1 mark)

5 (b) Draw the displayed formula of the repeating unit of poly(chloroethene).

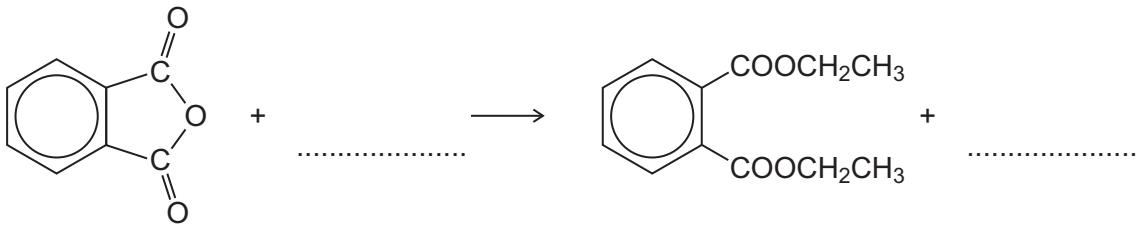
(1 mark)

Question 5 continues on the next page

Do not write outside the box

5 (c) The ester diethyl phthalate (DEP) is used in food packaging and in cosmetics.

5 (c) (i) Complete the following equation showing the formation of DEP from phthalic anhydride.



DEP

(2 marks)

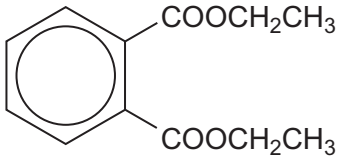
5 (c) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of DEP.

.....

(1 mark)

5 (c) (iii) One of the peaks in the ^{13}C n.m.r. spectrum of DEP is at $\delta = 62$ ppm.
Table 3 on the Data Sheet can be used to identify a type of carbon atom responsible for this peak.

Draw a circle around **one** carbon atom of this type in the structure below.



(1 mark)

5 (d) The mass spectrum of DEP includes major peaks at $m/z = 222$ (the molecular ion) and at $m/z = 177$

Write an equation to show the fragmentation of the molecular ion to form the fragment that causes the peak at $m/z = 177$

.....

(2 marks)

Do not write outside the box

5 (e) Because of their many uses, phthalates have been tested for possible adverse effects to humans and to the environment.

The European Council for Plasticisers and Intermediates is an organisation that represents the manufacturers of plasticisers.

The text below is taken from a document written by the organisation.

'Research demonstrates that phthalates, at current and foreseeable exposure levels, do not pose a risk to human health or to the environment. Experimental evidence shows that phthalates are readily biodegradable and do not persist for long in the environment.'

5 (e) (i) Hydrolysis of DEP in an excess of water was found to follow first order kinetics.

Write a rate equation for this hydrolysis reaction using DEP to represent the ester.

.....

(1 mark)

5 (e) (ii) Suggest what needs to be done so that the public could feel confident that the research quoted above is reliable.

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(2 marks)

(Extra space) .....

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11

Do not write outside the box

6 (a) In the presence of the catalyst rhodium, the reaction between NO and H_2 occurs according to the following equation.

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

The kinetics of the reaction were investigated and the rate equation was found to be

$$\text{rate} = k[NO]^2[H_2]$$

The initial rate of reaction was 6.2×10^{-6} mol dm^{-3} s^{-1} when the initial concentration of NO was 2.9×10^{-2} mol dm^{-3} and the initial concentration of H_2 was 2.3×10^{-2} mol dm^{-3}.

6 (a) (i) Calculate the value of the rate constant under these conditions and give its units.

Calculation .....

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Units .....

.....

(3 marks)

6 (a) (ii) Calculate the initial rate of reaction if the experiment is repeated under the same conditions but with the concentrations of NO and of H_2 both doubled from their original values.

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(1 mark)

Do not write outside the box

6 (b) Using the rate equation and the overall equation, the following three-step mechanism for the reaction was suggested. X and Y are intermediate species.

Step **1** $NO + NO \longrightarrow X$

Step **2** $X + H_2 \longrightarrow Y$

Step **3** $Y + H_2 \longrightarrow N_2 + 2H_2O$

Suggest which **one** of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step.....

Explanation .....

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(2 marks)

(Extra space) .....

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6

Turn over for the next question

Do not write outside the box

Section B

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

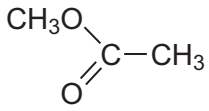
7 Organic chemists use a variety of methods to distinguish between compounds. These methods include analytical and spectroscopic techniques.

7 (a) The following compounds can be distinguished by observing what happens in test-tube reactions.

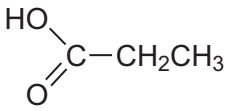
For each pair, suggest a suitable reagent or reagents that could be added separately to each compound in order to distinguish them.

Describe what you would observe with each compound.

7 (a) (i)



E



F

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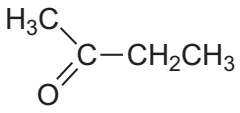
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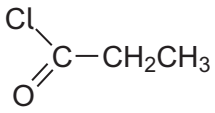
(3 marks)

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7 (a) (ii)



G



H

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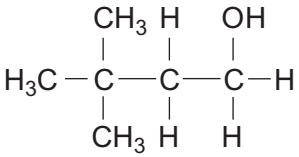
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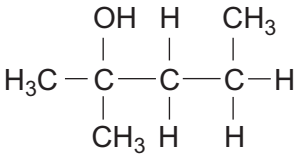
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(3 marks)

7 (a) (iii)



J



K

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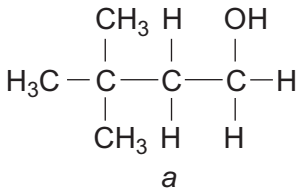
(3 marks)

Question 7 continues on the next page

Turn over ▶

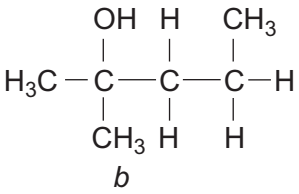
Do not write outside the box

7 (b) Compounds **J** and **K** can also be distinguished using spectroscopic techniques such as ^{1}H n.m.r.



a

J



b

K

7 (b) (i) Name compound **J**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **J**.

State the splitting pattern, if any, of the peak for the protons labelled *a*.

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(3 marks)

7 (b) (ii) Name compound **K**.

Give the total number of peaks in the ^{1}H n.m.r. spectrum of **K**.

State the splitting pattern, if any, of the peak for the protons labelled *b*.

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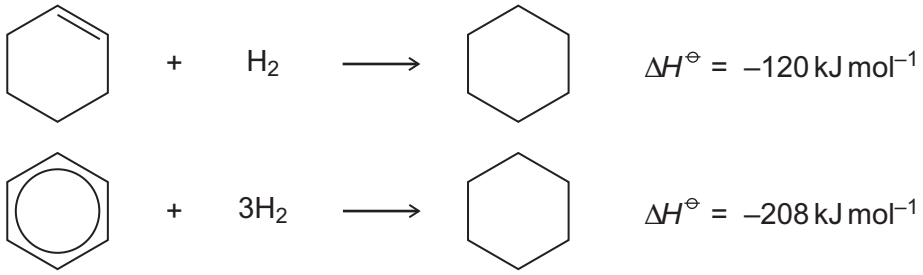
(3 marks)

15

Do not write outside the box

8 The hydrocarbons benzene and cyclohexene are both unsaturated compounds. Benzene normally undergoes substitution reactions, but cyclohexene normally undergoes addition reactions.

8 (a) The molecule cyclohexatriene does not exist and is described as hypothetical. Use the following data to state and explain the stability of benzene compared with the hypothetical cyclohexatriene.



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(4 marks)

(Extra space) .....

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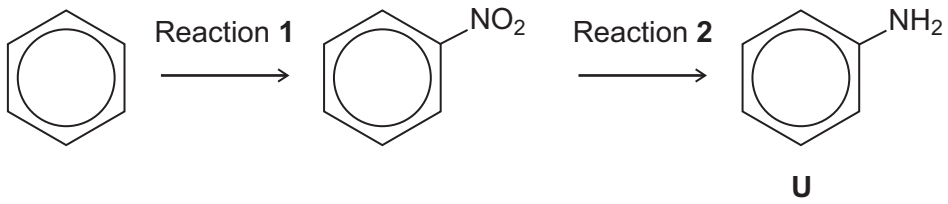
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Question 8 continues on the next page

Do not write outside the box

8 (b) Benzene can be converted into amine **U** by the two-step synthesis shown below.



U

The mechanism of Reaction **1** involves attack by an electrophile.

Give the reagents used to produce the electrophile needed in Reaction **1**.

Write an equation showing the formation of this electrophile.

Outline a mechanism for the reaction of this electrophile with benzene.

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(6 marks)

(Extra space) .....

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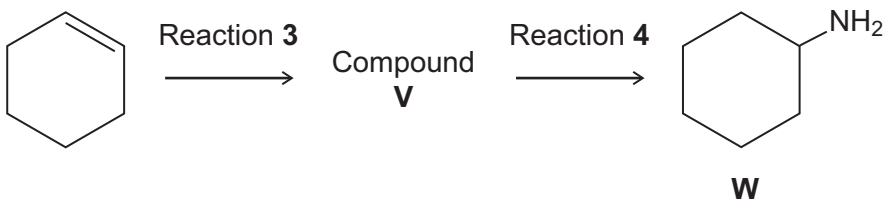
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Do not write outside the box

8 (c) Cyclohexene can be converted into amine **W** by the two-step synthesis shown below.



W

Suggest an identity for compound **V**.

For Reaction **3**, give the reagent used and name the mechanism.

For Reaction **4**, give the reagent and condition used and name the mechanism.

Equations and mechanisms with curly arrows are **not** required.

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(6 marks)

(Extra space) .....

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Question 8 continues on the next page

Do not write outside the box

8 (d) Explain why amine **U** is a weaker base than amine **W**.

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(3 marks)

(Extra space) .....

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19

END OF QUESTIONS

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Version 1



General Certificate of Education (A-level)
June 2011

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Final

Mark Scheme

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Question	Marking Guidance	Mark	Comments
1(a)	C A D	1 1 1	
1(b)(i)	Bromocresol green	1	Allow wrong spellings
1(b)(ii)	Purple to yellow	1	Must have both colours: Purple start – yellow finish

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Question	Marking Guidance	Mark	Comments
2(a)(i)	$-\log[H^+]$	1	penalise missing [ ] here **and not elsewhere**
2(a)(ii)	$[H^+][OH^-]$	1	Allow ( ) brackets, but must have charges
2(a)(iii)	Mark independently from a(ii) $[H^+] = 10^{-13.72} = 1.905 \times 10^{-14}$ $K_w = 1.905 \times 10^{-14} \times 0.154 = = (2.93 - 2.94) \times 10^{-15}$	 1 1	 If wrong no further mark
2(b)(i)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	1	Must have charges and all brackets, allow ( ) Acid/salt shown must be CH_3COOH not HA and correct formulae needed
2(b)(ii)	**In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp** **For values above 10, allow 3sfs - do not insist on 2 dp**		
	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ $([H^+]^2 = 1.75 \times 10^{-5} \times 0.154 = 2.695 \times 10^{-6} = 2.70 \times 10^{-6})$ $[H^+] = 1.64 \times 10^{-3}$ pH = 2.78 or 2.79	1 1 1	Allow HA If √ shown but not done gets pH = 5.57 (scores 2) Allow mark for pH conseq to their $[H^+]$ **here only**

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2(c)(i)	**In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp** **For values above 10, allow 3sfs - do not insist on 2 dp**		
	M1 Initially mol OH^- = (10 × 10^{-3}) × 0.154 **and** mol HA = (20 ×10^{-3}) × 0.154 **or** mol OH^- = 1.54 × 10^{-3} **and** mol HA = 3.08 × 10^{-3}	1	
	M2 $[H^+]$ = $K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$ or with numbers	1	Allow Henderson Hasselbach $pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$
	M3 mol ethanoic acid left = (mol ethanoate ions) = 1.54 × 10^{-3} $K_a = [H^+]$ **or** $pH = pK_a$ scores **M1**, **M2** and **M3**	1	If either mol acid in mixture or mol salt wrong - max 2 for M1 and M2 Any mention of $[H^+]^2$ - max 2 for M1 and M3
	M4 pH (= - log 1.75 × 10^{-5}) = 4.76 or 4.757	1	Not 4.75
	If no subtraction (so mol ethanoic acid in buffer = original mol) pH = 4.46 scores 2 for M1 and M2 If $[H^+]^2$ used, pH = 3.02 scores 2 for M1 and M3		

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2(c)(ii)	**In pH values penalise fewer than 3 sig figs each time but allow more than 2 dp** **For values above 10, allow 3sfs - do not insist on 2 dp**		
	M1 XS mol KOH (= $(20\times10^{-3}) \times 0.154$) = 3.08×10^{-3}	1	If no subtraction: max 1 for correct use of volume No subtraction and no use of volume scores zero If wrong subtraction or wrong moles Can only score **M2** and **M3** for process
	M2 $[OH^-]$ = $3.08 \times 10^{-3} \times \frac{10^3}{60}$ = 0.0513(3)	1	Mark for dividing their answer to **M1** by correct volume (method mark) If no volume or wrong volume or multiplied by volume, max 2 for **M1** and **M3** process
	M3 $[H^+]$ = $\frac{10^{-14}}{0.05133}$ (= 1.948×10^{-13} to 1.95×10^{-13}) **or** pOH = 1.29	1	Mark for K_w divided by their answer to **M2** If pOH route, give one mark for 14 – pOH
	M4 pH = 12.7(1)	1	Allow 3sf but not 12.70
	If no subtraction and no use of volume (pH = 11.79 scores zero) If no subtraction, max 1 for correct use of volume, ($60cm^3$) (pH = 13.01 scores 1) If volume not used, pH = 11.49 (gets 2) If multiplied by vol , pH = 10.27 (gets 2)		

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Question	Marking Guidance	Mark	Comments
3(a)	Forward and backward reactions proceeding at equal rate Amount (Conc or moles or proportion) of reactants and products remain constant	1 1	Not “reactants and products have equal conc”

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3(b)	**M1** $\frac{[R]^2}{[P][Q]^2}$	Allow ( ) but must have all brackets	1	If Kc wrong can only score **M3** (process mark) for dividing both R and P by volume)

3(c)	**M2** $[Q]^2 = \frac{[R]^2}{K_c[P]}$	Rearrangement of correct Kc expression	1	If wrong Kc used can only score **M3** for correct use of vol If wrong rearrangement can only score max 2 for **M3** and **M5** for correct √
	M3 $[Q]^2 = \frac{(5.24/10)^2}{68.0 \times (3.82/10)}$	Process mark for dividing both R and P by volume even in incorrect expression	1	If vol missed can only score max 2 for **M2** and **M5** for correct √ If vol used but then wrong maths can score **M2** **M3** and **M5** for correct √ If moles used wrongly, eg (2 × 5.24) or $(5.24 \times 10/10^3)$ can only score **M2** and **M5**
	M4 $[Q]^2 = 0.0106$	Correct calculation of Q^2	1	
	M5 $[Q] = 0.10(3)$	Correct taking of √	1	

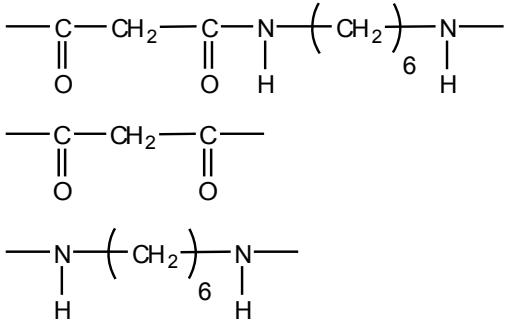
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3(c) cont.	Wrong rearrangement and no use of volume	zero	
	Wrong rearrangement	2 max	For Correct use of volume M3 and Correct taking of square root M5
	No use of volume	2 max **answer = 0.325** Ignore subsequent multiplying or dividing by 10. **0.0325 or 3.25** still score max 2	For Correct rearrangement M2 and Correct taking of square root M5
	Use of volume but maths error e.g. using $(5.24)^2/10$ when should be $(5.24/10)^2$	Scores 3 **also giving answer 0.325**	for M2, M3 and M5
	Use of volume but Q/10 also used or Q multiplied by 10 at end (i.e.muddling moles with concentration)	2 max **Gives answer 1.03**	For Correct rearrangement M2 and Correct taking of square root M5
	Wrong use of moles, e.g (5.24 × 2) or (5.24 $\times 10/10^3$)	2 max	For Correct rearrangement M2 and Correct taking of square root M5
	Wrong Kc used, e.g. missing powers	1 max	For Correct use of volume M3

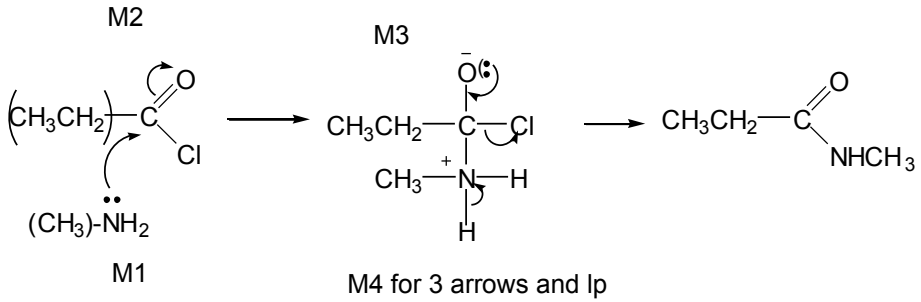
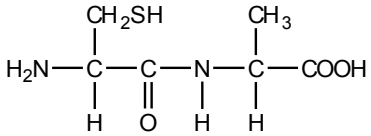
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3(d)	Increase or more or larger	1	Allow moves to left
3(e)	Increase or more or larger	1	Allow moves to left
3(f)	Decrease or less or smaller	1	NOT allow moves left
3(g)	No effect or unchanged or none	1	
3(h)	0.0147 or 0.0148 or 1.47×10^{-2} or 1.48×10^{-2} Allow 0.015 or 1.5×10^{-2} If not 0.0147, look at 3(c) for conseq correct use of their [Q] in new Kc = $1.39 \times [Q]^2$	1	Not allow just 1/68.0 ignore units

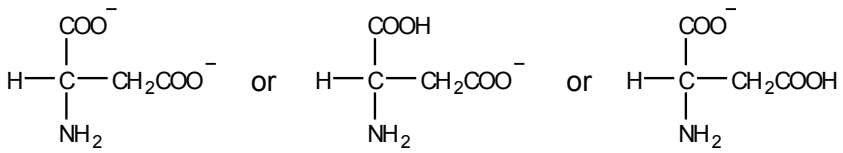
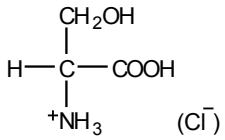
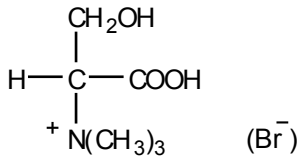
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Question	Marking Guidance	Mark	Comments
4(a)(i)		1 1	Allow –CONH- or - COHN - Mark two halves separately lose 1 each for missing trailing bonds at one or both ends or error in peptide link or either or both of H or OH on ends Not allow $-(C_6H_{12})-$ Ignore *n*
4(a)(ii)	**M1** in polyamides - H bonding **M2** in polyalkenes - van der Waals forces **M3** Stronger forces (of attraction) in polyamides Or H bonding is stronger (must be a comparison of correct forces to score M3)	1 1 1	 Penalise forces between atoms or van der Waals bonds Do not award if refer to stronger bonds

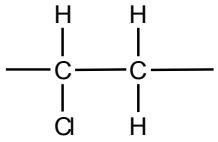
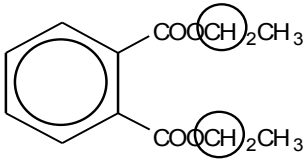
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4(b)(i)	(nucleophilic) addition elimination  M4 for 3 arrows and lp Not allow N–H_2	1 4	Minus sign on NH_2 loses M1 M2 not allowed independent of M1, but allow M1 for correct attack on C+ + rather than δ+ on C=O loses M2 If Cl lost with C=O breaking, max 1 for M1 M3 for correct structure <u>with charges</u> but lp on O is part of M4 only allow M4 after correct/ very close M3 For M4, ignore NH_3 removing H^+ but lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
4(b)(ii)	<u>N-methylpropanamide</u>	1	Not N-methylpropaneamide
4(c)	 	1	Allow –CONH- or - COHN -
4(d)(i)	<u>2-amino-3-hydroxypropanoic acid</u>	1	

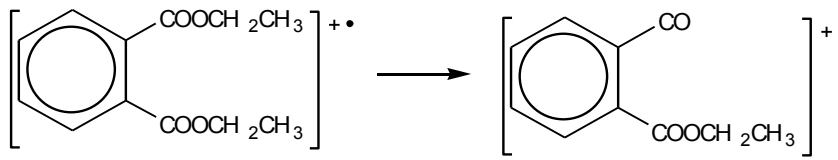
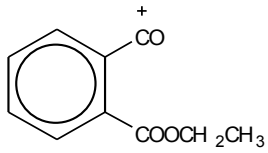
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4(d)(ii)	 or or Must be salts of aspartic acid	1	allow $-CO_2^-$ allow NH_2-
4(d)(iii)	Penalise use of aspartic acid once in d(iii) and d(iv) 	1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
4(d)(iv)	Penalise use of aspartic acid once in d(iii) and d(iv) 	1	allow $-CO_2^-$ must show C-N bond don't penalize position of + on $N(CH_3)_3$

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Question	Marking Guidance	Mark	Comments
5(a)	Benzene-1,2-dicarboxylic acid	1	Allow 1,2-benzenedicarboxylic acid
5(b)		1	Must show all bonds including trailing bonds Ignore *n*
5(c)(i)	2 C_2H_5OH H_2O	1 1	*NB Two ethanols* *but only one water*
5(c)(ii)	6 or six	1	
5(c)(iii)		1	Ignore overlap with O to the left or H to the right, but must only include this one carbon. either or allow both (as they are identical)

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5(d)	 $\dot{O}CH_2CH_3$ [DEP] $^{+\cdot}$ OR $[C_{12}H_{14}O_4]^{+\cdot} \rightarrow [C_{10}H_9O_3]^{+} + [C_2H_5O]^{\cdot}$	1 LHS 1 RHS	Allow + on C or O in  Dot must be on O in radical
5(e)(i)	Rate = *k*[DEP]	1	Must have brackets but can be ( )
5(e)(ii)	Any **two** of • experiment repeated/continued <u>over a long period</u> • repeated by independent body/other scientists/avoiding bias • investigate breakdown products • results made public	2 Max	Not just repetition Ignore animal testing

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Question	Marking Guidance	Mark	Comments
6(a)(i)	$k = \frac{6.2\times10^{-6}}{(2.9\times10^{-2})^2 \times 2.3\times10^{-2}}$	1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc AE (-1) for copying numbers wrongly or swapping two numbers
	= 0.32 (min 2sfs)	1	
	$mol^{-2}\,dm^6\,s^{-1}$ Units must be conseq to their *k*	1	Any order If k calculation wrong, allow units conseq to their k
6(a)(ii)	4.95×10^{-5} to 4.97×10^{-5} or 5.0×10^{-5} (min 2 sfs) (ignore units)	1	rate = their *k* × 1.547×10^{-4}
6(b)	Step 2 One H_2 (and two NO) (appear in rate equation) or species (in step 2) in ratio/proportion as in the rate equation	1 1	If wrong no further mark

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Question	Marking Guidance				Mark	Comments	
7(a)(i)	Single reagent	If wrong single reagent, CE = zero Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on For "no reaction" allow "nothing"					
	Different reagents	If different tests on E and F; **both** reagents and any follow on chemistry must be correct for first (reagent) mark. Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction. Second and third marks are for correct observations. i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.					
		Na_2CO_3/$NaHCO_3$ named carbonate	metal e.g.Mg	named indicator	1	PCl_5 PCl_3 $SOCl_2$	
	E ester	no reaction	no reaction	no effect	1	No reaction	
	F acid	Effervescence or CO_2	Effervescence or H_2	acid colour	1	fumes	

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<table>
<tr><td rowspan="6">7(a)(ii)</td><td>Single reagent</td><td colspan="7">If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on
For “no reaction” allow “nothing”</td></tr>
<tr><td>Different reagents</td><td colspan="7">If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.
i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.</td></tr>
<tr><td></td><td>$AgNO_3$</td><td>Na_2CO_3/$NaHCO_3$ named carbonate</td><td>water</td><td>named indicator</td><td rowspan="3">1

1

1</td><td>Named alcohol</td><td>Named amine or ammonia</td></tr>
<tr><td>G ketone</td><td>no reaction</td><td>no reaction</td><td>no reaction</td><td>no effect</td><td>no reaction</td><td>no reaction</td></tr>
<tr><td>H Acyl chloride</td><td>(white) ppt</td><td>Effervescence or CO_2 or fumes or exothermic</td><td>fumes</td><td>acid colour</td><td>Smell or fumes</td><td>fumes</td></tr>
<tr><td colspan="8">Allow iodoform test or Brady’s reagent (2,4,dnph) test (both positive for G)</td></tr>
</table>

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<table>
<tr><td rowspan="6">7(a)(iii)</td><td>Single reagent</td><td colspan="6">If wrong single reagent, CE = zero
Incomplete single reagent (e.g. carbonate) or wrong formula (e.g.$NaCO_3$) loses reagent mark, but mark on
For “no reaction” allow “nothing”</td></tr>
<tr><td>Different reagents</td><td colspan="6">If different tests on E and F; both reagents and any follow on chemistry must be correct for first (reagent) mark.
Reagent must react: i.e. not allow Tollens on G (ketone) – no reaction.
Second and third marks are for correct observations.
i.e. for different tests on E and F, if one reagent is correct and one wrong, can score max 1 for correct observation with correct reagent.</td></tr>
<tr><td></td><td>$K_2Cr_2O_7$/ H^+</td><td>$KMnO_4$/ H^+</td><td>Lucas test ($ZnCl_2$/HCl)</td><td>1</td><td></td><td>Penalise missing H^+ but mark on</td></tr>
<tr><td>J
Primary alcohol</td><td>goes green</td><td>decolourised / goes brown</td><td>No cloudiness</td><td>1</td><td></td><td></td></tr>
<tr><td>K
Tertiary alcohol</td><td>no reaction</td><td>no reaction</td><td>Rapid cloudiness</td><td>1</td><td></td><td></td></tr>
<tr><td colspan="6">If uses subsequent tests e.g. Tollens/Fehlings, test must be on product of oxidation</td></tr>
</table>

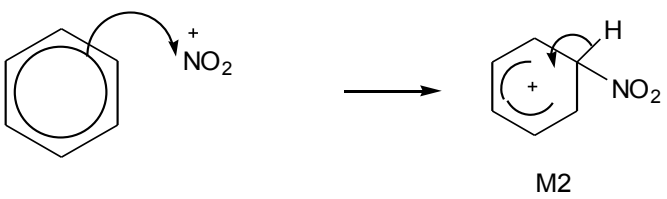
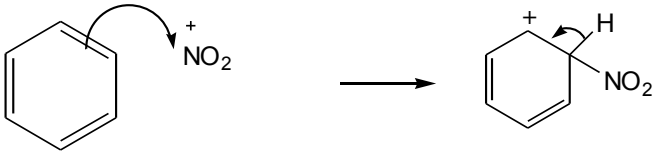
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7(b)(i)	3,3-dimethylbutan-1-ol 4 Triplet or three	1 1 1	Allow 3,3-dimethyl-1-butanol
7(b)(ii)	2-methylpentan-2-ol 5 Singlet or one or no splitting	1 1 1	Allow 2-methyl-2-pentanol

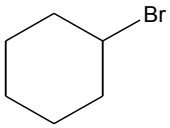
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Question	Marking Guidance	Mark	Comments
8(a)	**M1** Benzene is more stable than cyclohexatriene	1	more stable than cyclohexatriene must be stated or implied If benzene more stable than cyclohexene, then penalise M1 but mark on If benzene less stable: can score M2 only
	M2 Expected $\Delta H^{\ominus}$ hydrogenation of C_6H_6 is 3(–120) = –360 kJ mol^{-1}	1	Allow in words e.g. expected $\Delta H^{\ominus}$ hydrog is three times the $\Delta H^{\ominus}$ hydrog of cyclohexene
	M3 Actual $\Delta H^{\ominus}$ hydrogenation of benzene is 152 kJ mol^{-1} (less exothermic) or 152 kJ mol^{-1} different from expected	1	Ignore energy needed
	M4 Because of delocalisation or electrons spread out or resonance	1	

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8(b)	**No mark for name of mechanism**		
	Conc HNO_3 Conc H_2SO_4	1 1	If either or both conc missing, allow one; this one mark can be gained in equation
	$2\ H_2SO_4 + HNO_3 \rightarrow 2\ HSO_4^- + NO_2^+ + H_3O^+$ **OR** $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + NO_2^+ + H_2O$ **OR via two equations** $H_2SO_4 + HNO_3 \rightarrow\ HSO_4^- + H_2NO_3^+$ $H_2NO_3^+ \rightarrow\ NO_2^+ + H_2O$	1	Allow + anywhere on NO_2^+
	M1 M3  M2 **OR** M1 M3  M2	3	M1 arrow from within hexagon to N or + on N Allow NO_2^+ in mechanism horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3 + on H in intermediate loses M2 not M3

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8(c)	**If intermediate compound V is wrong or not shown, max 4 for 8(c)**		
	M1  or Cl or chlorocyclohexane or bromocyclohexane	1	
	Reaction 3 **M2** HBr **M3** Electrophilic addition	1 1	Allow M2 and M3 independent of each other
	Reaction 4 **M4** Ammonia if wrong do not gain M5 **M5** Excess ammonia or sealed in a tube or under pressure **M6** Nucleophilic substitution	1 1 1	Allow M4 and M6 independent of each other If CE e.g. acid conditions, lose M4 and M5
8(d)	Lone or electron <u>pair on N</u> Delocalised or spread into ring in U Less available (to accept protons) or less able to donate (to H^+)	1 1 1	No marks if reference to “lone pair on N” missing,

UMS conversion calculator www.aqa.org.uk/umsconversion

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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4	
5	
6	
7	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2011

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 26 January 2011 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

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Section A

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

1 The rate of hydrolysis of an ester **X** ($HCOOCH_2CH_2CH_3$) was studied in alkaline conditions at a given temperature. The rate was found to be first order with respect to the ester and first order with respect to hydroxide ions.

1 (a) (i) Name ester **X**.

.....

(1 mark)

1 (a) (ii) Using **X** to represent the ester, write a rate equation for this hydrolysis reaction.

.....

(1 mark)

1 (a) (iii) When the initial concentration of **X** was 0.024 mol dm^{-3} and the initial concentration of hydroxide ions was 0.035 mol dm^{-3}, the initial rate of the reaction was 8.5×10^{-5} mol dm^{-3} s^{-1}.
Calculate a value for the rate constant at this temperature and give its units.

Calculation .....

.....

.....

.....

Units .....

.....

(3 marks)

1 (a) (iv) In a second experiment at the same temperature, water was added to the original reaction mixture so that the total volume was doubled.
Calculate the initial rate of reaction in this second experiment.

.....

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(1 mark)

Do not write outside the box

1 (a) (v) In a third experiment at the same temperature, the concentration of **X** was half that used in the experiment in part **1 (a) (iii)** and the concentration of hydroxide ions was three times the original value.
Calculate the initial rate of reaction in this third experiment.

.....

.....

(1 mark)

1 (a) (vi) State the effect, if any, on the value of the rate constant *k* when the temperature is lowered but all other conditions are kept constant. Explain your answer.

Effect .....

Explanation .....

.....

(2 marks)

1 (b) Compound **A** reacts with compound **B** as shown by the overall equation

$$A + 3B \rightarrow AB_3$$

The rate equation for the reaction is

$$\text{rate} = k[A][B]^2$$

A suggested mechanism for the reaction is

Step **1** $A + B \rightarrow AB$

Step **2** $AB + B \rightarrow AB_2$

Step **3** $AB_2 + B \rightarrow AB_3$

Deduce which one of the three steps is the rate-determining step.

Explain your answer.

Rate-determining step .....

Explanation .....

.....

(2 marks)

11

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ANSWER IN THE SPACES PROVIDED

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2 This question is about the pH of several solutions.

Give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for pH.

.....

(1 mark)

2 (a) (ii) Calculate the pH of 0.154 mol dm^{-3} hydrochloric acid.

.....

.....

(1 mark)

2 (a) (iii) Calculate the pH of the solution formed when 10.0 cm^3 of 0.154 mol dm^{-3} hydrochloric acid are added to 990 cm^3 of water.

.....

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(2 marks)

2 (b) The acid dissociation constant, K_a, for the weak acid HX has the value 4.83×10^{-5} mol dm^{-3} at 25 °C.
A solution of HX has a pH of 2.48

Calculate the concentration of HX in the solution.

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(4 marks)

Question 2 continues on the next page

Turn over ▶

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2 (c) Explain why the pH of an acidic buffer solution remains almost constant despite the addition of a small amount of sodium hydroxide.

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(2 marks)

2 (d) The acid dissociation constant, K_a, for the weak acid HY has the value 1.35×10^{-5} mol dm^{-3} at 25 °C.

A buffer solution was prepared by dissolving 0.0236 mol of the salt NaY in 50.0 cm^3 of a 0.428 mol dm^{-3} solution of the weak acid HY

2 (d) (i) Calculate the pH of this buffer solution.

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(4 marks)

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2 (d) (ii) A 5.00 x 10^{-4} mol sample of sodium hydroxide was added to this buffer solution.

Calculate the pH of the buffer solution after the sodium hydroxide was added.

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(4 marks)

18

Turn over for the next question

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3 Synthesis gas is a mixture of carbon monoxide and hydrogen. Methanol can be manufactured from synthesis gas in a reversible reaction as shown by the following equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H^{\ominus} = -91\ kJ\,mol^{-1}$$

3 (a) A sample of synthesis gas containing 0.240 mol of carbon monoxide and 0.380 mol of hydrogen was sealed together with a catalyst in a container of volume 1.50 dm^3. When equilibrium was established at temperature T_1 the equilibrium mixture contained 0.170 mol of carbon monoxide.

Calculate the amount, in moles, of methanol and the amount, in moles, of hydrogen in the equilibrium mixture.

Methanol .....

Hydrogen .....

(2 marks)

3 (b) A different sample of synthesis gas was allowed to reach equilibrium in a similar container of volume 1.50 dm^3 at temperature T_1

At equilibrium, the mixture contained 0.210 mol of carbon monoxide, 0.275 mol of hydrogen and 0.0820 mol of methanol.

3 (b) (i) Write an expression for the equilibrium constant K_c for this reaction.

.....

.....

(1 mark)

3 (b) (ii) Calculate a value for K_c for the reaction at temperature T_1 and state its units.

Calculation .....

.....

.....

.....

.....

Units .....

.....

(4 marks)

3 (b) (iii) State the effect, if any, on the value of K_c of adding more hydrogen to the equilibrium mixture.

.....

(1 mark)

Do not write outside the box

3 (c) The temperature of the mixture in part **3 (b)** was changed to T_2 and the mixture was left to reach a new equilibrium position. At this new temperature the equilibrium concentration of methanol had increased.
Deduce which of T_1 or T_2 is the higher temperature and explain your answer.

Higher temperature .....

Explanation .....

.....

.....

(3 marks)

3 (d) The following reaction has been suggested as an alternative method for the production of methanol.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The hydrogen used in this method is obtained from the electrolysis of water.

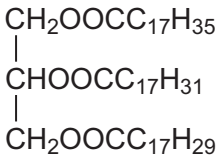
Suggest **one** possible environmental disadvantage of the production of hydrogen by electrolysis.

.....

.....

(1 mark)

3 (e) One industrial use of methanol is in the production of biodiesel from vegetable oils such as



Give the formula of **one** compound in biodiesel that is formed by the reaction of methanol with the vegetable oil shown above.

.....

(1 mark)

13

Do not write outside the box

4 (a) Name compound **Y**, $HOCH_2CH_2COOH$

.....

(1 mark)

4 (b) Under suitable conditions, molecules of **Y** can react with each other to form a polymer.

4 (b) (i) Draw a section of the polymer showing **two** repeating units.

(1 mark)

4 (b) (ii) Name the type of polymerisation involved.

.....

(1 mark)

4 (c) When **Y** is heated, an elimination reaction occurs in which one molecule of **Y** loses one molecule of water. The organic product formed by this reaction has an absorption at 1637 cm^{-1} in its infrared spectrum.

4 (c) (i) Identify the bond that causes the absorption at 1637 cm^{-1} in its infrared spectrum.

.....

(1 mark)

4 (c) (ii) Write the displayed formula for the organic product of this elimination reaction.

(1 mark)

4 (c) (iii) The organic product from part **4 (c) (ii)** can also be polymerised.
Draw the repeating unit of the polymer formed from this organic product.

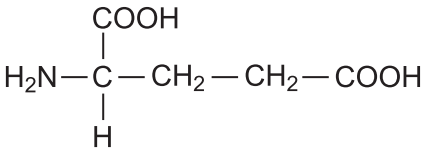
(1 mark)

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4 (d) At room temperature, 2-aminobutanoic acid exists as a solid.
Draw the structure of the species present in the solid form.

(1 mark)

4 (e) The amino acid, glutamic acid, is shown below.



Draw the structure of the organic species formed when glutamic acid reacts with each of the following.

4 (e) (i) an excess of sodium hydroxide

(1 mark)

4 (e) (ii) an excess of methanol in the presence of concentrated sulfuric acid

(1 mark)

4 (e) (iii) ethanoyl chloride

(1 mark)

Question 4 continues on the next page

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4 (f) A tripeptide was heated with hydrochloric acid and a mixture of amino acids was formed. This mixture was separated by column chromatography.
Outline briefly why chromatography is able to separate a mixture of compounds.
Practical details are **not** required.

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(3 marks)

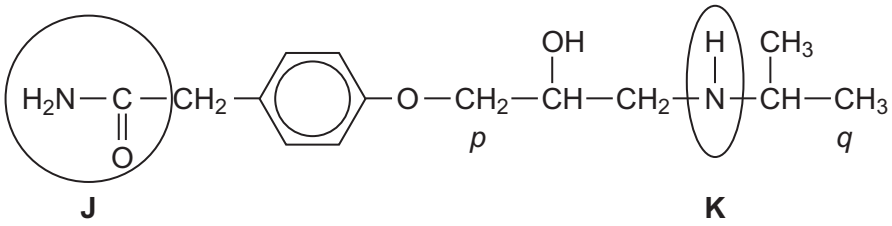
13

Turn over for the next question

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ANSWER IN THE SPACES PROVIDED

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5 Atenolol is an example of the type of medicine called a beta blocker. These medicines are used to lower blood pressure by slowing the heart rate. The structure of atenolol is shown below.



5 (a) Give the name of each of the circled functional groups labelled **J** and **K** on the structure of atenolol shown above.

Functional group labelled **J** .....

Functional group labelled **K** .....

(2 marks)

5 (b) The ^{1}H n.m.r. spectrum of atenolol was recorded.

One of the peaks in the ^{1}H n.m.r. spectrum is produced by the CH_2 group labelled *p* in the structure of atenolol.
Use **Table 2** on the Data Sheet to suggest a range of δ values for this peak.
Name the splitting pattern of this peak.

Range of δ values .....

Name of splitting pattern .....

(2 marks)

5 (c) N.m.r. spectra are recorded using samples in solution.
The ^{1}H n.m.r. spectrum was recorded using a solution of atenolol in $CDCl_3$

5 (c) (i) Suggest why $CDCl_3$ and **not** $CHCl_3$ was used as the solvent.

.....

.....

(1 mark)

5 (c) (ii) Suggest why $CDCl_3$ is a more effective solvent than CCl_4 for polar molecules such as atenolol.

.....

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(1 mark)

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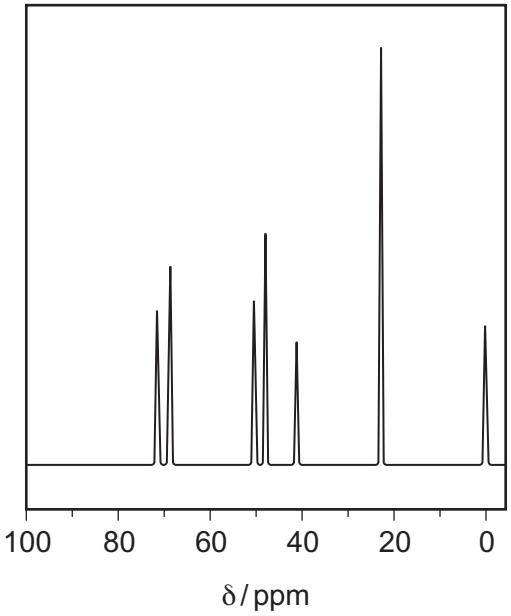
5 (d) The ^{13}C n.m.r. spectrum of atenolol was also recorded.

Use the structure of atenolol given to deduce the total number of peaks in the ^{13}C n.m.r. spectrum of atenolol.

.....

(1 mark)

5 (e) Part of the ^{13}C n.m.r. spectrum of atenolol is shown below. Use this spectrum and **Table 3** on the Data Sheet, where appropriate, to answer the questions which follow.



5 (e) (i) Give the formula of the compound that is used as a standard and produces the peak at $\delta = 0$ ppm in the spectrum.

.....

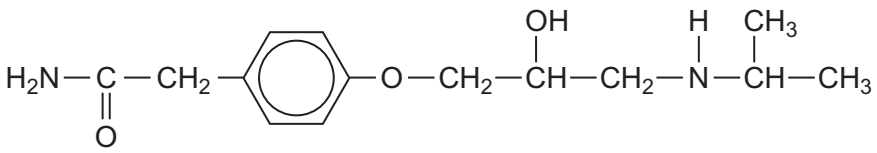
(1 mark)

5 (e) (ii) One of the peaks in the ^{13}C n.m.r. spectrum above is produced by the CH_3 group labelled *q* in the structure of atenolol.
Identify this peak in the spectrum by stating its δ value.

.....

(1 mark)

5 (e) (iii) There are three CH_2 groups in the structure of atenolol. One of these CH_2 groups produces the peak at $\delta = 71$ in the ^{13}C n.m.r. spectrum above.
Draw a circle around this CH_2 group in the structure of atenolol shown below.



(1 mark)

Question 5 continues on the next page

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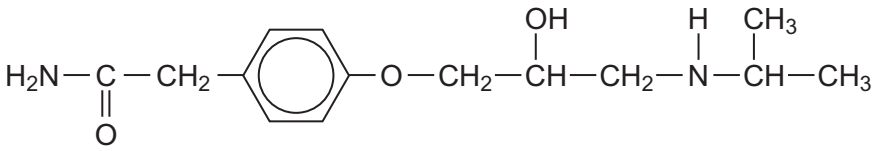
5 (f) Atenolol is produced industrially as a racemate (an equimolar mixture of two enantiomers) by reduction of a ketone. Both enantiomers are able to lower blood pressure. However, recent research has shown that one enantiomer is preferred in medicines.

5 (f) (i) Suggest a reducing agent that could reduce a ketone to form atenolol.

.....

(1 mark)

5 (f) (ii) Draw a circle around the asymmetric carbon atom in the structure of atenolol shown below.



(1 mark)

5 (f) (iii) Suggest how you could show that the atenolol produced by reduction of a ketone was a racemate and **not** a single enantiomer.

.....

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(2 marks)

5 (f) (iv) Suggest **one** advantage and **one** disadvantage of using a racemate rather than a single enantiomer in medicines.

Advantage .....

.....

Disadvantage .....

.....

(2 marks)

16

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ANSWER IN THE SPACES PROVIDED

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Section B

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

6 Many synthetic routes need chemists to increase the number of carbon atoms in a molecule by forming new carbon–carbon bonds. This can be achieved in several ways including

- reaction of an aromatic compound with an acyl chloride
- reaction of an aldehyde with hydrogen cyanide.

6 (a) Consider the reaction of benzene with CH_3CH_2COCl

6 (a) (i) Write an equation for this reaction and name the organic product.
Identify the catalyst required in this reaction.
Write equations to show how the catalyst is used to form a reactive intermediate and how the catalyst is reformed at the end of the reaction.

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(5 marks)

(*Extra space)* .....

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6 (a) (ii) Name and outline a mechanism for the reaction of benzene with this reactive intermediate.

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(4 marks)

(Extra space) .....

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Question 6 continues on the next page

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6 (b) Consider the reaction of propanal with HCN

6 (b) (i) Write an equation for the reaction of propanal with HCN and name the product.

.....

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(2 marks)

(*Extra space)* .....

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6 (b) (ii) Name and outline a mechanism for the reaction of propanal with HCN

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(5 marks)

(Extra space) .....

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6 (b) (iii) The rate-determining step in the mechanism in part **6 (b) (ii)** involves attack by the nucleophile.
Suggest how the rate of reaction of propanone with HCN would compare with the rate of reaction of propanal with HCN
Explain your answer.

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(2 marks)

(Extra space) .....

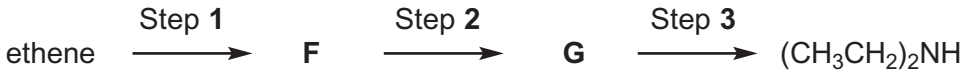
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18

Turn over for the next question

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7 The compound $(CH_3CH_2)_2NH$ can be made from ethene in a three-step synthesis as shown below.



7 (a) Name the compound $(CH_3CH_2)_2NH$

.....

(1 mark)

7 (b) Identify compounds **F** and **G**.

Compound **F** .....

Compound **G** .....

(2 marks)

7 (c) For the reactions in Steps **1**, **2** and **3**,

- give a reagent or reagents
- name the mechanism.

Balanced equations and mechanisms using curly arrows are **not** required.

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(6 marks)

(*Extra space*) .....

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7 (d) Identify **one** organic impurity in the product of Step **3** and give a reason for its formation.

.....

.....

.....

(2 marks)

(Extra space) .....

.....

11

END OF QUESTIONS

There are no questions printed on this page

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Version 1



General Certificate of Education (A-level)
January 2011

Chemistry CHEM4

(Specification 2420)

Unit 4: Kinetics, Equilibria and Organic Chemistry

Post-Standardisation

Mark Scheme

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation events which all examiners participate in and is the scheme which was used by them in this examination. The standardisation process ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for standardisation each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed and legislated for. If, after the standardisation process, examiners encounter unusual answers which have not been raised they are required to refer these to the Principal Examiner.

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Question	Marking Guidance		Mark	Comments
1(a)(i)	propyl methanoate		1	must be correct spelling
1(a)(ii)	rate = $k[X][OH^-]$		1	allow $HCOOCH_2CH_2CH_3$ (or close) for X allow ( ) but penalise missing minus
1(a)(iii)	$k = \frac{8.5 \times 10^{-5}}{(0.024)(0.035)}$	In (a)(iii), if wrong orders allow	1	mark is for insertion of numbers in correct expression for k If expression for k is upside down, only score units conseq to their expression
	= 0.10(12) 2sf minimum	1 for conseq answer	1	
	$mol^{-1}\,dm^3\,s^{-1}$	1 for conseq units	1	any order
1(a)(iv)	$2.1(3) \times 10^{-5}$		1	or $2.1(2) \times 10^{-5}$ ignore units allow 2 sf **NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k** **See * below**

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1(a)(v)	1.3×10^{-4} (1.28×10^{-4})	1	allow (1.26×10^{-4}) to (1.3×10^{-4}) ignore units allow 2 sf **NB If wrong check the orders in part (a)(iii) and allow (a)(iv) if conseq to wrong k** **See ** below**
	For example, if orders given are 1st in X and second in OH^- [The mark in a(ii) and also first mark in a(iii) have already been lost] So allow mark * in (iv) for rate = their k $\times(0.012)(0.0175)^2$ = their k $\times(3.7 \times 10^{-6})$ (allow answer to 2sf) ** in (v) for rate = their k $\times$ $(0.012)(0.105)^2$ = their k $\times(1.32 \times 10^{-4})$ (allow answer to 2sf) **The numbers will of course vary for different orders.**		
1(a)(vi)	Lowered fewer particles/collisions have energy $>E_a$ **OR** fewer have sufficient (activation) energy (to react)	1 1	if wrong, no further mark not just fewer successful collisions
1(b)	Step 2 (this step with previous) involves one mol/molecule/particle A and two Bs or 1:2 ratio or same amounts (of reactants) as in rate equation	1 1	if wrong, no further mark

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Question	Marking Guidance	Mark	Comments
2(a)(i)	$-\log[H^+]$ or $\log 1/[H^+]$	1	penalise missing square brackets here only
2(a)(ii)	0.81	1	2dp required, no other answer allowed
2(a)(iii)	**M1** mol $H^+ = 1.54 \times 10^{-3}$ **M2** pH = 2.81	1 1	if wrong no further mark if 1.5×10^{-3} allow M1 but not M2 for 2.82 allow more than 2dp but not fewer
2(b)	**M1** $[H^+] = 3.31 \times 10^{-3}$ **M2** $K_a = \frac{[H^+][X^-]}{[HX]}$ or $\frac{[H^+]^2}{[HX]}$ or using numbers **M3** $[HX] = \frac{[H^+]^2}{K_a} = \frac{(3.31\times10^{-3})^2}{4.83\times10^{-5}}$ **M4** [HX] = 0.227	1 1 1 1	 do not penalise ( ) or one or more missing [ ] allow conseq on their $[H^+]^2/(4.83 \times 10^{-5})$ (AE) if upside down, no further marks after M2 allow 0.225 – 0.23
2(c)	**M1** extra/added OH^- removed by reaction with H^+ or the acid **M2** correct discussion of equm shift i.e. $HX \rightleftharpoons H^+ + X^-$ moves to right **OR** ratio $\frac{[HX]}{[X^-]}$ remains almost constant	1 1	

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2(d)(i)	**M1** mol HY = $(50\times10^{-3}) \times 0.428 = 0.0214$	**OR** $[Y^-] = .0236 \times \frac{1000}{50} = 0.472$	1	mark for answer
	M2 $[H^+] = 1.35\times10^{-5} \times \frac{0.0214}{0.0236}$ **OR** $1.35\times10^{-5} = [H^+] \times \frac{0.0236}{0.0214}$	**OR** $[H^+] = 1.35\times10^{-5} \times \frac{0.428}{0.472}$ **OR** $1.35\times10^{-5} = [H^+] \times \frac{0.472}{0.428}$	1	must be numbers not just rearrangement of Ka expression If either HY value or Y^- value wrong, (apart from AE -1) lose M2 and M3
	M3 $[H^+] = 1.22\times10^{-5}$		1	mark for answer
	M4 pH = 4.91		1	allow more than 2dp but not fewer **allow M4 for correct pH calculation using their $[H^+]$ (this applies in 2(d)(i) only)**
	If Henderson Hasselbalch equation used:			**If Henderson Hasselbalch equation used:**
	M1 mol HY = $(50\times10^{-3}) \times 0.428 = 0.0214$	**OR** $[Y^-] = .0236 \times \frac{1000}{50} = 0.472$	1	mark for answer
	M2 p*K*a = 4.87		1	
	M3 $\log(\frac{0.0214}{0.0236}) = -0.043$	$\log(\frac{0.428}{0.472}) = -0.043$	1	If either HY value or Y^- value wrong, (apart from AE-1) lose M3 and M4
	M4 pH = 4.87 – (– 0.043) = 4.91		1	allow more than 2dp but not fewer

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2(d)(ii)				Can score full marks for correct consequential use of their HY and Y^- values from d(i)
	M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$		1	AE in subtraction loses just M1 If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount, lose M1 and M3
	M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$		1	AE in addition loses just M2 If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained
	M3 $[H^+] = 1.35 \times 10^{-5} \times \frac{0.0209}{0.0241}$ $(= 1.17 \times 10^{-5})$	if convert to concentrations $[H^+] = 1.35 \times 10^{-5} \times \frac{0.418}{0.482}$ $(= 1.17 \times 10^{-5})$	1	if HY/Y^- upside down, no further marks
	M4 pH = 4.93		1	allow more than 2dp but not fewer NOT allow M4 for correct pH calculation using their $[H^+]$ (this allowance applies in 2(d)(i) only)

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	If Henderson Hasselbalch equation used:		**If Henderson Hasselbalch equation used:** Can score full marks for correct consequential use of their HY and Y^- values from d(i)
	M1 Mol HY after adding NaOH = $0.0214 - 5.0 \times 10^{-4} = 0.0209$	1	AE in subtraction loses just M1 If wrong initial mol HY (i.e. not conseq to part d(i)) or no subtraction or subtraction of wrong amount lose M1 and M3
	M2 Mol Y^- after adding NaOH = $0.0236 + 5.0 \times 10^{-4} = 0.0241$	1	AE in addition loses just M2 If wrong mol Y^- (i.e. not conseq to part d(i)) or no addition or addition of wrong amount lose M2 and next mark gained
	M3 $\log\left(\frac{0.0209}{0.0241}\right) = -0.062$	1	if HY/Y^- upside down, no further marks
	M4 pH = $4.87 - (-0.062) = 4.93$	1	allow more than 2dp but not fewer

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Question	Marking Guidance	Mark	Comments
3(a)	mol CH_3OH = 0.07(0) mol H_2 = 0.24(0)	1 1	
3(b)(i)	$\frac{[CH_3OH]}{[CO][H_2]^2}$ or $\frac{(0.082/1.5)}{(0.210/1.5)(0.275/1.5)^2}$	1	allow ( ) but expression using formulae must have brackets alternative expression using numbers must include volumes
3(b)(ii)	**M1** divides by vol **M2** $\frac{(0.082/1.5)}{(0.210/1.5)(0.275/1.5)^2}$ (= $\frac{(0.05467)}{(0.14)(0.1833)^2}$) **M3** 11.6 or 11.7 **M4** $mol^{-2}\,dm^6$	1 1 1 1	Mark independently from (b)(i) any AE is –1 if volume missed, can score only M3 and M4 mark is for correct insertion of correct numbers in correct Kc expression in b(ii) If Kc expression wrong, can only score M1 & M4 If numbers rounded, allow M2 but check range for M3 mark for answer above 11.7 up to 12.2 scores 2 for M1 and M2 if vol missed, can score M3 for 5.16 (allow range 4.88 to 5.21) Units conseq to their Kc in (b)(ii)
3(b)(iii)	no effect or no change or none	1	

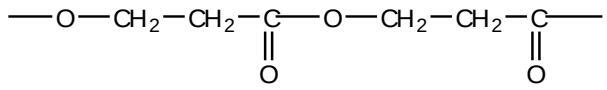
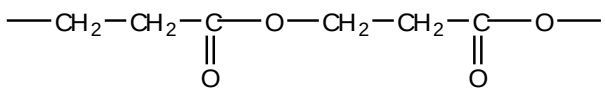
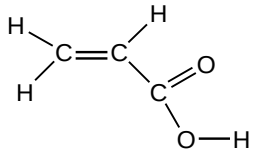
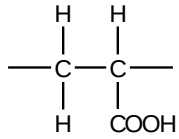
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3(c)	**M1** T_1			1	if wrong - no further marks
	M2	(forward) reaction is exothermic **OR** gives out heat	<u>backward</u> reaction is endothermic	1	only award M3 if M2 is correct
	M3	shifts to RHS <u>to replace lost heat</u> **OR** <u>to increase the temperature</u> **OR** <u>to oppose fall in temp</u>	<u>backward reaction</u> takes in heat **OR** to lower the temperature	1	not just to oppose the change

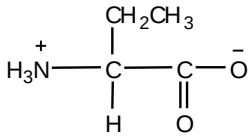
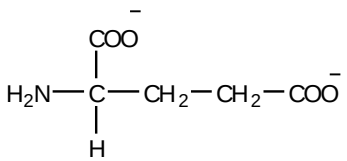
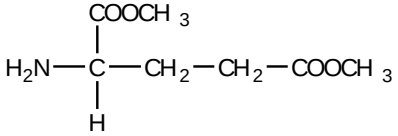
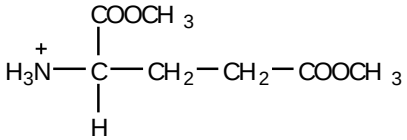
3(d)	fossil fuels used **OR** CO_2 H_2O produced/given off/formed which are <u>greenhouse gases</u> **OR** SO_2 produced/given off/formed which causes acid rain **OR** Carbon produced/given off/formed causes global dimming	1	not allow electricity is expensive ignore just global warming ignore energy or hazard discussion

3(e)	$C_{17}H_{35}COOCH_3$ or $C_{17}H_{31}COOCH_3$ or $C_{17}H_{29}COOCH_3$ **OR** $CH_3OOCC_{17}H_{35}$ or $CH_3OOCC_{17}H_{31}$ or $CH_3OOCC_{17}H_{29}$	1	

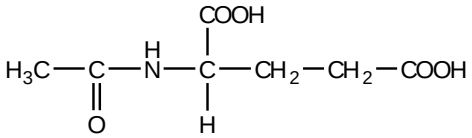
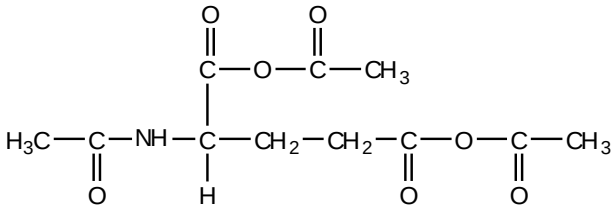
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Question	Marking Guidance	Mark	Comments
4(a)	3-hydroxypropanoic acid	1	allow 3-hydroxypropionic acid must be correct spelling
4(b)(i)	must show trailing bonds  or can start at any point in the sequence, e.g. 	1	not allow dimer allow –O–$CH_2CH_2COOCH_2CH_2CO$- or –$CH_2CH_2COOCH_2CH_2COO$- ignore ( ) or *n* NB answer has a total of 6 carbons and 4 oxygens
4(b)(ii)	condensation (polymerisation)	1	Allow close spelling
4(c)(i)	C=C or carbon-carbon <u>double</u> bond	1	
4(c)(ii)		1	must show **ALL** bonds including O–H
4(c)(iii)	must show trailing bonds 	1	allow polyalkene conseq on their c(ii) ignore *n*

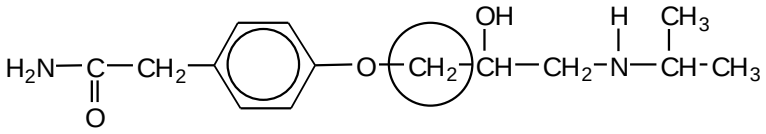
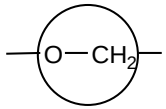
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4(d)		1	allow NH_3^+— allow COO^-
4(e)(i)		1	In 4(e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly NB two carboxylate groups Allow COONa or COO^-Na^+ but not covalent bond to Na allow NH_2–
4(e)(ii)	 **OR** 	1	In 4(e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly NB two ester groups allow NH_2– or $^+NH_3$–

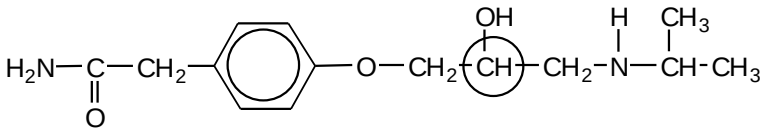
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4(e)(iii)		1	In 4(e), do not penalise a slip in the number of carbons in the $-CH_2CH_2-$ chain, but all must be bonded correctly allow anhydride formation on either or both COOH groups (see below) with or without amide group formation 
4(f)	**M1** phase or eluent or solvent (or named solvent) is <u>moving or mobile</u> **M2** stationary phase or solid or alumina/silica/resin **M3** separation depends on balance between solubility or affinity (of compounds) in each phase **OR** different adsorption or retention **OR** (amino acids have) different R_f values **OR** (amino acids) travel at different speeds or take different times	1 1 1	

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Question	Marking Guidance	Mark	Comments
5(a)	**J** (acid) amide **K** (secondary) amine or amino	1 1	not peptide, not N-substituted amide penalise primary or tertiary allow N-substituted amine
5(b)	(δ =) 3.1-3.9 doublet **OR** duplet	1 1	Not 3.7 – 4.1 Not secondary name required not the number 2
5(c)(i)	Solvent must be proton-free **OR** $CHCl_3$ has protons or has H or gives a peak	1	
5(c)(ii)	$CDCl_3$ is polar **OR** CCl_4 is non-polar	1	
5(d)	11 **OR** eleven	1	
5(e)(i)	$Si(CH_3)_4$ **OR** SiC_4H_{12}	1	ignore TMS
5(e)(ii)	a single number or a range within 21-25	1	penalise anything outside this range
5(e)(iii)		1	allow ring around the C only and also allow 

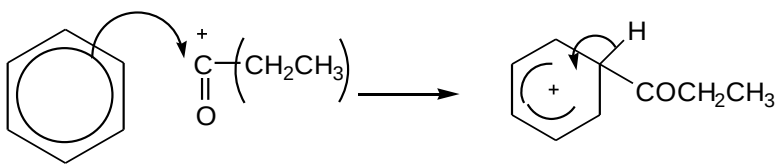
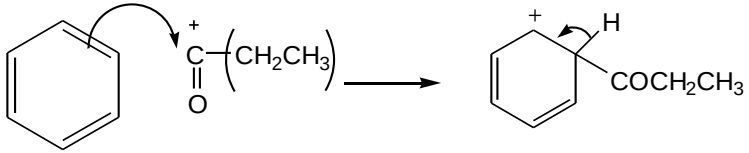
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5(f)(i)	$NaBH_4$	1	ignore name if formula correct ignore solvent allow $LiAlH_4$ Zn/HCl Sn/HCl H_2/Ni H_2/Pt
5(f)(ii)		1	allow ring around the C only
5(f)(iii)	(plane) polarised light **OR** light in a polarimeter polarised light is not rotated or is unaffected	1 1	 penalise bent/diffracted/deflected/reflected Not just solution is optically inactive
5(f)(iv)	**adv** cheaper medicine due to cost or difficulty <u>of separation</u> or both can lower blood pressure **OR** more effective/beneficial <u>with a reason</u> **disadv** may be side effects from one enantiomer in the mixture or only half the product works or one enantiomer may be ineffective or double dose required	1 1	or no need to separate

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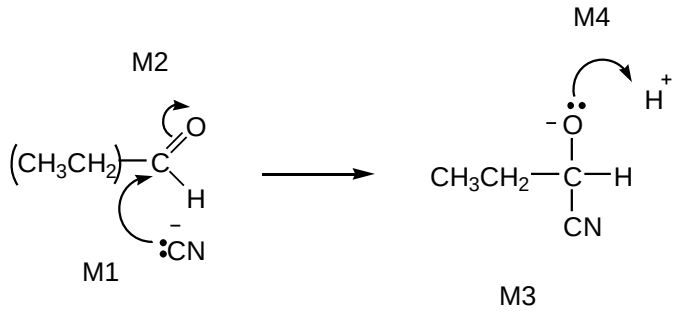
Question	Marking Guidance	Mark	Comments
6(a)(i)	$C_6H_6 + CH_3CH_2COCl \rightarrow C_6H_5COCH_2CH_3 + HCl$ **OR** $C_6H_6 + CH_3CH_2CO^+ \rightarrow C_6H_5COCH_2CH_3 + H^+$	1	allow C_2H_5 penalise $C_6H_5–CH_3CH_2CO$ allow + on C or O in equation
	phenylpropanone **OR** ethylphenylketone **OR** phenylethylketone	1	Ignore 1 in formula, but penalise other numbers
	$AlCl_3$	1	can score in equation
	$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$	1	allow C_2H_5 allow + on C or O in equation
	$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$	1	

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6(a)(ii)	electrophilic substitution M1 M3  M2 for structure **OR** M1 M3  M2	1 3	can allow in (a)(i) if no contradiction M1 arrow from circle or within it to C or to + on C horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M2 penalise C_6H_5–CH_3CH_2CO (even if already penalized in (a)(i)) M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3

6(b)(i)	$CH_3CH_2\underline{CHO}$ + HCN → $CH_3CH_2CH(OH)CN$ **OR** $C_2H_5CH(OH)CN$ 2-hydroxybutan<u>e</u>nitrile **OR** 2-hydroxybutan<u>o</u>nitrile	1 1	aldehyde must be -CHO brackets optional no others

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6(b)(ii)	<u>nucleophilic addition</u>  	1 4	 M1 includes lp and arrow to Carbonyl C and minus charge (on either C or N) Not allow M2 before M1, but allow M1 to C^+ after non-scoring carbonyl arrow Ignore δ+, δ– on carbonyl group, but if wrong way round or full + charge on C lose M2 M3 for correct structure including minus sign. Allow C_2H_5 M4 for lp and curly arrow to H^+
6(b)(iii)	(propanone) slower **OR** <u>propanal</u> faster inductive effects of alkyl groups **OR** C of C=O less δ+ in propanone **OR** alkyl groups in ketone hinder attack **OR** easier to attack at end of chain	1 1	if wrong, no further marks

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Question	Marking Guidance	Mark	Comments
7(a)	diethylamine **OR** ethyl ethanamine **OR** ethyl aminoethane	1	ignore N-

7(b)

For 7(b) and (c)

There are three valid routes for this synthesis called Routes **A, B** and **C** below

- Decide which route fits the answer best (this may not be the best for part b) to give the candidate the best possible overall mark.
- Mark part (b)
- For this best route mark the mechanism and reagent independently
- Migration from one route to another is not allowed
- Either name or formula is allowed in every case.
- Ignore conditions unless they are incorrect.

	Route A	Route B	Route C	
F	CH_3CH_2Br or CH_3CH_2Cl	C_2H_6	CH_3CH_2OH	1
G	$CH_3CH_2NH_2$ ethylamine **OR** ethanamine **OR** aminoethane	CH_3CH_2Br **OR** CH_3CH_2Cl	CH_3CH_2Br **OR** CH_3CH_2Cl	1

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			Route A	Route B	Route C	
7(c)	Step 1	Reagent(s)	HBr **OR** HCl	$\underline{H_2 / Ni}$ (Not $NaBH_4$)	H_2O & H_3PO_4 **OR** H_2O & H_2SO_4	1
		Mechanism	Electrophilic addition	addition (allow electrophilic **OR** catalytic but not nucleophilic) ignore hydrogenation	Electrophilic addition	1
	Step 2	Reagent(s)	NH_3	Cl_2 **OR** Br_2	HBr **OR** KBr & H_2SO_4 **OR** PCl_3 **OR** PCl_5 **OR** $SOCl_2$	1
		Mechanism	Nucleophilic substitution	(free) radical substitution	Nucleophilic substitution	1
	Step 3	Reagent(s)	CH_3CH_2Br **OR** CH_3CH_2Cl	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	$CH_3CH_2NH_2$ **OR** NH_3 but penalise excess ammonia here	1
		Mechanism	Nucleophilic substitution	Nucleophilic substitution	Nucleophilic substitution	1

7(d)	tertiary amine **OR** triethylamine **OR** $(CH_3CH_2)_3N$ Quaternary ammonium salt **OR** tetraethylammonium bromide **OR** chloride **OR** ion **OR** $(CH_3CH_2)_4N^+$ (Br^- **OR** Cl^-)	1	
	further substitution will take place **OR** diethylamine is a better nucleophile than ethylamine	1	

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General principles applied to marking CHEM4 papers by CMI+ (January 2011)

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**
-

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

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D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

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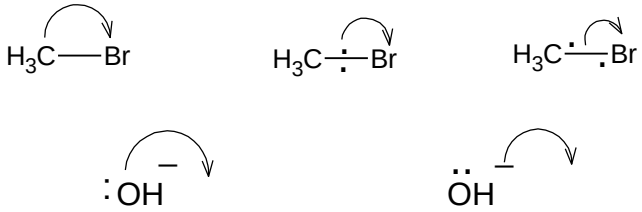
G. Marking calculations

In general

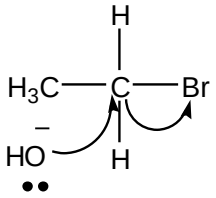
- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.
The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

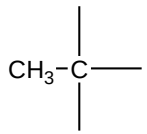
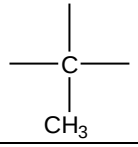
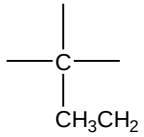
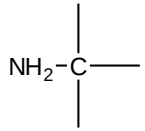
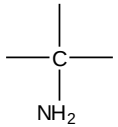
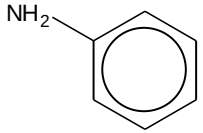
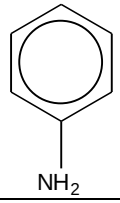
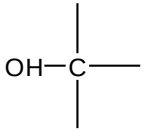
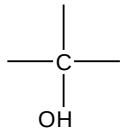
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

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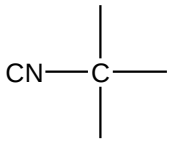
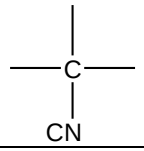
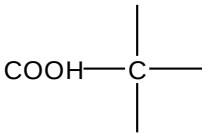
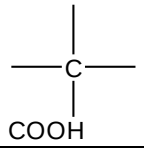
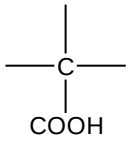
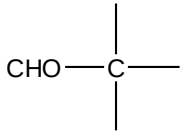
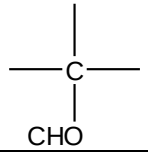
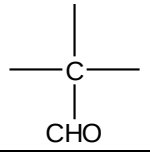
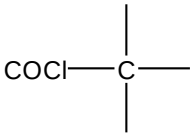
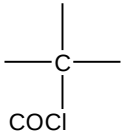
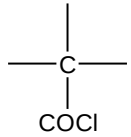
I. Organic structures

In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C ─ HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C ─ C bonds in alkyl groups, given that CH_3─ is considered to be interchangeable with H_3C─ even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2─ C will be allowed, although H_2N─ C would be preferred.
- Poor presentation of vertical C ─ CH_3 bonds or vertical C ─ NH_2 bonds should **not** be penalised. For other functional groups, such as ─ OH and ─ CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.
  By way of illustration, the following would apply.

					
allowed	**allowed**	not allowed			
					
allowed	**allowed**	**allowed**	**allowed**	not allowed	not allowed

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not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C ─ H bonds in a structure should **not** be penalised. The exceptions will include structures in mechanisms when the C ─ H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethane

N.B. Exceptions may be made in the context of balancing equations

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

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J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

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Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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7	
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TOTAL	



General Certificate of Education
Advanced Level Examination
June 2010

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Thursday 17 June 2010 1.30 pm to 3.15 pm

For this paper you must have:
- the Periodic Table/Data Sheet, provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. Do not write outside the box around each page or on blank pages.
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 75 minutes on **Section A** and about 30 minutes on **Section B**.



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Do not write outside the box

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

Do not write outside the box

Section A

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

1 A reaction mechanism is a series of steps by which an overall reaction may proceed. The reactions occurring in these steps may be deduced from a study of reaction rates. Experimental evidence about initial rates leads to a rate equation. A mechanism is then proposed which agrees with this rate equation.

Ethanal dimerises in dilute alkaline solution to form compound **X** as shown in the following equation.

$$2CH_3CHO \longrightarrow \underset{\mathbf{X}}{CH_3CH(OH)CH_2CHO}$$

A chemist studied the kinetics of the reaction at 298 K and then proposed the following rate equation.

$$\text{Rate} = k[CH_3CHO][OH^-]$$

1 (a) Give the IUPAC name of compound **X**.

.....

(1 mark)

1 (b) The initial rate of the reaction at 298 K was found to be 2.2×10^{-3} mol dm^{-3} s^{-1} when the initial concentration of ethanal was 0.10 mol dm^{-3} and the initial concentration of sodium hydroxide was 0.020 mol dm^{-3}.
Calculate a value for the rate constant at this temperature and give its units.

Calculation .....

.....

.....

Units .....

(3 marks)

1 (c) The sample of **X** produced consists of a racemic mixture (racemate). Explain how this racemic mixture is formed.

.....

.....

.....

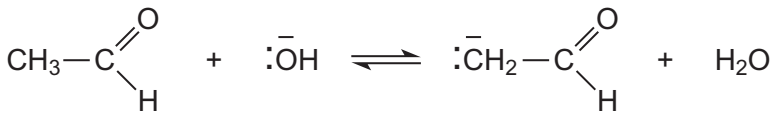
(2 marks)

Question 1 continues on the next page

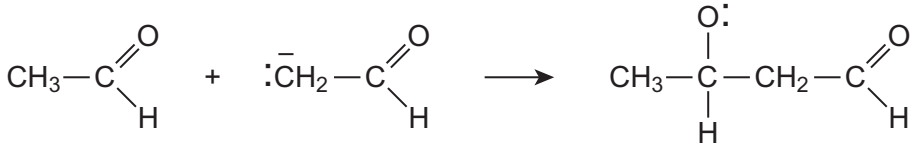
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1 (d) A three-step mechanism has been proposed for this reaction according to the following equations.

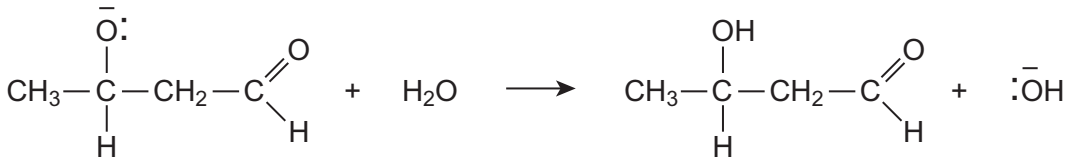
Step **1**



Step **2**



Step **3**



1 (d) (i) Using the rate equation, predict which of the three steps is the rate-determining step. Explain your answer.

Rate-determining step .....

Explanation .....

.....

(2 marks)

1 (d) (ii) Deduce the role of ethanal in Step **1**.

.....

(1 mark)

Do not write outside the box

1 (d) (iii) Use your knowledge of reaction mechanisms to deduce the type of reaction occurring in Step **2**.

.....

(1 mark)

1 (d) (iv) In the space below draw out the mechanism of Step **2** showing the relevant curly arrows.

(2 marks)

1 (e) In a similar three-step mechanism, one molecule of **X** reacts further with one molecule of ethanal. The product is a trimer containing six carbon atoms.

Deduce the structure of this trimer.

(1 mark)

13

Do not write outside the box

2 The reaction of methane with steam produces hydrogen for use in many industrial processes. Under certain conditions the following reaction occurs.

$$CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \qquad \Delta H^{\ominus} = +165\ kJ\,mol^{-1}$$

2 (a) Initially, 1.0 mol of methane and 2.0 mol of steam were placed in a flask and heated with a catalyst until equilibrium was established. The equilibrium mixture contained 0.25 mol of carbon dioxide.

2 (a) (i) Calculate the amounts, in moles, of methane, steam and hydrogen in the equilibrium mixture.

Moles of methane .....

Moles of steam .....

Moles of hydrogen .....

(3 marks)

2 (a) (ii) The volume of the flask was 5.0 dm^3. Calculate the concentration, in mol dm^{-3}, of methane in the equilibrium mixture.

.....

.....

(1 mark)

2 (b) The table below shows the equilibrium concentration of each gas in a different equilibrium mixture in the same flask and at temperature *T*.

gas	$CH_4(g)$	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
concentration / mol dm^{-3}	0.10	0.48	0.15	0.25

2 (b) (i) Write an expression for the equilibrium constant, K_c, for this reaction.

.....

.....

.....

(1 mark)

Do not write outside the box

2 (b) (ii) Calculate a value for K_c at temperature T and give its units.

Calculation .....

.....

.....

.....

Units of K_c .....

(3 marks)

2 (c) The mixture in part (b) was placed in a flask of volume greater than 5.0 dm^3 and allowed to reach equilibrium at temperature T.
State and explain the effect on the amount of hydrogen.

Effect on amount of hydrogen .....

Explanation .....

.....

.....

.....

(3 marks)

2 (d) Explain why the amount of hydrogen decreases when the mixture in part **(b)** reaches equilibrium at a lower temperature.

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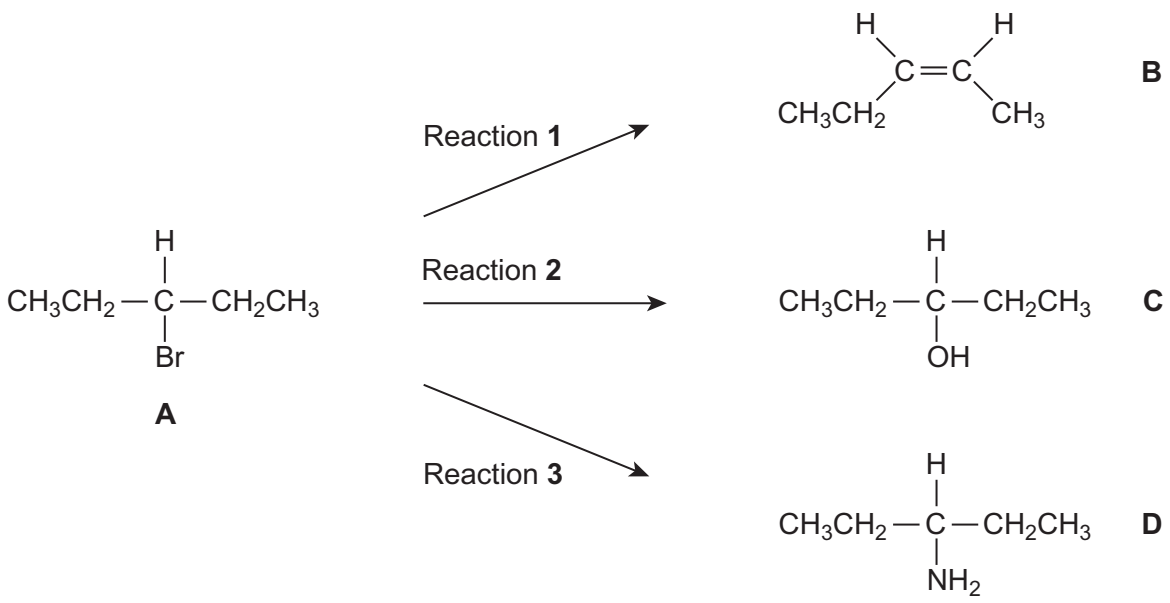
(2 marks)

13

Turn over for the next question

Do not write outside the box

3 Haloalkanes are useful compounds in synthesis.
Consider the three reactions of the haloalkane **A** shown below.



3 (a) (i) Draw a **branched-chain** isomer of **A** that exists as optical isomers.

(1 mark)

3 (a) (ii) Name the type of mechanism in Reaction **1**.

.....

(1 mark)

3 (a) (iii) Give the full IUPAC name of compound **B**.

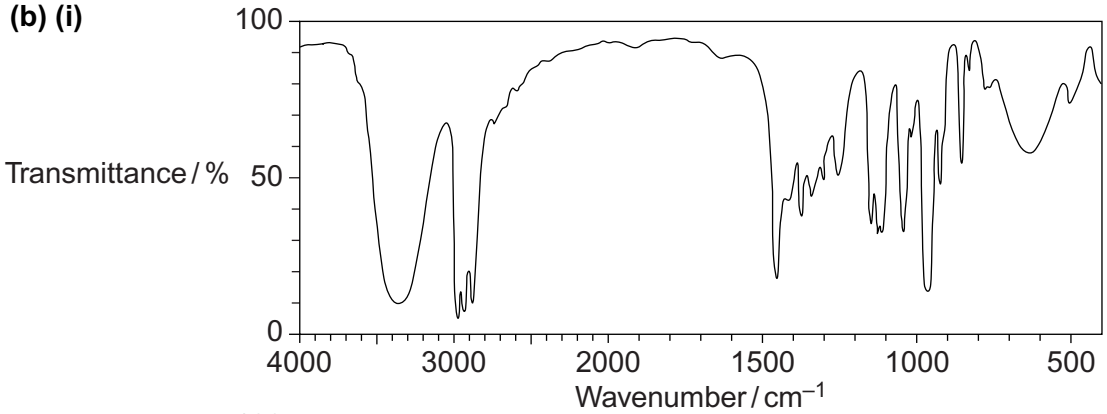
.....

(1 mark)

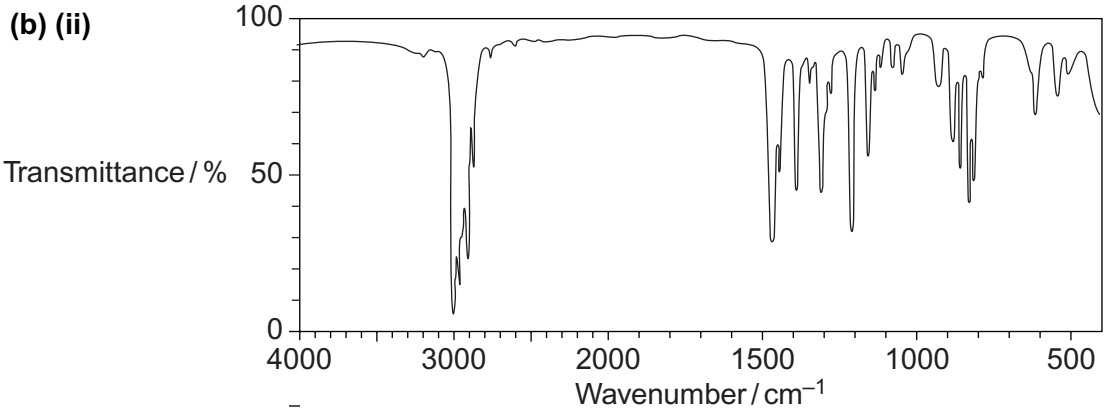
Do not write outside the box

3 (b) The infrared spectra shown below are those of the four compounds, **A**, **B**, **C** and **D**. Using **Table 1** on the Data Sheet, write the correct letter in the box next to each spectrum.

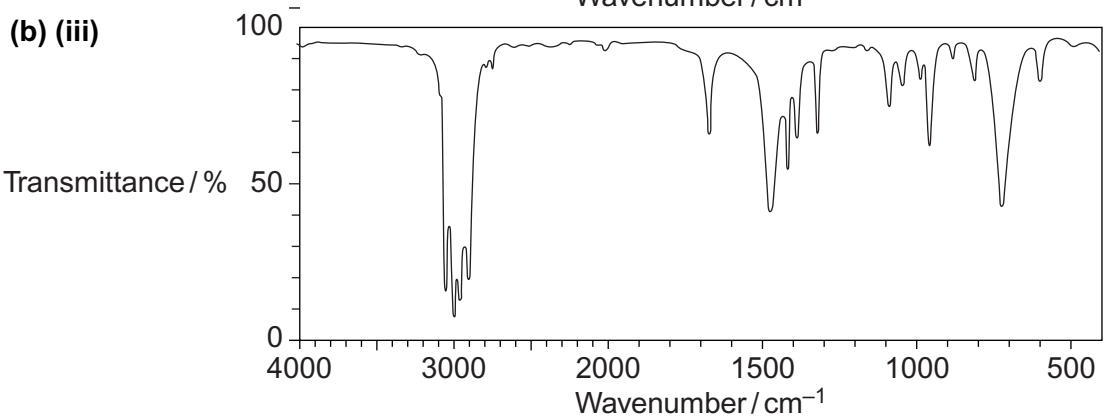
3 (b) (i)



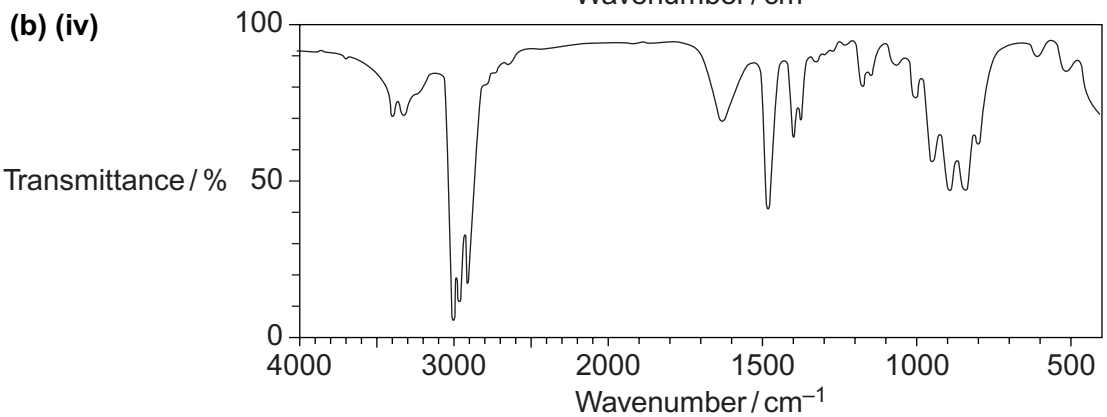
3 (b) (ii)



3 (b) (iii)



3 (b) (iv)



(4 marks)

Question 3 continues on the next page

Turn over ▶

Do not write outside the box

3 (c) Draw the repeating unit of the polymer formed by **B** and name the type of polymerisation involved.

Repeating unit

Type of polymerisation .....

(2 marks)

3 (d) (i) Outline a mechanism for Reaction **3**.

(4 marks)

3 (d) (ii) State the conditions used in Reaction **3** to form the maximum amount of the primary amine, **D**.

.....

(1 mark)

Do not write outside the box

3 (d) (iii) Draw the structure of the secondary amine formed as a by-product in Reaction **3**.

(1 mark)

3 (e) **D** is a primary amine which has three peaks in its ^{13}C n.m.r. spectrum.

3 (e) (i) An isomer of **D** is also a primary amine and also has three peaks in its ^{13}C n.m.r. spectrum. Draw the structure of this isomer of **D**.

(1 mark)

3 (e) (ii) Another isomer of **D** is a tertiary amine. Its ^{1}H n.m.r. spectrum has three peaks. One of the peaks is a doublet. Draw the structure of this isomer of **D**.

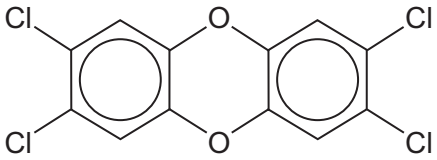
(1 mark)

17

Turn over ▶

Do not write outside the box

4 In 2008, some food products containing pork were withdrawn from sale because tests showed that they contained amounts of compounds called dioxins many times greater than the recommended safe levels.
Dioxins can be formed during the combustion of chlorine-containing compounds in waste incinerators. Dioxins are very unreactive compounds and can therefore remain in the environment and enter the food chain.
Many dioxins are polychlorinated compounds such as tetrachlorodibenzodioxin (TCDD) shown below.



In a study of the properties of dioxins, TCDD and other similar compounds were synthesised. The mixture of chlorinated compounds was then separated before each compound was identified by mass spectrometry.

4 (a) Fractional distillation is **not** a suitable method to separate the mixture of chlorinated compounds before identification by mass spectrometry.
Suggest how the mixture could be separated.

.....

(1 mark)

4 (b) The molecular formula of TCDD is $C_{12}H_4O_2Cl_4$
Chlorine exists as two isotopes ^{35}Cl (75%) and ^{37}Cl (25%).
Deduce the number of molecular ion peaks in the mass spectrum of TCDD and calculate the *m*/*z* value of the most abundant molecular ion peak.

Number of molecular ion peaks .....

.....

m/*z* value of the most abundant molecular ion peak .....

.....

(2 marks)

4 (c) Suggest **one** operating condition in an incinerator that would minimise the formation of dioxins.

.....

.....

(1 mark)

Do not write outside the box

4 (d) TCDD can also be analysed using ^{13}C n.m.r.

4 (d) (i) Give the formula of the compound used as the standard when recording a ^{13}C spectrum.

.....

(1 mark)

4 (d) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of TCDD.

.....

(1 mark)

6

Turn over for the next question

Do not write outside the box

5 In this question, give all values of pH to two decimal places.

Calculating the pH of aqueous solutions can involve the use of equilibrium constants such as K_w and K_a

K_w is the ionic product of water. The value of K_w is $5.48 \times 10^{-14}\,mol^2\,dm^{-6}$ at 50 °C.

5 (a) (i) Write an expression for pH.

.....

(1 mark)

5 (a) (ii) Write an expression for K_w

.....

(1 mark)

5 (b) (i) Calculate the pH of pure water at 50 °C.

.....

.....

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(2 marks)

5 (b) (ii) Suggest why this pure water is **not** acidic.

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(1 mark)

5 (b) (iii) Calculate the pH of $0.140\,mol\,dm^{-3}$ aqueous sodium hydroxide at 50 °C.

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(3 marks)

Do not write outside the box

5 (c) Calculate the pH of the solution formed when 25.0 cm^3 of 0.150 mol dm^{-3} aqueous sulfuric acid are added to 30.0 cm^3 of 0.200 mol dm^{-3} aqueous potassium hydroxide at 25 °C. Assume that the sulfuric acid is fully dissociated.

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(6 marks)

5 (d) (i) Write an expression for the acid dissociation constant, K_a, for ethanoic acid.

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(1 mark)

5 (d) (ii) The value of K_a for ethanoic acid is 1.74×10^{-5} mol dm^{-3} at 25 °C.
Calculate the pH of a 0.136 mol dm^{-3} aqueous solution of ethanoic acid at this temperature.

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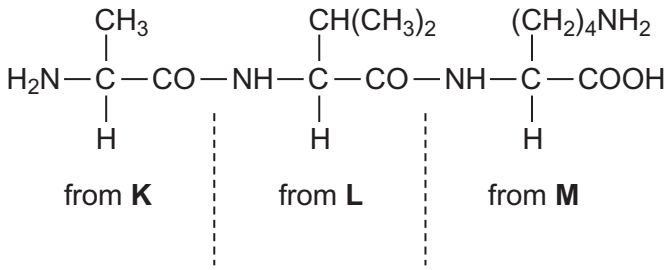
(3 marks)

18

Turn over ▶

Do not write outside the box

6 (a) Consider the tripeptide shown below that is formed from three amino acids, **K**, **L** and **M**.



6 (a) (i) Name the process by which the tripeptide is split into three amino acids.

.....

(1 mark)

6 (a) (ii) Give the IUPAC name for the amino acid **K**.

.....

(1 mark)

6 (a) (iii) Draw the structure of the zwitterion of amino acid **L**.

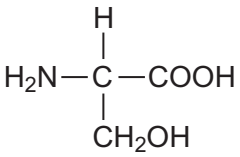
(1 mark)

6 (a) (iv) Draw the structure of the species formed by amino acid **M** at low pH.

(1 mark)

Do not write outside the box

6 (b) Consider the amino acid serine.



6 (b) (i) Draw the structure of the product formed when serine reacts with an excess of CH_3Br

(1 mark)

6 (b) (ii) Draw the structure of the dipeptide formed by two molecules of serine.

(1 mark)

6

Turn over for the next question

Do not write outside the box

Section B

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

7 Esters have many important commercial uses such as solvents and artificial flavourings in foods.

Esters can be prepared in several ways including the reactions of alcohols with carboxylic acids, acid anhydrides, acyl chlorides and other esters.

7 (a) Ethyl butanoate is used as a pineapple flavouring in sweets and cakes.

Write an equation for the preparation of ethyl butanoate from an acid and an alcohol.

Give a catalyst used for the reaction.

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(4 marks)

Do not write outside the box

7 (b) Butyl ethanoate is used as a solvent in the pharmaceutical industry.

Write an equation for the preparation of butyl ethanoate from an acid anhydride and an alcohol.

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(3 marks)

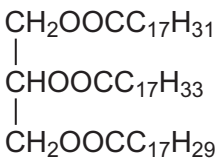
7 (c) Name and outline a mechanism for the reaction of CH_3COCl with CH_3OH to form an ester.

(5 marks)

Question 7 continues on the next page

Do not write outside the box

7 (d) The ester shown below occurs in vegetable oils. Write an equation to show the formation of biodiesel from this ester.



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(3 marks)

Do not write outside the box

7 (e) Draw the repeating unit of the polyester Terylene that is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.

Although Terylene is biodegradeable, it is preferable to recycle objects made from Terylene.

Give **one** advantage and **one** disadvantage of recycling objects made from Terylene.

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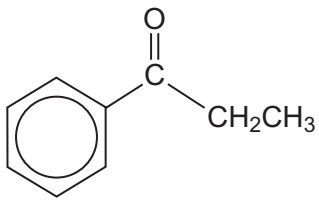
(4 marks)

19

Turn over for the next question

Do not write outside the box

8 Consider compound **P** shown below that is formed by the reaction of benzene with an electrophile.



P

8 (a) Give the **two** substances that react together to form the electrophile and write an equation to show the formation of this electrophile.

.....

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(3 marks)

8 (b) Outline a mechanism for the reaction of this electrophile with benzene to form **P**.

(3 marks)

Do not write outside the box

8 (c) Compound **Q** is an isomer of **P** that shows optical isomerism. **Q** forms a silver mirror when added to a suitable reagent.

Identify this reagent and suggest a structure for **Q**.

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(2 marks)

8

END OF QUESTIONS

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Version 1.1

General Certificate of Education
June 2010

Chemistry CHEM4

Kinetics, Equilibria and Organic Chemistry

Mark Scheme

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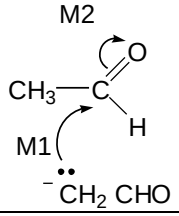
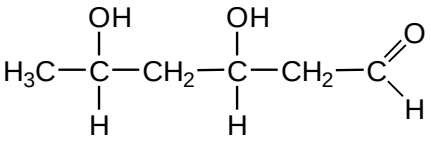
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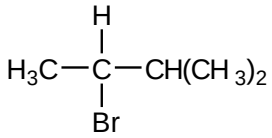
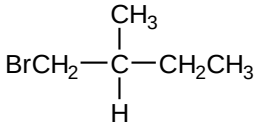
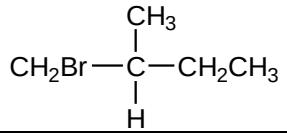
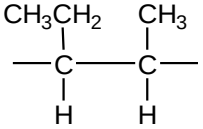
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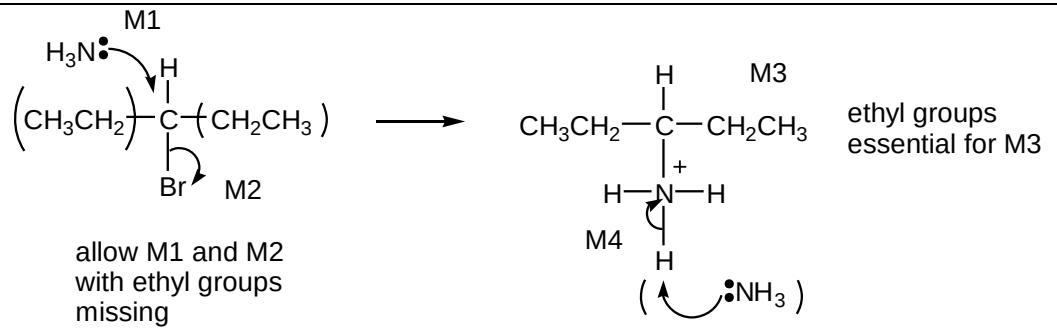
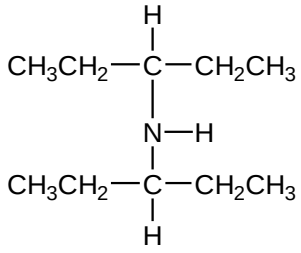
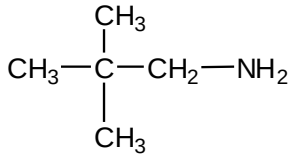
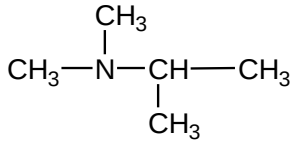
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Q	Part	Sub Part	Marking Guidance	Mark	Comments
1	(a)		3-hydroxybutanal ignore number 1 i.e. allow 3-hydroxybutan-1-al	1	not hydroxy**l**
1	(b)		$k = \frac{2.2 \times 10^{-3}}{(0.10)(0.02)}$ = 1.1 $mol^{-1}dm^3s^{-1}$	1 1 1	
1	(c)		planar or flat C=O or molecule equal probability of attack from above or below	1 1	allow planar molecule must be equal; not attack of OH^-
1	(d)	(i)	Step 1 if wrong – no mark for explanation. involves ethanal and OH^- or species/"molecules" in rate equation	1 1	
1	(d)	(ii)	(B-L) acid or proton donor	1	not Lewis acid
1	(d)	(iii)	nucleophilic addition	1	QOL
1	(d)	(iv)		2	not allow M2 before M1, but allow M1 attack on C+ after non-scoring carbonyl arrow ignore error in product
1	(e)			1	

Q	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)	(i)	mol CH_4 = 0.75	1	
			mol H_2O = 1.5	1	
			mol H_2 = 1(.0)	1	
2	(a)	(ii)	0.15 (mol dm^{-3})	1	conseq = (mol CH_4)/5
2	(b)	(i)	$\frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$ not just numbers	1	do not penalise ( ) If wrong Kc no marks for calc but allow units conseq to their Kc
2	(b)	(ii)	$\frac{(0.15)(0.25)^4}{(0.10)(0.48)^2}$	1	No marks for calc if concs used wrongly or wrong values inserted
			0.025(4)	1	
			$mol^2\ dm^{-6}$	1	allow 1 here for correct units from wrong Kc
2	(c)		increase	1	if wrong, no further marks in (c)
			lower P M1	1	not “greater volume” for M1
			eqm shifts to side with more moles (Le Chatelier) M2	1	but allow “moves to form a greater volume” for M2
2	(d)		(forward reaction is) endothermic or backward reaction is exothermic	1	
			eqm shifts in exothermic direction or to oppose reduction of or change in temp	1	This mark must have reference to temp change or exothermic reaction

Q	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)	(i)	 must be **branched** and chiral or  or 	1	not allow C_3H_7 allow C_2H_5 bonded to C either way round
3	(a)	(ii)	elimination allow base – elimination	1	but penalise any other qualification
3	(a)	(iii)	Z-pent-2-ene or cis-pent-2-ene either Z or cis is necessary (allow Z-2-pentene or cis-2-pentene)	1	with or without brackets around Z with or without hyphens
3	(b)	(i)	C	1	
3	(b)	(ii)	A	1	
3	(b)	(iii)	B	1	
3	(b)	(iv)	D	1	
3	(c)		 allow C_2H_5 bonded via C or H addition or radical or step or chain growth	1 1	must have both trailing bonds ignore brackets or n QOL not additional

3	(d)	(i)	 allow M1 and M2 with ethyl groups missing ethyl groups essential for M3	4	Allow SN1, i.e M2 first then attack of NH_3 on carbocation. Allow C_2H_5 in M3 bonded either way Allow with or without NH_3 to remove H^+ in M4, but lose mark if Br^- used. ignore $\delta+$ or $\delta-$ unless wrong + on central C instead of $\delta+$ loses M2
3	(d)	(ii)	<u>excess</u> NH_3 ignore reflux	1	allow conc ammonia in sealed tube
3	(d)	(iii)	 NOT $-C_5H_{11}$	1	Allow C_2H_5 bonded either way
3	(e)	(i)		1	
3	(e)	(ii)		1	NOT $(C_2H_5)_2NCH_3$ which is tertiary with 3 peaks but its spectrum has no doublet.

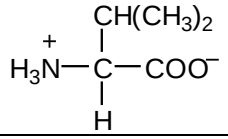
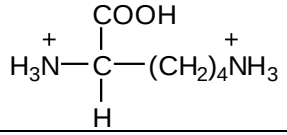
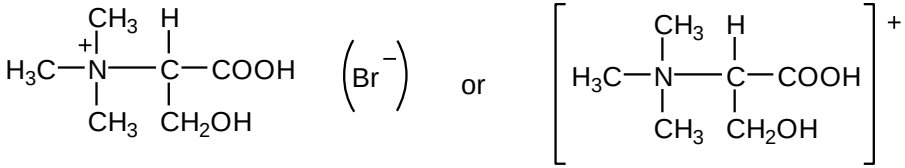
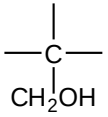
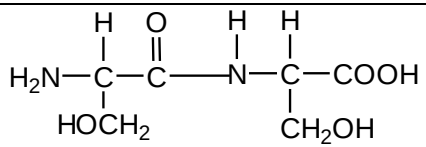
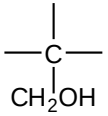
Q	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		chromatography (allow GLC TLC GC HPLC)	1	allow any qualification
4	(b)		5 Allow 320(.0) or 322(.0)	1 1	
4	(c)		Use of excess air/oxygen or high temperature (over 800 ^{o}C) or remove chlorine-containing compounds before incineration	1	
4	(d)	(i)	$Si(CH_3)_4$ allow SiC_4H_{12} allow displayed formula and do not penalise sticks	1	Not TMS
4	(d)	(ii)	3	1	

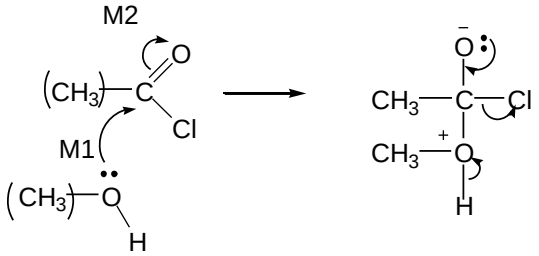
Q	Part	Sub Part	Marking Guidance		Mark	Comments
5	(a)	(i)	$-\log[H^+]$		1	penalise missing [ ] here **and not elsewhere**
5	(a)	(ii)	$[H^+][OH^-]$		1	
5	(b)	(i)	$[H^+] = 2.34 \times 10^{-7}$ pH = 6.63 *Penalise fewer than 3 sig figs but allow more than 2 dp*		1 1	
5	(b)	(ii)	$[H^+] = [OH^-]$		1	
5	(b)	(iii)	$[H^+] = K_w/[OH^-]$ $(= 5.48 \times 10^{-14} / 0.140) = 3.91 \times 10^{-13}$ pH = 12.4(1) *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values above 10, allow 3sfs - do not insist on 2 dp.* *For values below 1, allow 2dp – do not insist on 3 sig figs*	M1 M2 M3	1 1 1	if upside down or CE, allow M3 only for correct use of their $[H^+]$ not 12.40 (AE from 12.407)
			Not allow pH = 14 – pOH but can award M3 only for pH = 13.1(46) Can award all three marks if $pK_w = 13.26$ is used			

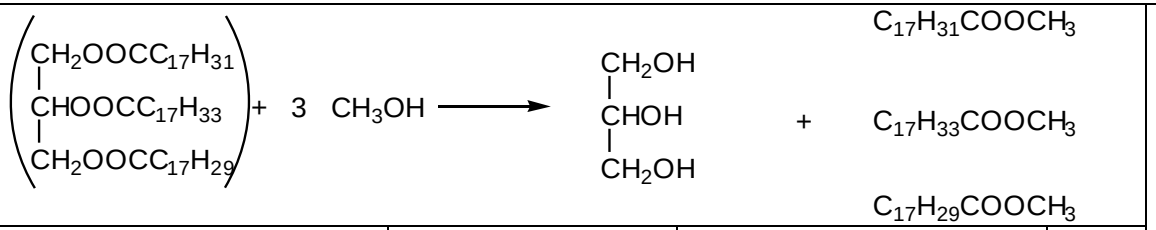
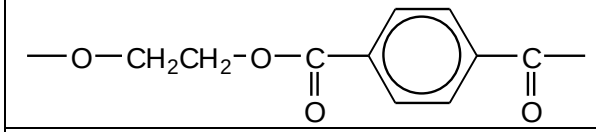
5	(c)		mol NaOH = mol OH^- = $(30\times10^{-3}) \times 0.20 = 6.0 \times 10^{-3}$	M1	1	mark for answer
			mol $H_2SO_4 = (25\times10^{-3}) \times 0.15 = 3.75\times10^{-3}$	M2	1	mark for answer
			mol $H^+ = (25\times10^{-3}) \times 0.15 \times 2 = 7.5\times10^{-3}$ OR XS mol $H_2SO_4 = 0.75\times10^{-3}$	M3	1	if factor of 2 missed or used wrongly, CE - lose M3 and next mark gained. In this case they must then use K_w to score any more. see examples below
			XS mol $H^+ = 1.5\times10^{-3}$	M4	1	
			$[H^+] = (1.5\times10^{-3}) \times (1000/55) = 0.0273$	M5	1	if no use or wrong use of volume, lose M5 and M6 except if 1000 missed AE -1 (pH = 4.56)
			pH = 1.56 *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values above 10, allow 3sfs - do not insist on 2 dp.* *For values below 1, allow 2dp – do not insist on 3 sig figs*	M6	1	

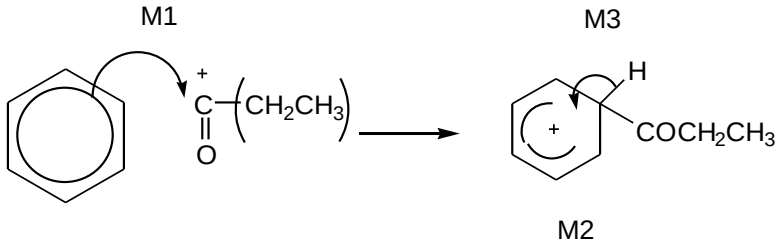
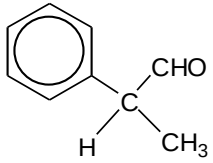
5	(d)	(i)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$	Must have all 3 brackets but don't penalize ( ) see note to Q5(a)(i)	1	not HA This mark could score in (d) (ii)

5	(d)	(ii)	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers or $[H^+] = [CH_3COO^-]$		1	allow HA here This mark could score in (d) (i)
			$[H^+] = (\sqrt{(1.74\times10^{-5} \times 0.136)} = \sqrt{(2.366\times10^{-6}} =) 1.54\times10^{-3}$		1	mark for answer if 1.5×10^{-3} penalise here if miss √ but it is shown, AE -1 so allow 2 for pH = 5.63
			pH = 2.81 can give three marks here for (d)(ii) *Do not insist on 2 dp* *Penalise fewer than 3 sig figs but allow more than 3 sfs* *For values below 1, allow 2dp – do not insist on 3 sig figs*		1	allow pH = 2.82 conseq

Q	Part	Sub Part	Marking Guidance	Mark	Comments
6	(a)	(i)	hydrolysis	1	not hydration
6	(a)	(ii)	2-aminopropanoic acid	1	ignore alanine QoL
6	(a)	(iii)		1	allow $-CO_2^-$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(a)	(iv)		1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(b)	(i)		1	allow $-CO_2H$ allow limit as  + on N or outside [ ]
6	(b)	(ii)		1	allow $-CO_2H$ allow $-CONH-$ or $-COHN-$ allow NH_2- allow limit as 

Q	Part	Sub Part	Marking Guidance		Mark	Comments
7	a		$CH_3CH_2CH_2COOH$	M1	1	not C_3H_7COOH
			CH_3CH_2OH or C_2H_5OH	M2	1	
			$\rightarrow CH_3CH_2CH_2COOCH_2CH_3 + H_2O$	M3	1	allow $C_3H_7COOC_2H_5$ penalise M3 for wrong products and unbalanced equation
			H_2SO_4 or HCl or H_3PO_4 conc or dil or neither	M4	1	not HNO_3
7	b		$CH_3CH_2CH_2CH_2OH$	M1	1	not C_4H_9OH
			$(CH_3CO)_2O$	M2	1	
			$\rightarrow CH_3COOCH_2CH_2CH_2CH_3 + CH_3COOH$	M3	1	allow $CH_3COOC_4H_9$ penalise M3 for wrong products and unbalanced equation
7	c		(nucleophilic) addition-elimination  		5	not acylation alone M2 not allowed indep of M1 but allow M1 for correct attack on C+ +C=O loses M2 only allow M4 after correct or v close M3 ignore Cl^- removing H^+

7	d		 (1) (1) (1)	3	ignore errors in initial triester First mark for $3CH_3OH$ Third mark for all three esters
7	e		not – C_2H_4 –  First mark for correct ester link second mark for the rest including trailing bonds	2	If ester link wrong, lose second mark also
			Adv reduces landfill saves raw materials lower cost for recycling than making from scratch reduces CO_2 emissions by not being incinerated	1	not allow cost without qualification ignore energy uses
			Disad difficulty/cost of collecting/sorting/processing product not suitable for original purpose, easily contaminated	1	not allow cost without qualification ignore energy uses

Q	Part	Sub Part	Marking Guidance	Mark	Comments
8	a		CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride OR $(CH_3CH_2CO)_2O$ OR propanoic anhydride penalize contradiction in formula and name e.g. propyl chloride	1	could score in equation
			$AlCl_3$ or $FeCl_3$ or names	1	could score in equation
			$CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO^+ + AlCl_4^-$ Allow RCOCl in equation but penalise above	1	allow + on C or O in equation
8	b			3	M1 arrow from circle or within it to C or to + on C Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure Ignore base removing H in M3
8	c		Tollens or ammoniacal silver nitrate	1	penalise wrong formula
				1	

General principles applied to marking CHEM4 papers by CMI+ June 2010

It is important to note that the guidance given here is generic and specific variations may be made at individual standardising meetings in the context of particular questions and papers.

Basic principles

- **Examiners should note that throughout the mark scheme, items that are underlined are required information to gain credit.**
- **Occasionally an answer involves incorrect chemistry and the mark scheme records CE = 0, which means a chemical error has occurred and no credit is given for that section of the clip or for the whole clip.**

A. The "List principle" and the use of "ignore" in the mark scheme

If a question requires **one** answer and a candidate gives two answers, no mark is scored if one answer is correct and one answer is incorrect. There is no penalty if both answers are correct.

N.B. Certain answers are designated in the mark scheme as those which the examiner should "Ignore". These answers are not counted as part of the list and should be ignored and will not be penalised.

B. Incorrect case for element symbol

The use of an incorrect case for the symbol of an element should be penalised **once only** within a clip.
For example, penalise the use of "h" for hydrogen, "CL" for chlorine or "br" for bromine.

C. Spelling

In general

- The names of chemical compounds and functional groups **must be spelled correctly** to gain credit.
- Phonetic spelling may be acceptable for some chemical terminology.

N.B. Some terms may be required to be spelled correctly or an idea needs to be articulated with clarity, as part of the "Quality of Language" (**QoL**) marking. These will be identified in the mark scheme and marks are awarded only if the QoL criterion is satisfied.

D. Equations

In general

- Equations **must** be balanced.
- When an equation is worth two marks, one of the marks in the mark scheme will be allocated to one or more of the reactants or products. This is independent of the equation balancing.
- State symbols are generally ignored, unless specifically required in the mark scheme.

E. Reagents

The command word "Identify", allows the candidate to choose to use **either** the name or the formula of a reagent in their answer. In some circumstances, the list principle may apply when both the name and the formula are used. Specific details will be given in mark schemes.

The guiding principle is that a reagent is a chemical which can be taken out of a bottle or container. Failure to identify complete reagents **will be penalised**, but follow-on marks (e.g. for a subsequent equation or observation) can be scored from an incorrect attempt (possibly an incomplete reagent) at the correct reagent. Specific details will be given in mark schemes.
For example, **no credit** would be given for

- the cyanide ion or CN^- when the reagent should be potassium cyanide or KCN;
- the hydroxide ion or OH^- when the reagent should be sodium hydroxide or NaOH;
- the $Ag(NH_3)_2^+$ ion when the reagent should be Tollens' reagent (or ammoniacal silver nitrate). In this example, no credit is given for the ion, but credit could be given for a correct observation following on from the use of the ion. Specific details will be given in mark schemes.

In the event that a candidate provides, for example, **both** KCN and cyanide ion, it would be usual to ignore the reference to the cyanide ion (because this is not contradictory) and credit the KCN. Specific details will be given in mark schemes.

F. Oxidation states

In general, the sign for an oxidation state will be assumed to be positive unless specifically shown to be negative.

G. Marking calculations

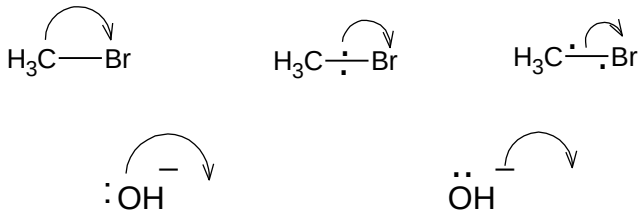
In general

- A correct answer alone will score **full marks** unless the necessity to show working is specifically required in the question.
- An arithmetic error may result in a one mark penalty if further working is correct.
- A chemical error will usually result in a two mark penalty.

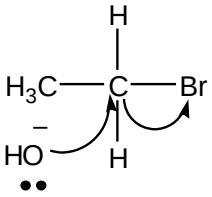
H. Organic reaction mechanisms

Curly arrows should originate either from a lone pair of electrons or from a bond.

The following representations should not gain credit **and will be penalised each time** within a clip.



For example, the following would score zero marks



When the curly arrow is showing the formation of a bond to an atom, the arrow can go directly to the relevant atom, alongside the relevant atom or **more than half-way** towards the relevant atom.

In free-radical substitution

- The absence of a radical dot should be penalised **once only** within a clip.
- The use of double-headed arrows or the incorrect use of half-headed arrows in free-radical mechanisms should be penalised **once only** within a clip

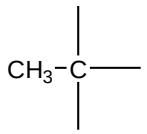
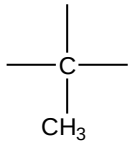
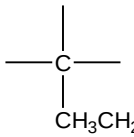
In mass spectrometry fragmentation equations, the absence of a radical dot on the molecular ion and on the free-radical fragment would be considered to be two independent errors and both would be penalised if they occurred within the same clip.

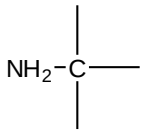
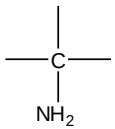
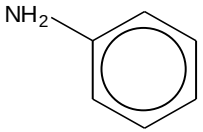
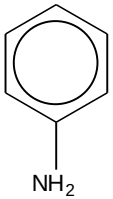
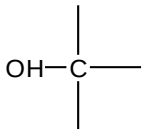
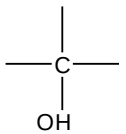
I. Organic structures

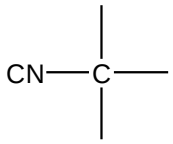
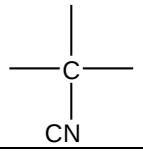
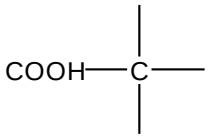
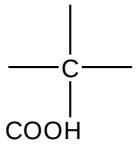
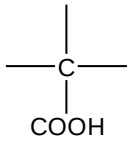
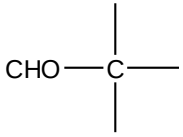
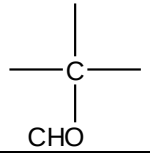
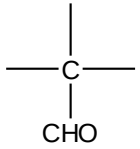
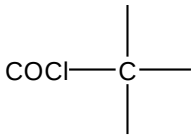
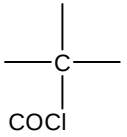
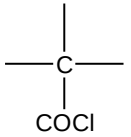
In general

- Displayed formulae must show all of the bonds and all of the atoms in the molecule, but need not show correct bond angles.
- Bonds should be drawn correctly between the relevant atoms. This principle applies in all cases where the attached functional group contains a carbon atom, e.g nitrile, carboxylic acid, aldehyde and acid chloride. The carbon-carbon bond should be clearly shown. Wrongly bonded atoms will be penalised **on every occasion**. (see the examples below)
- The same principle should also be applied to the structure of alcohols. For example, if candidates show the alcohol functional group as C — HO, they should be penalised **on every occasion**.
- Latitude should be given to the representation of C — C bonds in alkyl groups, given that CH_3— is considered to be interchangeable with H_3C— even though the latter would be preferred.
- Similar latitude should be given to the representation of amines where NH_2— C will be allowed, although H_2N— C would be preferred.
- Poor presentation of vertical C — CH_3 bonds or vertical C — NH_2 bonds should **not** be penalised. For other functional groups, such as — OH and — CN, the limit of tolerance is the half-way position between the vertical bond and the relevant atoms in the attached group.

  By way of illustration, the following would apply.

		
allowed	**allowed**	not allowed

					
allowed	**allowed**	**allowed**	**allowed**	not allowed	not allowed

					
not allowed	not allowed	not allowed	not allowed	not allowed	
					
not allowed	not allowed	not allowed	not allowed	not allowed	not allowed

- In most cases, the use of "sticks" to represent C — H bonds in a structure should not be penalised. The exceptions will include structures in mechanisms when the C — H bond is essential (e.g. elimination reactions in haloalkanes) and when a displayed formula is required.
- Some examples are given here of **structures** for specific compounds that should **not** gain credit

CH_3COH	for	ethanal
CH_3CH_2HO	for	ethanol
$OHCH_2CH_3$	for	ethanol
C_2H_6O	for	ethanol
CH_2CH_2	for	ethene
$CH_2.CH_2$	for	ethene
$CH_2:CH_2$	for	ethene

N.B. Exceptions <u>may</u> be made in the context of balancing equation

- Each of the following **should gain credit** as alternatives to correct representations of the structures.

$CH_2 = CH_2$	for	ethene, $H_2C=CH_2$
$CH_3CHOHCH_3$	for	propan-2-ol, $CH_3CH(OH)CH_3$

J. Organic names

As a general principle, non-IUPAC names or incorrect spelling or incomplete names should **not** gain credit.
Some illustrations are given here.

but-2-ol	should be **butan-2-ol**
2-hydroxybutane	should be **butan-2-ol**
butane-2-ol	should be **butan-2-ol**
2-butanol	should be **butan-2-ol**
2-methpropan-2-ol	should be **2-methylpropan-2-ol**
2-methylbutan-3-ol	should be **3-methylbutan-2-ol**
3-methylpentan	should be **3-methylpentane**
3-mythylpentane	should be **3-methylpentane**
3-methypentane	should be **3-methylpentane**
propanitrile	should be **propanenitrile**
aminethane	should be **ethylamine** (although aminoethane can gain credit)
2-methyl-3-bromobutane	should be **2-bromo-3-methylbutane**
3-bromo-2-methylbutane	should be **2-bromo-3-methylbutane**
3-methyl-2-bromobutane	should be **2-bromo-3-methylbutane**
2-methylbut-3-ene	should be **3-methylbut-1-ene**
difluorodichloromethane	should be **dichlorodifluoromethane**

Centre Number						Candidate Number				
Surname										
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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8	
9	
TOTAL	

General Certificate of Education
Advanced Level Examination
January 2010

Chemistry CHEM4

Unit 4 Kinetics, Equilibria and Organic Chemistry

Wednesday 27 January 2010 9.00 am to 10.45 am

For this paper you must have:
- the Periodic Table/Data Sheet provided as an insert (enclosed)
- a calculator.

Time allowed
- 1 hour 45 minutes

Instructions
- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page.
- Answer **all** questions.
- You must answer the questions in the spaces provided. **Answers written in margins or on blank pages will not be marked.**
- All working must be shown.
- Do all rough work in this book. Cross through any work you do not want to be marked.

Information
- The marks for questions are shown in brackets.
- The maximum mark for this paper is 100.
- The Periodic Table/Data Sheet is provided as an insert.
- Your answers to the questions in **Section B** should be written in continuous prose, where appropriate.
- You will be marked on your ability to:
  – use good English
  – organise information clearly
  – use accurate scientific terminology.

Advice
- You are advised to spend about 70 minutes on **Section A** and about 35 minutes on **Section B**.

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SECTION A

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

1 A mixture was prepared using 1.00 mol of propanoic acid, 2.00 mol of ethanol and 5.00 mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation.

$$CH_3CH_2COOH + CH_3CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_3 + H_2O \qquad \Delta H^{\ominus} = -22\,kJ\,mol^{-1}$$

The equilibrium mixture contained 0.54 mol of the ester ethyl propanoate.

1 (a) (i) Calculate the amounts, in moles, of propanoic acid, of ethanol and of water in this equilibrium mixture.

Moles of propanoic acid .....

Moles of ethanol .....

Moles of water .....

(3 marks)

1 (a) (ii) Write an expression for the equilibrium constant, K_c, for this equilibrium.

.....

.....

(1 mark)

1 (a) (iii) Calculate a value for K_c for this equilibrium at this temperature. Explain why this K_c value has no units.

Calculation .....

.....

.....

.....

Explanation .....

.....

(3 marks)

(Extra space) .....

.....

Areas outside the box will not be scanned for marking

1 (b) For this equilibrium, predict the effect of an increase in temperature on each of the following.

1 (b) (i) the amount, in moles, of ester at equilibrium

.....

(1 mark)

1 (b) (ii) the time taken to reach equilibrium

.....

(1 mark)

1 (b) (iii) the value of K_c

.....

(1 mark)

10

Turn over for the next question

Areas outside the box will not be scanned for marking

2 In this question, give all values of pH to 2 decimal places.

2 (a) (i) Write an expression for the term pH.

.....

(1 mark)

2 (a) (ii) Calculate the concentration, in mol dm^{-3}, of an aqueous solution of sulfuric acid that has a pH of 0.25

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(2 marks)

2 (b) A student carried out a titration by adding an aqueous solution of sodium hydroxide from a burette to an aqueous solution of ethanoic acid. The end-point was reached when 22.60 cm^3 of the sodium hydroxide solution had been added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

2 (b) (i) Write an equation for the reaction between sodium hydroxide and ethanoic acid.

.....

(1 mark)

2 (b) (ii) Calculate the concentration, in mol dm^{-3}, of the sodium hydroxide solution used.

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(2 marks)

Areas outside the box will not be scanned for marking

2 (b) (iii) A list of indicators is shown below.

Indicator	pH range
thymol blue	1.2–2.8
bromophenol blue	3.0–4.6
litmus	5.0–8.0
cresol purple	7.6–9.2

Select from the list the most suitable indicator for the end-point of this titration.

.....

(1 mark)

2 (b) (iv) Suggest why the concentration of sodium hydroxide in a solution slowly decreases when left open to air.

.....

.....

(1 mark)

2 (c) At 298 K, the value of the acid dissociation constant, K_a, for ethanoic acid in aqueous solution is 1.74×10^{-5} mol dm^{-3}

2 (c) (i) Write an expression for the acid dissociation constant, K_a, for ethanoic acid.

.....

.....

(1 mark)

2 (c) (ii) Calculate the pH of 0.410 mol dm^{-3} ethanoic acid at this temperature.

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(3 marks)

(Extra space) .....

.....

Question 2 continues on the next page

Areas outside the box will not be scanned for marking

2 (c) (iii) Calculate the pH of the buffer solution formed when 10.00 cm^3 of 0.100 mol dm^{-3} potassium hydroxide are added to 25.00 cm^3 of 0.410 mol dm^{-3} ethanoic acid.

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(6 marks)

(Extra space) .....

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18

There are no questions printed on this page

DO NOT WRITE ON THIS PAGE
ANSWER IN THE SPACES PROVIDED

Turn over ▶

Areas outside the box will not be scanned for marking

3 Propanone and iodine react in acidic conditions according to the following equation.

$$CH_3COCH_3 + I_2 \longrightarrow ICH_2COCH_3 + HI$$

A student studied the kinetics of this reaction using hydrochloric acid and a solution containing propanone and iodine. From the results the following rate equation was deduced.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

3 (a) Give the overall order for this reaction.

.....

(1 mark)

3 (b) When the initial concentrations of the reactants were as shown in the table below, the initial rate of reaction was found to be 1.24×10^{-4} mol dm^{-3} s^{-1}.

	initial concentration / mol dm^{-3}
CH_3COCH_3	4.40
I_2	5.00×10^{-3}
H^+	0.820

Use these data to calculate a value for the rate constant, k, for the reaction and give its units.

Calculation .....

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Units .....

(3 marks)

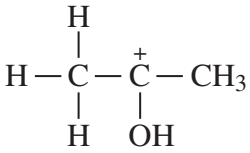
3 (c) Deduce how the initial rate of reaction changes when the concentration of iodine is doubled but the concentrations of propanone and of hydrochloric acid are unchanged.

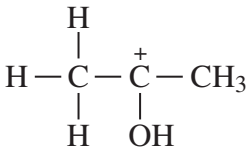
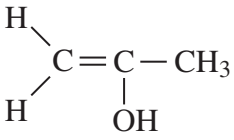
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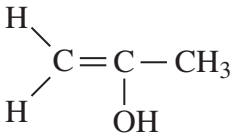
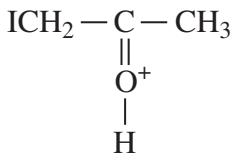
(1 mark)

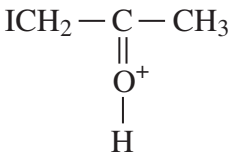
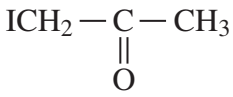
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3 (d) The following mechanism for the overall reaction has been proposed.

Step **1** $CH_3COCH_3 + H^+ \longrightarrow$ 

Step **2**  $\longrightarrow$  $+ H^+$

Step **3**  $+ I_2 \longrightarrow$  $+ I^-$

Step **4**  $\longrightarrow$  $+ H^+$

Use the rate equation to suggest which of the four steps could be the rate-determining step. Explain your answer.

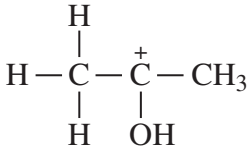
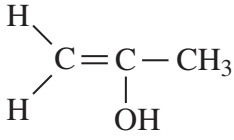
Rate-determining step .....

Explanation .....

.....

(2 marks)

3 (e) Use your understanding of reaction mechanisms to predict a mechanism for Step **2** by adding one or more curly arrows as necessary to the structure of the carbocation below.

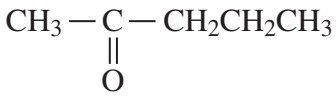
Step **2**  $\longrightarrow$  $+ H^+$

(1 mark)

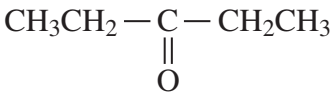
8

Areas outside the box will not be scanned for marking

4 Two isomeric ketones are shown below.



Q



R

4 (a) Name and outline a mechanism for the reaction of compound **Q** with HCN and name the product formed.

Name of mechanism .....

Mechanism

Name of product .....

(6 marks)

Areas outside the box will not be scanned for marking

4 (b) Some students were asked to suggest methods to distinguish between isomers **Q** and **R**.

One student suggested testing the optical activity of the products formed when **Q** and **R** were reacted separately with HCN.

By considering the optical activity of these products formed from **Q** and **R**, explain why this method would **not** distinguish between **Q** and **R**.

.....

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(3 marks)

(Extra space) .....

.....

.....

4 (c) Other students suggested using mass spectrometry and the fragmentation patterns of the molecular ions of the two isomers to distinguish between them.

They predicted that only one of the isomers would have a major peak at *m/z* = 57 in its mass spectrum so that this method would distinguish between **Q** and **R**.

4 (c) (i) Identify the isomer that has a major peak at *m/z* = 57 in its mass spectrum.

.....

(1 mark)

4 (c) (ii) Write an equation for the fragmentation of the molecular ion of this isomer to form the species that produces the peak at *m/z* = 57.

.....

(2 marks)

4 (c) (iii) Predict the *m/z* value of a major peak in the mass spectrum of the other isomer.

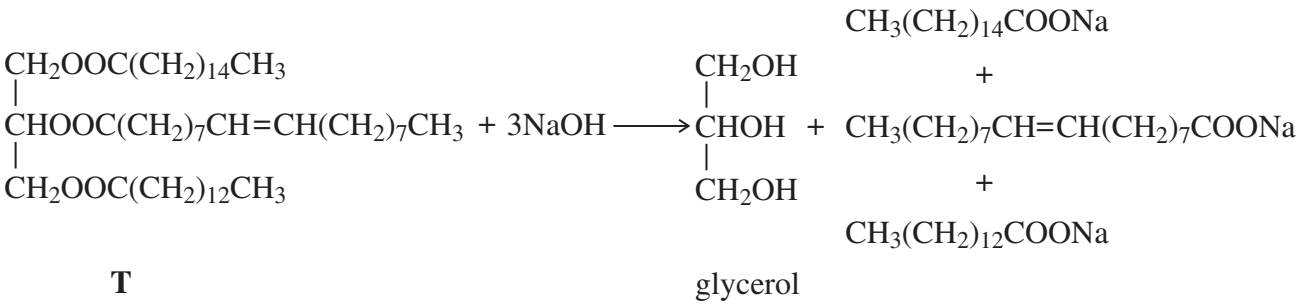
.....

(1 mark)

13

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5 The triester, **T**, shown below is found in palm oil. When **T** is heated with an excess of sodium hydroxide solution, the alcohol glycerol is formed together with a mixture of three other products as shown in the following equation.



T glycerol

5 (a) (i) Give the IUPAC name for glycerol.

.....

(1 mark)

5 (a) (ii) Give a use for the mixture of sodium salts formed in this reaction.

.....

(1 mark)

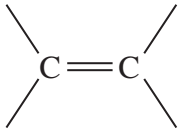
5 (b) When **T** is heated with an excess of methanol, glycerol is formed together with a mixture of methyl esters.

5 (b) (i) Give a use for this mixture of methyl esters.

.....

(1 mark)

5 (b) (ii) One of the methyl esters in the mixture has the IUPAC name methyl (*Z*)-octadec-9-enoate. Draw **two** hydrogen atoms on the diagram below to illustrate the meaning of the letter *Z* in the name of this ester.



(1 mark)

Areas outside the box will not be scanned for marking

5 (b) (iii) One of the other methyl esters in the mixture has the formula $CH_3(CH_2)_{12}COOCH_3$
Write an equation for the complete combustion of one molecule of this ester.

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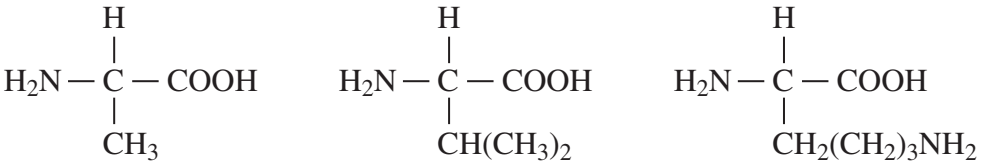
(1 mark)

5

Turn over for the next question

Areas outside the box will not be scanned for marking

6 The three amino acids shown below were obtained by hydrolysis of a protein.



alanine valine lysine

6 (a) (i) Draw the zwitterion of alanine.

(1 mark)

6 (a) (ii) Draw the species formed when valine is dissolved in an alkaline solution.

(1 mark)

6 (a) (iii) Draw the species formed by lysine at low pH.

(1 mark)

Areas outside the box will not be scanned for marking

6 (b) Draw the two dipeptides formed by the reaction of alanine with valine.

(2 marks)

6 (c) Name a suitable method by which the mixture of amino acids formed by hydrolysis of the protein can be separated.

.....

(1 mark)

6

Turn over for the next question

Areas outside the box will not be scanned for marking

7 Organic chemists use a variety of methods to identify unknown compounds. When the molecular formula of a compound is known, spectroscopic and other analytical techniques are used to distinguish between possible structural isomers. Use your knowledge of such techniques to identify the compounds described below.

Use the three tables of spectral data on the Data Sheet where appropriate.

Each part below concerns a different pair of structural isomers.
Draw **one** possible structure for each of the compounds **A** to **J**, described below.

7 (a) Compounds **A** and **B** have the molecular formula C_3H_6O
A has an absorption at 1715 cm^{-1} in its infrared spectrum and has only one peak in its ^1H n.m.r. spectrum.
B has absorptions at 3300 cm^{-1} and at 1645 cm^{-1} in its infrared spectrum and does **not** show *E*–*Z* isomerism.

A **B**

(2 marks)

7 (b) Compounds **C** and **D** have the molecular formula C_5H_{12}
In their ^1H n.m.r. spectra, **C** has three peaks and **D** has only one.

C **D**

(2 marks)

Areas outside the box will not be scanned for marking

7 (c) Compounds **E** and **F** are both esters with the molecular formula $C_4H_8O_2$
In their ^1H n.m.r. spectra, **E** has a quartet at $\delta = 2.3$ ppm and **F** has a quartet at $\delta = 4.1$ ppm.

E **F**

(2 marks)

7 (d) Compounds **G** and **H** have the molecular formula $C_6H_{12}O$
Each exists as a pair of optical isomers and each has an absorption at about 1700 cm^{-1} in its infrared spectrum. **G** forms a silver mirror with Tollens' reagent but **H** does not.

G **H**

(2 marks)

7 (e) Compounds **I** and **J** have the molecular formula $C_4H_{11}N$ and both are secondary amines. In their ^{13}C n.m.r. spectra, **I** has two peaks and **J** has three.

I **J**

(2 marks)

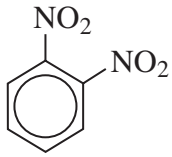
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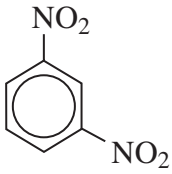
SECTION B

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

8 Three isomers of $C_6H_4(NO_2)_2$ are shown below.



W



X



Y

8 (a) (i) Give the number of peaks in the ^{13}C n.m.r. spectrum of each isomer.

.....

.....

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(3 marks)

8 (a) (ii) Draw the displayed formula of the compound used as a standard in recording these spectra.

(1 mark)

Areas outside the box will not be scanned for marking

8 (b) Isomer **X** is prepared from nitrobenzene by reaction with a mixture of concentrated nitric acid and concentrated sulfuric acid.

The two acids react to form an inorganic species that reacts with nitrobenzene to form **X**.

8 (b) (i) Give the formula of this inorganic species formed from the two acids and write an equation to show its formation.

.....

.....

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(2 marks)

8 (b) (ii) Name and outline a mechanism for the reaction of this inorganic species with nitrobenzene to form **X**.

(4 marks)

Question 8 continues on the next page

Areas outside the box will not be scanned for marking

8 (c) Isomer **Y** is used in the production of the polymer Kevlar.

Y is first reduced to the diamine shown below.



8 (c) (i) Identify a suitable reagent or mixture of reagents for the reduction of **Y** to form this diamine. Write an equation for this reaction using [H] to represent the reducing agent.

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(2 marks)

8 (c) (ii) This diamine is then reacted with benzene-l,4-dicarboxylic acid to form Kevlar. Draw the repeating unit of Kevlar.

(2 marks)

Areas outside the box will not be scanned for marking

8 (c) (iii) Kevlar can be used as the inner lining of bicycle tyres. The rubber used for the outer part of the tyre is made of polymerised alkenes.

State the difference in the biodegradability of Kevlar compared to that of rubber made of polymerised alkenes.

Use your knowledge of the bonding in these polymer molecules to explain this difference.

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(4 marks)

(Extra space) .....

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18

Turn over for the next question

Areas outside the box will not be scanned for marking

9 (a) Name and outline a mechanism for the reaction of $CH_3CH_2NH_2$ with CH_3CH_2COCl

Name the amide formed.

(6 marks)

Areas outside the box will not be scanned for marking

9 (b) Haloalkanes such as CH_3Cl are used in organic synthesis.

Outline a three-step synthesis of $CH_3CH_2NH_2$ starting from methane. Your first step should involve the formation of CH_3Cl

In your answer, identify the product of the second step and give the reagents and conditions for each step.

Equations and mechanisms are **not** required.

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(6 marks)

(Extra space) .....

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12

END OF QUESTIONS

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Version 1.0: 02/2010

General Certificate of Education

Chemistry 2421

CHEM4 Kinetics, Equilibria and Organic Chemistry

Mark Scheme

2010 examination - January series

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Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

Further copies of this Mark Scheme are available to download from the AQA Website: www.aqa.org.uk

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Registered address: AQA, Devas Street, Manchester M15 6EX
Dr Michael Cresswell Director General

Question	Part	Sub part		Mark	Comments
1	(a)	(i)	acid 0.46 alcohol 1.46 water 5.54	1 1 1	
1	(a)	(ii)	$K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{[ester][water]}{[acid][alcohol]}$	1	penalise ( ) allow molecular formulae or minor slip in formulae
1	(a)	(iii)	$\frac{(0.54/V)(5.54/V)}{(0.46/V)(1.46/V)}$ Allow without V 4.45 or 4.5 cancel (as equal no of moles on each side of equation)	1 1 1	Conseq on values in (a)(i) If values used wrongly or wrong values inserted or wrong Kc no marks for calc Part 1(a)(iii) for info 0.46 × 1.46 = 0.6716 Possible wrong answers acid 0.46 √ / alcohol 1.46 √ / water 4.46 X — gives Kc = 3.59 √√ acid 0.46 √ / alcohol 1.46 √ / water 0.54 X — gives Kc = 0.434 √√
1	(b)	(i)	decrease or be reduced or fewer	1	
1	(b)	(ii)	decrease or be reduced or less time or faster or quicker	1	
1	(b)	(iii)	decrease or be reduced	1	

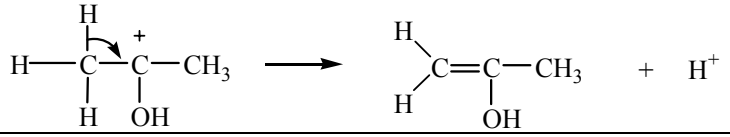
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Question	Part	Sub part		Mark	Comments
2	(a)	(i)	$-\log[H^+]$	1	or $\log 1/[H^+]$ penalise ( )
2	(a)	(ii)	$[H^+] = 0.56$ $[H_2SO_4] = ½ \times 0.56 = 0.28$	1 1	mark for the answer; allow 2dp or more
2	(b)	(i)	$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ ***OR*** $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$	1	Allow CH_3CO_2H etc
2	(b)	(ii)	mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or 1.03×10^{-2} $[NaOH] = 1.025 \times 10^{-2} / 22.6 \times 10^{-3} = 0.45(4)$ ***OR*** $[NaOH] = 1.03 \times 10^{-2} / 22.6 \times 10^{-3} = 0.456$ or 0.46	1 1	 mark for answer if not 0.454 look back for error
2	(b)	(iii)	cresol purple	1	
2	(b)	(iv)	NaOH reacts with <u>carbon dioxide</u> (in the air)	1	
2	(c)	(i)	$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ allow molecular formulae or minor slip in formulae	1	penalise ( ) allow H_3O^+ not allow HA etc

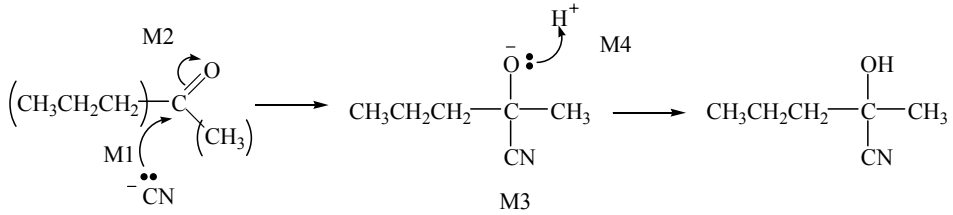
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2	(c)	(ii)	$K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers $[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$ pH = 2.57 can give three ticks here for (c)(ii) penalise decimal places < 2 >	1 1 1	allow HA etc here This can be scored in part(c)(i) but doesn't score there. mark for 2.67×10^{-3} or 2.7×10^{-3} either gives 2.57 pH mark conseq on their $[H^+]$ so 5.15 gets 2 marks where square root not taken
2	(c)	(iii)	**M1** mol OH^- = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$ **M2** orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$ or 1.025×10^{-2} or 1.03×10^{-2} **M3** mol <u>HA</u> in buffer = orig mol HA – mol OH^- = 0.00925 or 0.0093 **M4** mol A^- in buffer = mol OH^- = 1.0×10^{-3} **M5** $[H^+] = (\frac{Ka \times [CH_3COOH]}{[CH_3COO^-]} =)$ $\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010}$ or $\frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$ $(= 1.61 \times 10^{-4}$ or $1.62 \times 10^{-4})$ **M6** pH = 3.79 can give six ticks for 3.79 NB Unlike Qu 2(c)(ii), this pH mark is NOT awarded conseq to their $[H^+]$ unless following AE	1 1 1 1 1 1	If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4 If A^- is wrong, max 3 for M1, M2 and M3 or use of pH = pKa – log [HA]/ $[A^-]$ Mark is for insertion of correct numbers in correct expression for $[H^+]$ if [HA]/[A^-] upside down lose M5 & M6 If wrong method e.g. $[H^+]^2/[HA]$ max 3 for M1, M2 and M3 Some may calculate concentrations [HA] = 0.264 and $[A^-]$ = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK) BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75 (this gets 3 for M1, M2 & M4)

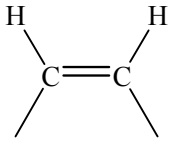
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Question	Part	Sub Part		Mark	Comment
3	(a)		2 or two or second	1	
3	(b)		$k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$ $= 3.44 \times 10^{-5}$ (min 3sfs) $mol^{-1}dm^3s^{-1}$	1 1 1	mark is for insertion of numbers into a correctly rearranged rate equ , k = etc if upside down, (or use of I_2 data) score only units mark any order
3	(c)		no change or no effect or stays the same or 1.24×10^{-4}	1	
3	(d)		1 or 2 or 1 and 2 rate equ doesn't involve I_2 or only step which includes 2 species in rate equ	1 1	if wrong no further mark but mark on from no answer
3	(e)			1	any second arrow loses the mark

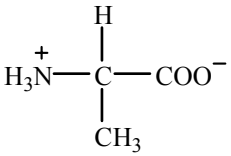
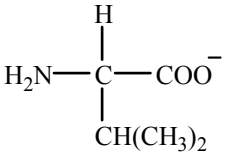
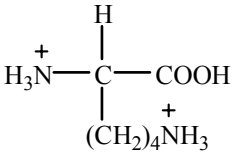
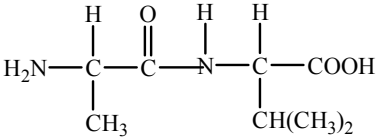
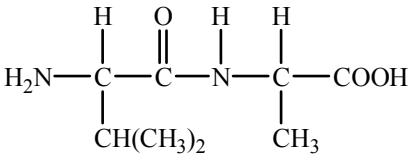
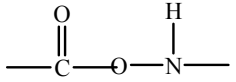
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Question	Part	Sub Part		Mark	Comments
4	(a)		nucleophilic addition  M3 for completely correct structure not including lp M4 for lp and arrow 2-hydroxy-2-methylpentan(e)nitrile	1 4 1	Attack by HCN loses M1 and M2 M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2 M2 only allowed if correct carbon attacked allow minus charge on N i.e. :CN^- allow C_3H_7 in M3 allow without – allow 2-hydroxy-2-methylpentanonitrile
4	(b)		Product from **Q** is a racemic mixture/ equal amounts of enantiomers racemic mixture is inactive or inactive explained Product from **R** is inactive (molecule) or has no chiral centre	1 1 1	if no reference to products then no marks; not **Q** is optically active or has a chiral centre etc
4	(c)	(i)	**mark the three sections of Qu 4(c) separately** **R** or $CH_3CH_2COCH_2CH_3$	1	
4	(c)	(ii)	$[CH_3CH_2COCH_2CH_3]^{+\cdot}$ ***OR*** $[C_5H_{10}O]^{+\cdot}$ $\rightarrow$ $[CH_3CH_2CO]^+ + {}^{\cdot}CH_2CH_3$ ***OR*** $\rightarrow$ $[C_3H_5O]^+ + {}^{\cdot}C_2H_5$	1 1	allow molecular formulae allow without brackets if brackets not shown, allow dot anywhere on radical or + anywhere on ion
4	(c)	(iii)	m/z = 43 or 71	1	

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Question	Part	Sub Part		Mark	Question
5	(a)	(i)	propan(e)-1,2,3-triol or 1,2,3- propan(e)triol	1	not propyl ignore hyphen, commas
5	(a)	(ii)	soaps	1	allow anionic surfactant not cationic surfactant not detergents, not shampoos
5	(b)	(i)	(bio)<u>diesel</u>	1	Allow fuel for <u>diesel</u> engines not biofuel, not oils
5	(b)	(ii)		1	ignore anything else attached except any more H atoms.
5	(b)	(iii)	$CH_3(CH_2)_{12}COOCH_3 + 21½\ O_2 \rightarrow 15CO_2 + 15\ H_2O$ ***OR*** $C_{15}H_{30}O_2$ or 43/2	1	**not** allow equation doubled

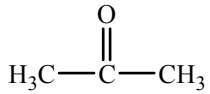
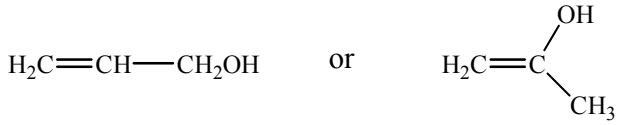
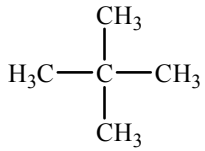
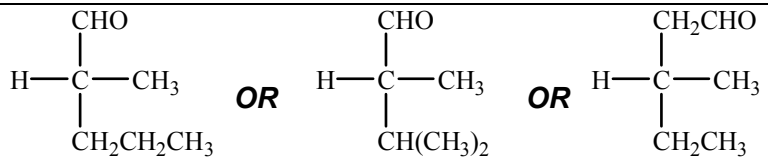
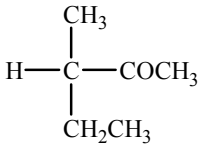
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Question	Part	Sub Part		Mark	Comments
6	(a)	(i)		1	allow $-CO_2^-$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(a)	(ii)		1	allow $-CO_2^-$ allow NH_2- allow C_3H_7
6	(a)	(iii)		1	allow $-CO_2H$ allow $^+NH_3-$ don't penalize position of + on NH_3
6	(b)		 	1 1	allow $-CO_2H$ allow NH_2- allow C_3H_7 allow as zwitterions if error in peptide link e.g.  if twice, penalise both times not polymers if wrong amino acid in both can score Max 1

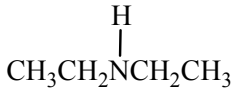
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6	(c)		chromatography or electrophoresis	1	ignore qualification to chromatography

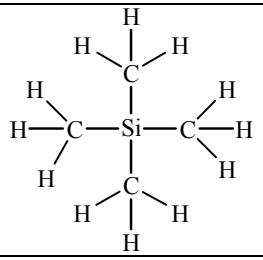
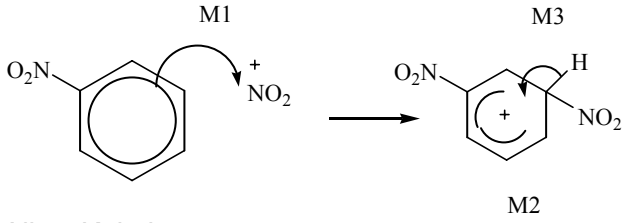
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Question	Part	Sub Part		Mark	Comments
7	(a)		A 	1	allow CH_3COCH_3
			B 	1	must show C=C Penalise sticks once per pair
7	(b)		C $CH_3CH_2CH_2CH_2CH_3$	1	
			D 	1	NOT cyclopentane which is only C_5H_{10} Penalise sticks once per pair
7	(c)		E $CH_3CH_2COOCH_3$	1	Allow $C_2H_5CO_2CH_3$
			F $CH_3COOCH_2CH_3$	1	Allow $CH_3CO_2CH_2CH_3$ or $CH_3CO_2C_2H_5$ Penalise sticks once per pair
7	(d)		G  allow C_3H_7 allow C_3H_7 allow C_2H_5	1	not C_5H_{11} nor C_4H_9 Penalise sticks once per pair
			H  allow C_2H_5	1	

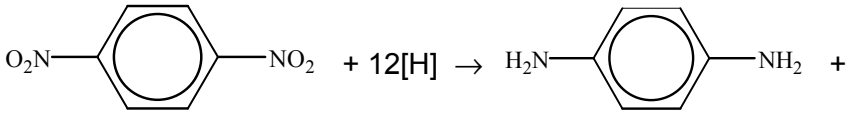
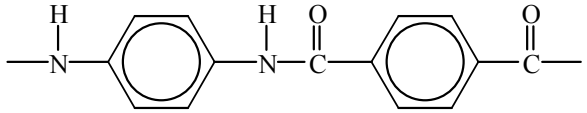
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7	(e)		I 	1	allow C_2H_5
			J 	1	NOT C_3H_7 Penalise sticks once per pair

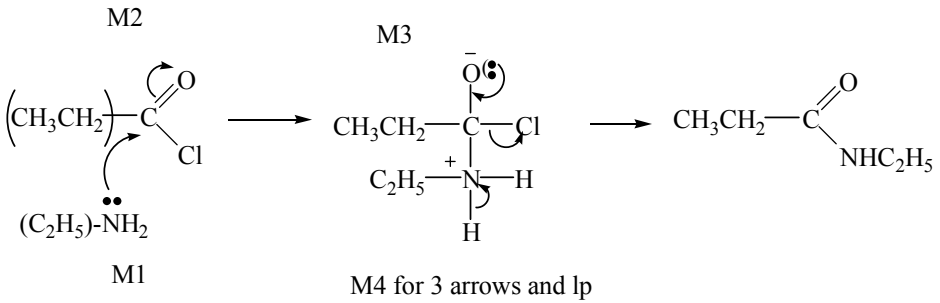
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Question	Part	Sub Part		Mark	Comments
(8)	(a)	(i)	**W** 3 **X** 4 **Y** 2	1 1 1	
(8)	(a)	(ii)		1	displayed formula shows ALL bonds
(8)	(b)	(i)	NO_2^+ $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$ ***OR*** $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$	1 1	allow + anywhere can score in equation or use two equations via $H_2NO_3^+$
(8)	(b)	(ii)	electrophilic substitution  Allow Kekule structures + must be on N of $^+NO_2$ (which must be correct) both NO_2 must be correctly positioned and bonded to gain M2	1 3	Not Friedel Crafts M1 arrow from circle or within it to N or to + on N horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure ignore base removing H in M3

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8	(c)	(i)	H_2/Ni or H_2/Pt or Sn/HCl or Fe/HCl (conc or dil or neither) allow dil H_2SO_4 ignore mention of NaOH  $4H_2O$ Or $6H_2$	1 1	Not $NaBH_4$ Not $LiAlH_4$ Not Na/C_2H_5OH not conc H_2SO_4 or any HNO_3 allow $C_6H_4(NO_2)_2$ etc , allow NO_2– NH_2– i.e. be lenient on structures, the mark is for balancing equ
8	(c)	(ii)	 1st mark for correct peptide link 2nd mark for the rest correct including trailing bonds	 2	allow –CONH- ignore [ ]n as in polymer
8	(c)	(iii)	**M1** Kevlar is <u>biodegradeable</u> but polyalkenes not **M2** Kevlar has <u>polar</u> bonds / is a (poly) amide / has peptide link **M3** can be hydrolysed/attacked by nucleophiles/acids/bases/enzymes **M4** polyalkenes <u>non polar</u> /has <u>non-polar</u> bonds	1 1 1 1	allow Kevlar is <u>more</u> biodegradeable comment on structure of Kevlar comment on structure of polyalkenes but not just strong bonds

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Question	Part	Sub Part		Mark	Comments
9	(a)		(nucleophilic) addition-elimination	1	
				4	minus on NH_2 loses M1 M2 not allowed independent of M1, but allow M1 for correct attack on C+ +C=O loses M2 only allow M4 after correct or very close M3 lose M4 for Cl^- removing H^+ in mechanism, but ignore HCl as a product
			<u>N-ethylpropanamide</u>	1	Not N-ethylpropaneamide
9	(b)		CH_3CN or ethan(e)nitrile or ethanonitrile	1	not ethanitrile but allow correct formula with ethanitrile
			for each step wrong or no reagent loses condition mark	1	contradiction loses mark
			Step 1 Cl_2		
			uv or above 300 °C	1	wrong or no reagent loses condition mark
			Step 2 KCN	1	
			aq and alcoholic (both needed)	1	allow uv light / (sun)light / uv radiation
			Step 3 H_2/Ni or $LiAlH_4$ or Na/C_2H_5OH	1	not CN^- but mark on NOT HCN or KCN + acid, and this loses condition mark NOT $NaBH_4$ Sn/HCl (forms aldehyde!) ignore conditions

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