Centre Number						Candidate Number				
Surname	MODEL ANSWERS									
Other Names										
Candidate Signature										

For Examiner's Use	
Examiner's Initials	
Question	Mark
1	
2	
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10	
11	
TOTAL	

AQA

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**.

JUN15CHEM401

WMP/Jun15/CHEM4/E5

Section A

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

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

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

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

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

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}	1.167×10^{-4}
3	9.8×10^{-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 $k = \frac{rate}{[A]^2}$ $k = \frac{3.3 \times 10^{-5}}{(4.2 \times 10^{-3})^2}$

$k = 1.87$ mol^{-1}dm^{3}s^{-1}

Don't forget your units!

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]

The rate determining step does not involve B - it only involves A.

Remember if the order is zero then it does not affect rate and is therefore not in the rate determining step!

6

Turn over for the next question

Do not write outside the box

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

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

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

[2 marks]

K_c $Kc = \frac{[SO_2]^3}{[SO_2]^2[O_2]}$

Units $mol^{-1}dm^3$ = $\frac{mol dm^{-3} \times mol dm^{-3}}{mol dm^{-3} \times mol dm^{-3} \times mol dm^{-3}}$ = $\frac{1}{mol dm^{-3}}$ ∴ answer

9 (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]

$Kc = \frac{[SO_2]^3}{[SO_2]^2[O_2]}$ $\frac{[SO_2]^3}{[SO_2]^2 \times Kc} = [O_2]$

$\frac{(0.0720)}{(0.0550)^2 \times 27.9} = [O_2]$ $[O_2] = 0.0614 mol dm^{-3}$

conc × vol = moles

∴ moles of O_2 = 0.0614 × 1.4 = 0.086 moles

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]

No effect

Only temperature affects Kc

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 Increase SO_3

Explanation There are less moles on the Right Hand Side of the equation so when volume decreases pressure increases and therefore equilibrium position will shift to the right to oppose the change.

Always mention - if possible, the statement "equilibrium position shifts".

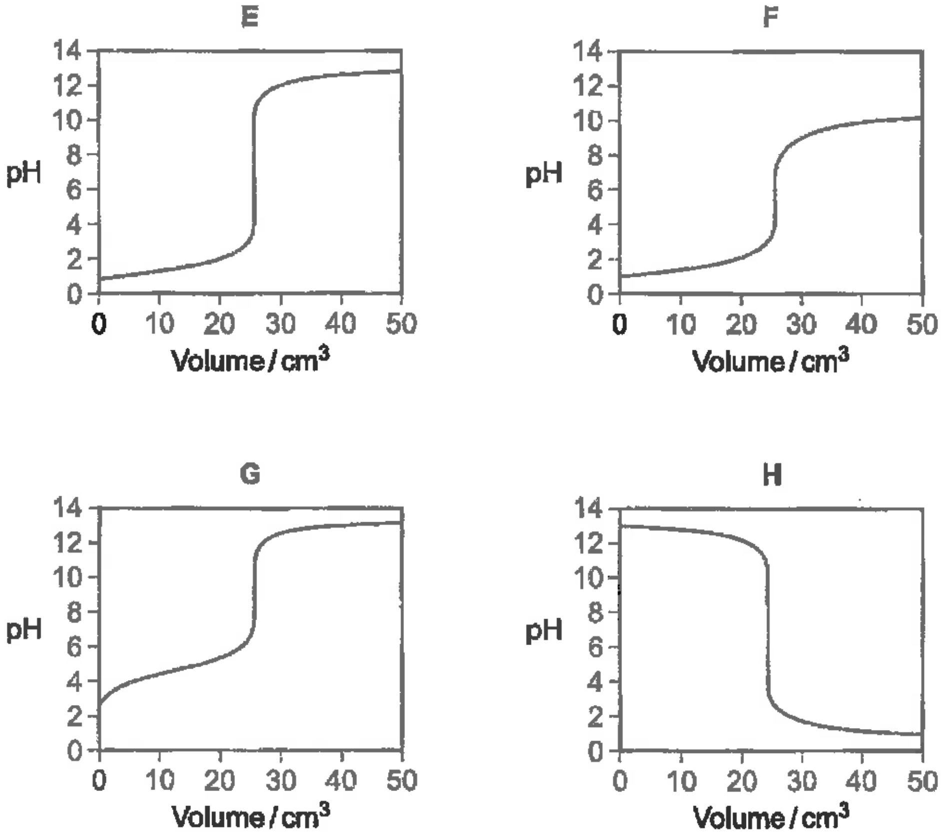
9

Turn over for the next question

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

G

[1 mark]

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

F

[1 mark]

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

H

[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]

Yellow to Red.

it says colour change so must have both colours for the 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]

Yellow

6

Turn over ▶

0 7

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 / °C	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]

Concentration of H_2O very high in comparison with $[H^+]$ and $[OH^-]$, therefore $[H_2O]$ is effectively constant.

without the $[H_2O]$ this is a Kc equation. Kw is just modified from this

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

[2 marks]

forward reaction is endothermic. therefore when temp is increased equilibrium position will move to the right hand side to oppose the change.

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]

$Kw = [H^+][OH^-]$ for pure water $[H^+] = [OH^-]$

$\therefore\ Kw = [H^+]^2 \quad 5.48\times10^{-14} = [H^+]^2$

$\sqrt{5.48\times10^{-14}} = [H^+] = 2.34\times10^{-7}$

$-\log_{10}(2.34\times10^{-7}) = pH \quad pH = 6.63$

pure water questions are where you use the $kw=[H^+]^2$ assumption.

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]

$Kw = [H^+][OH^-] \quad Kw = 5.48\times10^{-14}$

$\frac{5.48\times10^{-14}}{0.12} = [H^+] = 4.56\times10^{-13}$

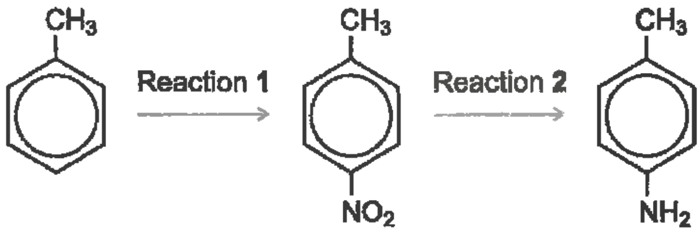
$-\log(4.56\times10^{-13}) = pH \quad pH = 12.34$

You need to know that NaOH is a strong base - hence using Kw

10

Turn over for the next question

5 Consider the following reaction sequence starting from methylbenzene.



J

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

[1 mark]

Electrophilic Substitution

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

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

[1 mark]

Sn/HCl or H_2/Ni

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

[1 mark]

CH_3–⟨O⟩–NO_2 + 6[H] → CH_3–⟨O⟩–NH_2 + $2H_2O$

Don't forget the water. you should realise that without it, it does not balance

$CH_3C_6H_4NO_2 + 6[H] \rightarrow CH_3C_6H_4NH_2 + 2H_2O$

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

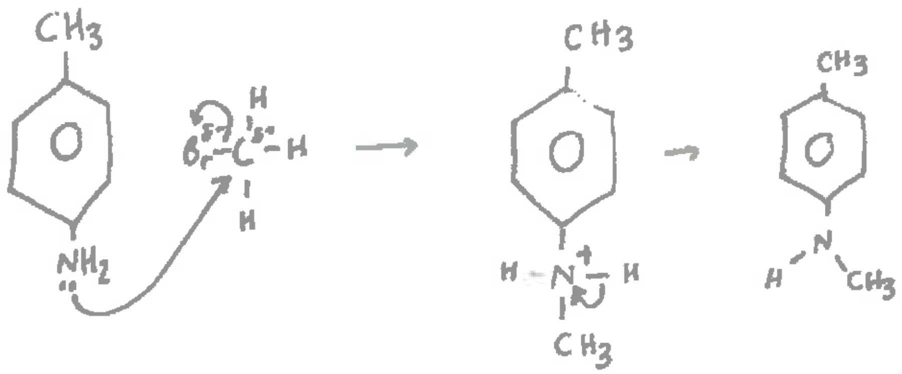
[1 mark]

making dyes, making cationic surfactants, making hair conditioners etc.

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]

The lone pair on the Nitrogen in j is pulled into the delocalised ring and therefore is less available, and hence a weaker base.

This question is all about availability of the lone pair. A base being a H^+ acceptor!

11

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

$(CH_3)_2CHOH + (CH_3CO)_2O \rightarrow CH_3COOCH(CH_3)_2 + CH_3COOH$

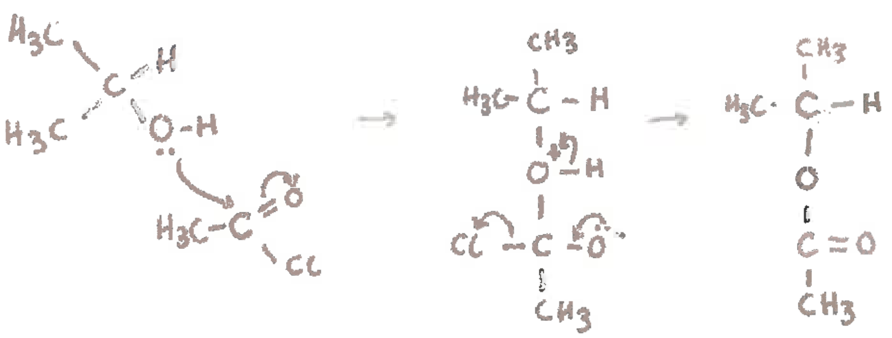
IUPAC name of the ester methylethylethanoate

tricky naming: don't forget the methyl branch!

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.

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array}$$

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

Saponification
You need to know this

$$\begin{array}{l} CH_2OOCC_{17}H_{31} \\ | \\ CHOOCC_{17}H_{33} \\ | \\ CH_2OOCC_{17}H_{29} \end{array} + 3NaOH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + \begin{array}{l} C_{17}H_{31}COONa \\ C_{17}H_{33}COONa \\ C_{17}H_{29}COONa \end{array}$$

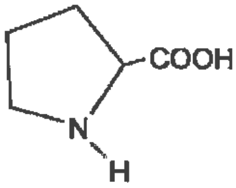
6 (b) (ii) Give the formula of the biodiesel molecule with the highest M_r that can be produced by reaction of this ester with methanol.
[1 mark]

$C_{17}H_{33}COOCH_3$

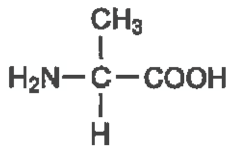
9

Turn over for the next question

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



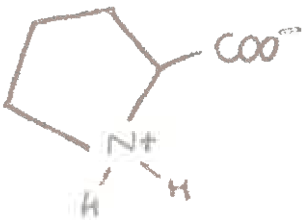
proline



alanine

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

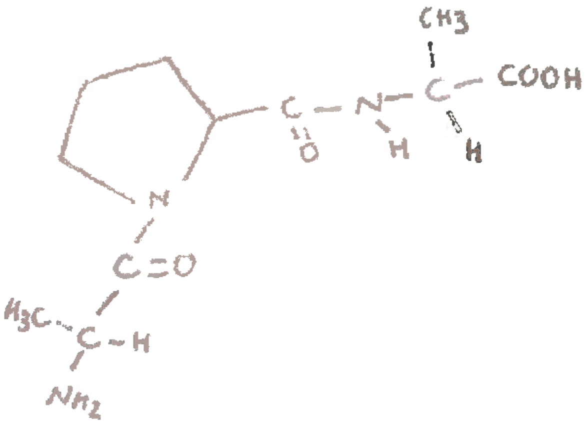
[1 mark]



Zwitterion is when there is both a +ve and negative charge. dipolar ion!

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

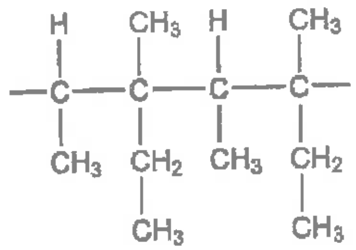
[2 marks]



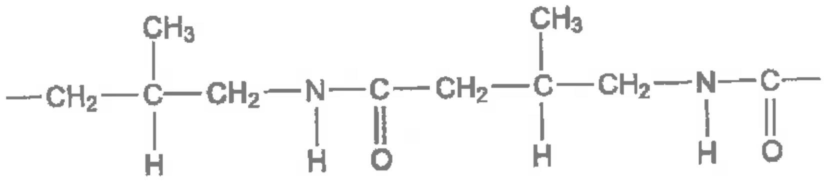
Do not write outside the box

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

L



M



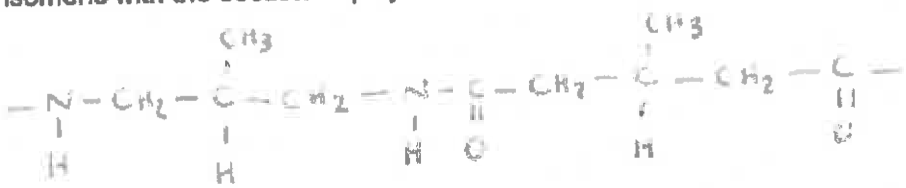
7 (b) (i) Give the IUPAC name of a monomer that forms polymer **L**. **[1 mark]**

3-methylpent-2-ene

7 (b) (ii) Give the IUPAC name of the monomer that forms polymer **M**. **[1 mark]**

4-amino-3-methylbutanoic acid

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]**

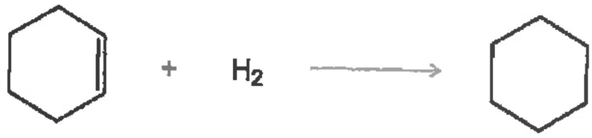
Non Polar (C-C bonds are strong).

7

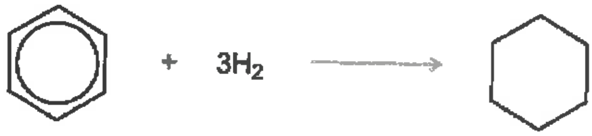
Turn over ▶

Do not write outside the box

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



$\Delta H^\circ = -120\ kJ\ mol^{-1}$



$\Delta H^\circ = -208\ kJ\ mol^{-1}$

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]

$-120 \times 3 = -360\ kJmol^{-1}$

$-360-(-208) = -152\ kJmol^{-1}$

the less negative the value the more stable it is as we would release less energy than expected if forming it

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

[1 mark]

Benzene has delocalised electron system.

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]

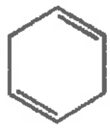
short → long

x, y then w

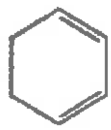
double shortest/strongest
single longest/weakest
benzene bonds in between double + single

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]

-240 kJ mol^{-1} $\quad -120 \times 2$.

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

[1 mark]

Less than -240 so between (-239 → -121)

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]

There is extra stability with 1,3 because you get some delocalisation as they are close enough together.

Similar to kekulé structure

would give resonance stability

would not

8

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]

$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ $0.186 = [CH_3COOH]$

$0.105 = [CH_3COO^-]$

$\frac{Ka \times [CH_3COOH]}{[CH_3COO^-]} = [H^+]$ $\frac{1.74 \times 10^{-5} \times 0.186}{0.105} = [H^+]$

$[H^+] = 3.08 \times 10^{-5}$ $-\log(3.08 \times 10^{-5}) = 4.51$

Remember you assume zero dissociation for a weak acid but total dissociation for a salt.

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]

$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ Because volume $1000cm^3$ then ∴ all conc. = moles!

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

CH_3COOH 0.251 + 0.015 = 0.266

CH_3COO^- 0.140 − 0.015 = 0.125

$\frac{1.74\times10^{-5} \times 0.266}{0.125} = [H^+] = 3.70\times10^{-5}$

$-\log(3.70\times10^{-5}) = pH$ pH = 4.43

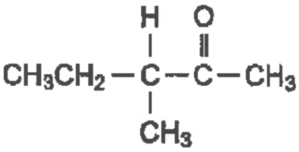
Adding H+ will increase the conc. of ethanoic acid (undissociated) but decrease conjugate $[CH_3COO^-]$

8

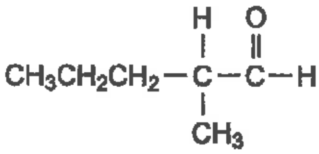
Turn over for the next question

Do not write outside the box

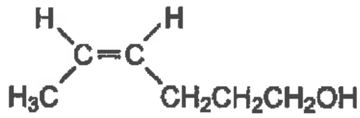
10 The following five isomers, **P**, **Q**, **R**, **S** and **T**, were investigated using test-tube reactions and also using n.m.r. spectroscopy.



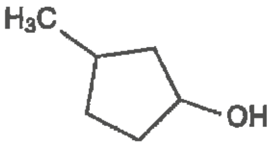
P



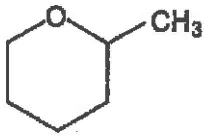
Q



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]

P is a ketone, S is an alcohol.
Acidified $K_2Cr_2O_7$ (potassium dichromate) with S it will change colour from orange to green, but no reaction with P.

with acidified dichromate
S would turn into an aldehyde, and eventually ~~an~~ a carboxylic acid
P already a ketone and cannot be oxidised further.

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]

Q is an aldehyde so add tollens reagent and it will form a silver mirror. fehlings could also be used to form a brick red ppt.

Either is fine

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]

P would give 5 peaks.

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]

$C_4H_{12}Si$. It gives one single peak upfield of others and it inert.

TMS - tetramethylsilane

CH_3
$CH_3-Si-CH_3$
CH_3

Question 10 continues on the next page

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

Figure 2

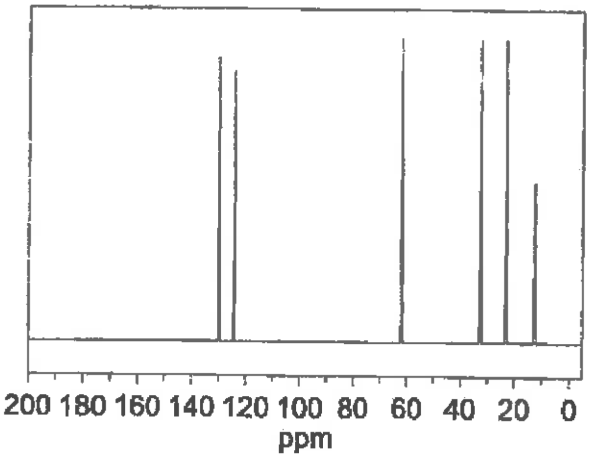
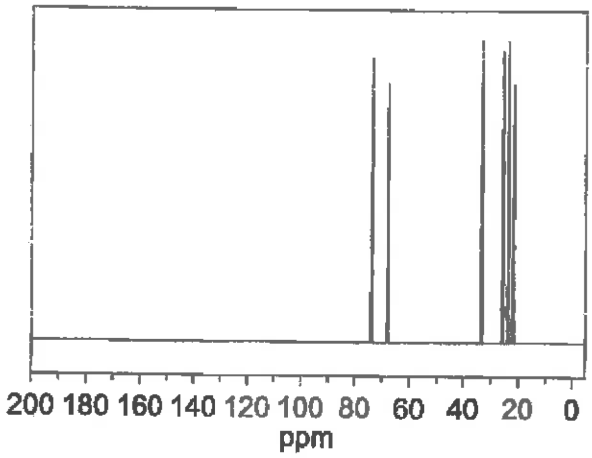
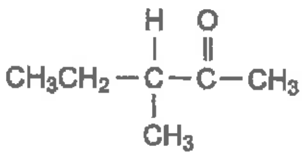


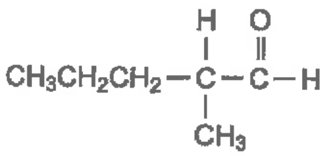
Figure 3



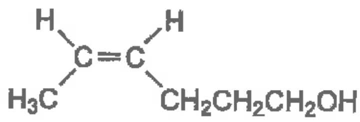
The structures of the five isomers are repeated to help you answer this question.



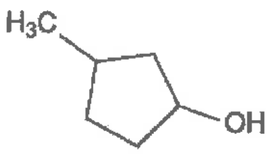
P



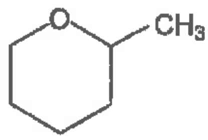
Q



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]

figure 2 is R as it has 2 peaks between 90 - 150 ppm showing C = C (alkene).

figure 3 is T as it has two peaks between 50 - 90 ppm showing C — O bonds. S would only give one peak here.

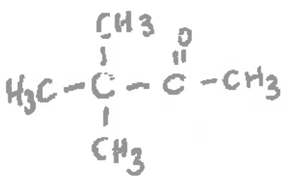
10 (f) **U** and **V** are other isomers of **P**, **Q**, **R**, **S** and **T**.
The [1]H n.m.r. spectrum of **U** consists of two singlets.
V is a cyclic alcohol that exists as optical isomers.

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

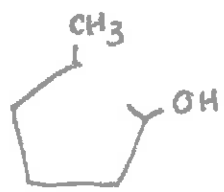
[2 marks]

U

$C_6H_{12}O_6$



V



tons of answers - just experiment with one that fits the brief!

17

2 3

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]

Reaction 1

Reagent: HBr

Structure: $CH_3CH_2-C(H)(Br)-CH_3$

Mechanism: Electrophilic addition

Reaction 2

Reagent: NH_3

Structure: $CH_3CH_2-C(H)(NH_2)-CH_3$

Mechanism: Nucleophilic Substitution

Reaction 3

Reagent: CH_3COCl

Structure: $CH_3CH_2-C(H)(N(H)C(=O)CH_3)-CH_3$

Mechanism: (Nucleophilic) addition-elimination

easy to forget you started with alkene in the 2,3 position so you would get the bromine in the 2 position!! this will affect all other answers.

9

END OF QUESTIONS