Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number | Candidate Number

Pearson Edexcel International Advanced Level

Time 1 hour 45 minutes

Paper reference **WCH14/01**

Chemistry

International Advanced Level
UNIT 4: Rates, Equilibria and Further Organic Chemistry

You must have:
Scientific calculator, Data Booklet, ruler

Total Marks

Instructions

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

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets – *use this as a guide as to how much time to spend on each question.*
- In the question marked with an **asterisk (*)**, marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

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B:1/1/1/1/1/

P 7 1 8 6 3 A 0 1 3 2

Pearson

SECTION A

Answer ALL the questions in this section.

You should aim to spend no more than 20 minutes on this section.

For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Which **continuous** monitoring method could be used to obtain rate data for the reaction shown?

$$C_4H_9Cl(l) + H_2O(l) \rightarrow C_4H_9OH(aq) + H^+(aq) + Cl^-(aq)$$

☒ **A** electrical conductivity

☒ **B** colorimetry

☒ **C** mass change

☒ **D** titration with alkali

(Total for Question 1 = 1 mark)

2 Nitrogen monoxide is reduced by hydrogen.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

The rate equation for the reaction is

$$\text{rate} = k\,[NO]^2\,[H_2]$$

(a) The concentrations of **both** reactants are tripled.

By what factor does the rate of reaction increase?

(1)

☒ **A** 3

☒ **B** 9

☒ **C** 18

☒ **D** 27

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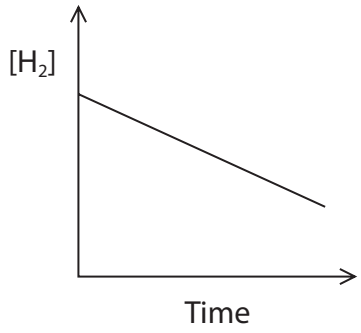
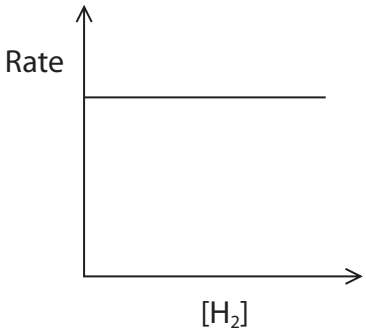
(b) Which graph is correct for this reaction?

(1)

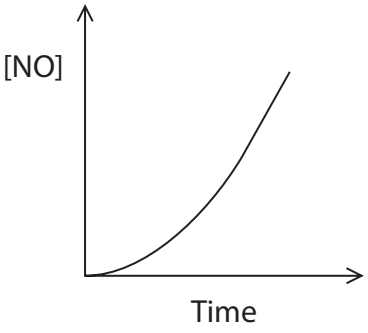
☒ **A**



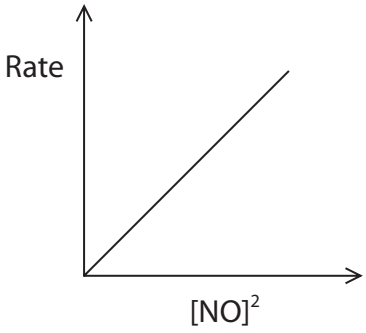
☒ **B**



☒ **C**



☒ **D**



(c) The reaction mechanism occurs in three steps.

Step **1** $NO + NO \rightleftharpoons N_2O_2$

Step **2** $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

Step **3** $N_2O + H_2 \rightarrow N_2 + H_2O$

Which is the rate-determining step in the mechanism?

(1)

☒ **A** Step **1**

☒ **B** Step **2**

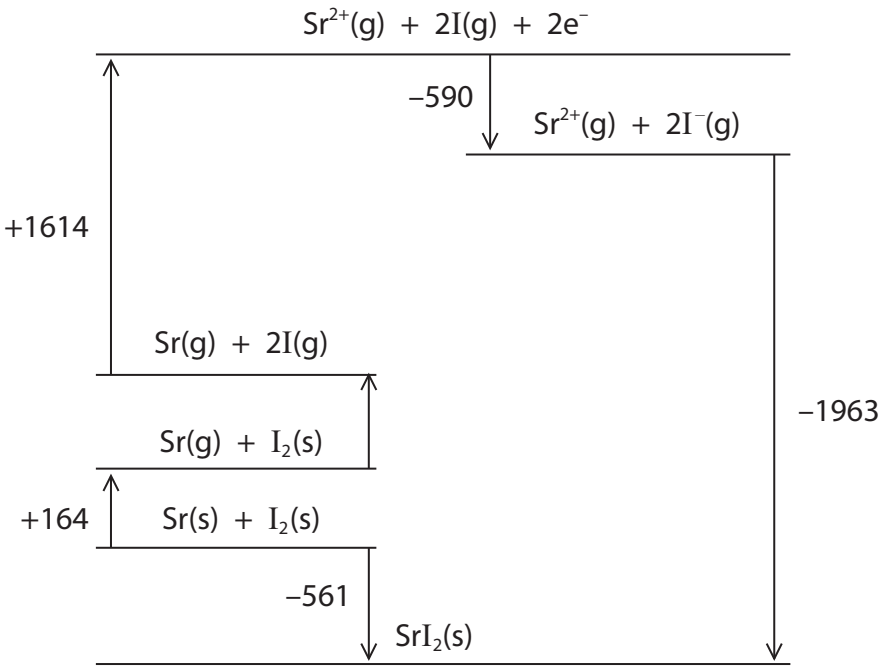
☒ **C** Step **3**

☒ **D** cannot be deduced from the information provided

(Total for Question 2 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

3 The Born–Haber cycle for strontium iodide, SrI_2, is shown.
All values are in kJ mol^{-1}. The cycle is **not** to scale.



(a) Which of the following statements is **not** true?

(1)

- ☒ **A** the lattice energy of strontium iodide is exothermic
- ☒ **B** the first electron affinity of iodine is −295 kJ mol^{-1}
- ☒ **C** the second ionisation energy of strontium is +1614 kJ mol^{-1}
- ☒ **D** the standard enthalpy change of atomisation of strontium is +164 kJ mol^{-1}

(b) Using the Born–Haber cycle, it can be calculated that the standard enthalpy change of atomisation of iodine, in kJ mol^{-1}, is

(1)

- ☒ **A** +542
- ☒ **B** +271
- ☒ **C** +214
- ☒ **D** +107

(c) Theoretical lattice energies are calculated assuming only ionic bonding is present.

Which of these is most likely to be the **theoretical** lattice energy of strontium iodide?

(1)

☒ **A** $-561\ kJ\ mol^{-1}$

☒ **B** $-1937\ kJ\ mol^{-1}$

☒ **C** $-1963\ kJ\ mol^{-1}$

☒ **D** $-1989\ kJ\ mol^{-1}$

(Total for Question 3 = 3 marks)

4 Which of these statements is **true**?

☒ **A** the enthalpy change of hydration of an ion is always negative

☒ **B** the enthalpy change of solution of an ionic compound is always negative

☒ **C** an endothermic enthalpy change of solution indicates that an ionic compound will be insoluble

☒ **D** the more exothermic the lattice energy of an ionic compound, the more soluble it is likely to be

(Total for Question 4 = 1 mark)

5 Which sequence shows the elements in order of **increasing** standard entropy?

☒ **A** $He(g) < O_2(g) < Hg(l) < Os(s)$

☒ **B** $O_2(g) < He(g) < Hg(l) < Os(s)$

☒ **C** $Os(s) < Hg(l) < He(g) < O_2(g)$

☒ **D** $Os(s) < Hg(l) < O_2(g) < He(g)$

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

6 This question is about the equilibrium system used in the industrial production of nitric acid.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H = -905\,kJ\,mol^{-1}$$

The process is carried out at a temperature of 800 °C, a total pressure of 10 atm and in the presence of a platinum-rhodium catalyst.

(a) Which conditions of temperature and pressure would be expected to give the greatest equilibrium yield of NO?

(1)

- ☒ **A** high temperature and high pressure
- ☒ **B** high temperature and low pressure
- ☒ **C** low temperature and high pressure
- ☒ **D** low temperature and low pressure

(b) Which of these statements **best** explains why only a small amount of energy is required to maintain this process?

(1)

- ☒ **A** the catalyst increases the equilibrium yield of NO
- ☒ **B** the catalyst decreases the activation energy
- ☒ **C** the reaction is thermodynamically feasible
- ☒ **D** the reaction is highly exothermic

(c) What are the units of the equilibrium constant, K_p, for this reaction?

(1)

- ☒ **A** atm^{-1}
- ☒ **B** atm
- ☒ **C** $dm^3\,mol^{-1}$
- ☒ **D** $mol\,dm^{-3}$

(Total for Question 6 = 3 marks)

Use this space for any rough working. Anything you write in this space will gain no credit.

7 In which equation is H_2O acting **only** as a Brønsted–Lowry acid?

- ☒ **A** $CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$
- ☒ **B** $NH_4^+ + H_2O \rightarrow H_3O^+ + NH_3$
- ☒ **C** $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
- ☒ **D** $2H_2O \rightarrow H_3O^+ + OH^-$

(Total for Question 7 = 1 mark)

8 What is the pH of a 0.050 mol dm^{-3} solution of barium hydroxide, $Ba(OH)_2$?

- ☒ **A** 13.3
- ☒ **B** 13.0
- ☒ **C** 12.7
- ☒ **D** 12.4

(Total for Question 8 = 1 mark)

9 What is the pH of a solution containing 0.100 mol dm^{-3} CH_3COOH and 0.200 mol dm^{-3} CH_3COONa?

[pK_a CH_3COOH = 4.76]

- ☒ **A** 5.06
- ☒ **B** 4.76
- ☒ **C** 4.46
- ☒ **D** 2.88

(Total for Question 9 = 1 mark)

10 Which of these indicators is **most** suitable for the titration of ammonia solution with hydrochloric acid?

- ☒ **A** methyl violet (pK_{in} = 0.8)
- ☒ **B** bromocresol green (pK_{in} = 4.7)
- ☒ **C** thymol blue (pK_{in} = 8.9)
- ☒ **D** alizarin yellow (pK_{in} = 12.5)

(Total for Question 10 = 1 mark)

11 Which compound is **both** completely miscible in water and has a higher boiling temperature than water?

- ☒ **A** CH_3COOH
- ☒ **B** CH_3COCH_3
- ☒ **C** $CH_3CH_2CH_2CHO$
- ☒ **D** $CH_3CH_2COOCH_2CH_3$

(Total for Question 11 = 1 mark)

12 Which compound forms a precipitate with Fehling's or Benedict's solutions **and** with iodine in the presence of alkali?

- ☒ **A** methanal
- ☒ **B** ethanal
- ☒ **C** propanone
- ☒ **D** butanone

(Total for Question 12 = 1 mark)

13 Which reaction does **not** produce a tertiary alcohol as one of the products?

- ☒ **A** $(CH_3)_2C{=}CH_2 + H_2O$
- ☒ **B** $(CH_3)_3CBr + H_2O$
- ☒ **C** $(CH_3)_3CCOC(CH_3)_3 + LiAlH_4$
- ☒ **D** $(CH_3)_3CCOOC(CH_3)_3 + NaOH$

(Total for Question 13 = 1 mark)

14 Which change **decreases** the retention time in gas chromatography?

- ☒ **A** decreasing the column temperature
- ☒ **B** increasing the carrier gas flow rate
- ☒ **C** decreasing the amount of sample
- ☒ **D** increasing the column length

(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

15 This question is about lactic acid, $CH_3CH(OH)COOH$.

(a) Give the IUPAC name of lactic acid.

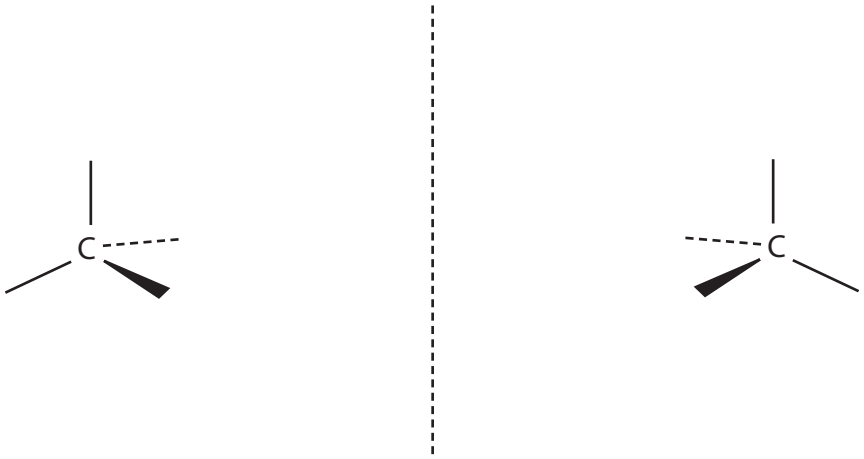
(1)

.....

(b) Lactic acid is a chiral molecule, existing as a pair of non-superimposable mirror images called enantiomers.

Complete the 3D diagrams of the enantiomers of lactic acid.

(2)



(c) Racemic lactic acid is synthesised in a two-step process.

In Step **1**, ethanal, CH_3CHO, is reacted with hydrogen cyanide, HCN, in the presence of KCN to form compound **X**.

In Step **2**, compound **X** is hydrolysed using dilute acid.

$$CH_3CHO + HCN \xrightarrow{\text{Step 1}} \text{compound } \mathbf{X} \xrightarrow{\text{Step 2}} CH_3CH(OH)COOH$$

(i) State what is meant by **racemic** lactic acid.

(1)

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.....

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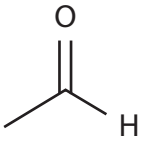
(ii) Complete the mechanism for the formation of **X** in Step **1**.
Include curly arrows, and any relevant lone pairs and dipoles.

(4)



CN^-

(iii) Write the **ionic** equation for the hydrolysis of **X** in Step **2**.
State symbols are **not** required.

(2)

(iv) Explain, with reference to your mechanism in (c)(ii), why the lactic acid formed in this process is racemic.

(2)

(d) Lactic acid is a weak acid.

(i) Calculate the mass, in g, of lactic acid, HA, required to make 1.00 dm^3 of an aqueous solution with a pH of 3.00.
Assume:

- $[HA]_{initial} = [HA]_{equilibrium}$
- $[H^+] = [A^-]$

[Lactic acid data: $pK_a = 3.86$ $M_r = 90.0$]

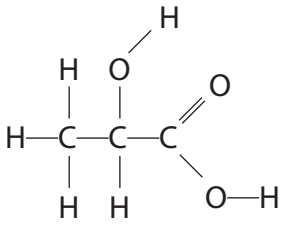
(4)

(ii) In practice, the initial concentration of lactic acid does not equal its equilibrium concentration.

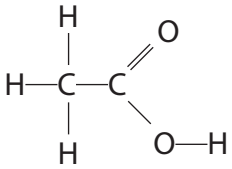
Explain how this affects the mass of acid needed to make a solution with a pH of 3.00 . No calculation is required.

(2)

(iii) Lactic acid is a stronger acid than ethanoic acid.



lactic acid



ethanoic acid

Give a possible reason why lactic acid is the stronger acid.

(1)

(Total for Question 15 = 19 marks)

16 Azomethane, $CH_3N_2CH_3$, decomposes to form nitrogen and ethane.

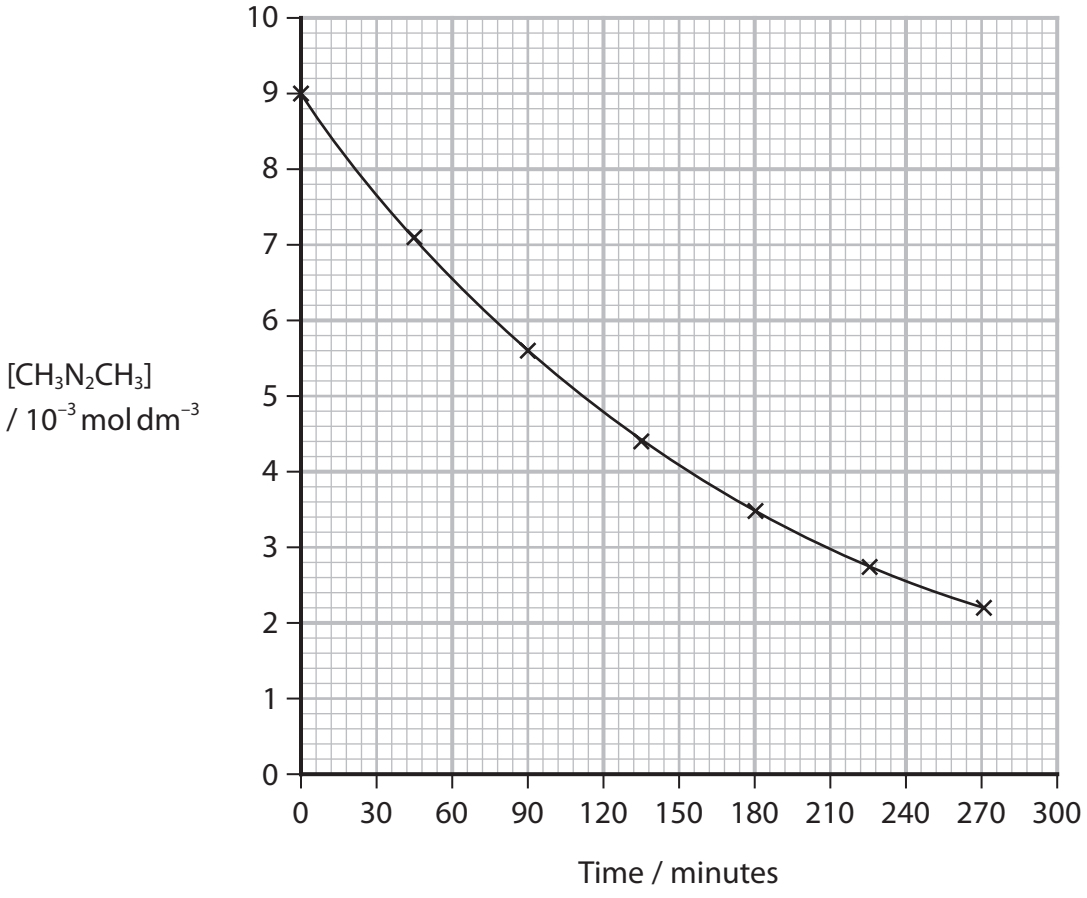
$$CH_3N_2CH_3(g) \rightarrow N_2(g) + C_2H_6(g)$$

(a) Write the rate equation for this first order reaction.

(1)

(b) The concentration of azomethane, $[CH_3N_2CH_3]$, was measured at various times during its decomposition at 573 K.

A graph of the data obtained is shown.



(i) Determine values for the half-life, $t_{1/2}$, of the decomposition of azomethane from the graph, stating whether or not these data confirm that the reaction is first order.
You must show your working on the graph.

(2)

.....

.....

(ii) Calculate the rate constant, k, **in s^{-1}**, for the decomposition of azomethane at 573 K, using your answer to (b)(i) and the expression shown.

$$t_{1/2} = \frac{\ln 2}{k}$$

(2)

(c) The rate constant for the decomposition of azomethane is $1.1 \times 10^{-6}\,s^{-1}$ at 523 K and $3.5 \times 10^{-3}\,s^{-1}$ at 623 K.

(i) Explain why the rate constant for this reaction is higher at 623 K than at 523 K.

(2)

.....

.....

.....

.....

(ii) The rate constant changes with temperature according to the expression shown.

$$\log_{10}\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Calculate the activation energy, E_a, for the decomposition of azomethane using this expression and the values for k at 523 K and 623 K.

Include units and give your answer to **two** significant figures.

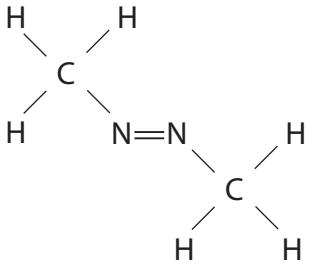
[$R = 8.31\,J\,mol^{-1}\,K^{-1}$]

(3)

(d) The activation energy for the decomposition of azomethane is high because the reaction involves covalent bond fission.

Identify on the structure of azomethane the covalent bond (or bonds) that break in this decomposition.

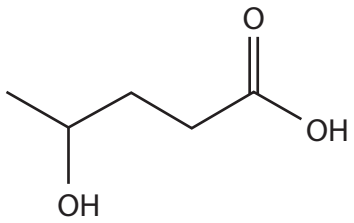
(1)



(Total for Question 16 = 11 marks)

17 This question is about reactions of carboxylic acids and their derivatives.

(a) Molecule **A** reacts in two ways in the presence of an acid catalyst.



molecule **A**

Reaction **1** is intramolecular, in which one molecule of **A** forms a cyclic ester **B**.

Reaction **2** is intermolecular, in which a condensation polymer **C** forms.

(i) Draw the structure of the cyclic ester **B**.

(1)

(ii) Draw the structure of the condensation polymer **C**, showing **two** repeat units.

(2)

(iii) Explain why the entropy change of the system, ΔS_{system}, is greater for Reaction **1** than for Reaction **2**.

(2)

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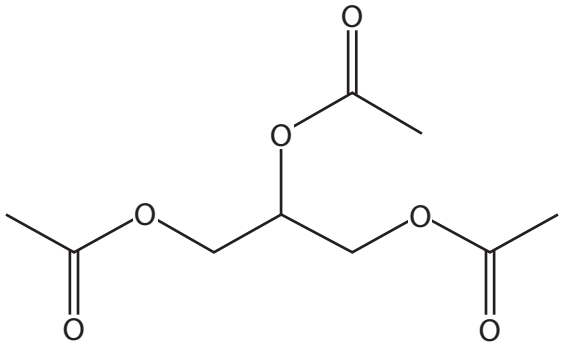
(b) The molecule shown is a triester, used as a food additive.



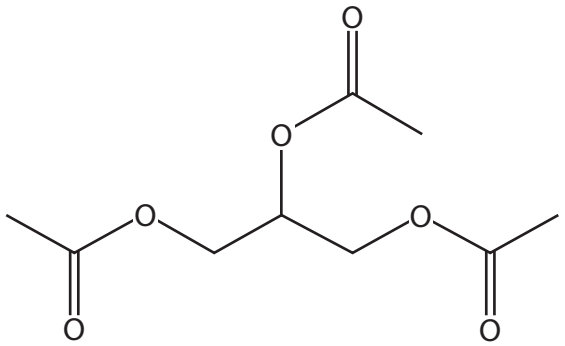
(i) Give the **molecular** formula of this triester.

(1)

.....

(ii) Complete the equation for the alkaline hydrolysis of this triester with **excess** aqueous sodium hydroxide, showing the structures of the products.

(3)



\+ ..... NaOH

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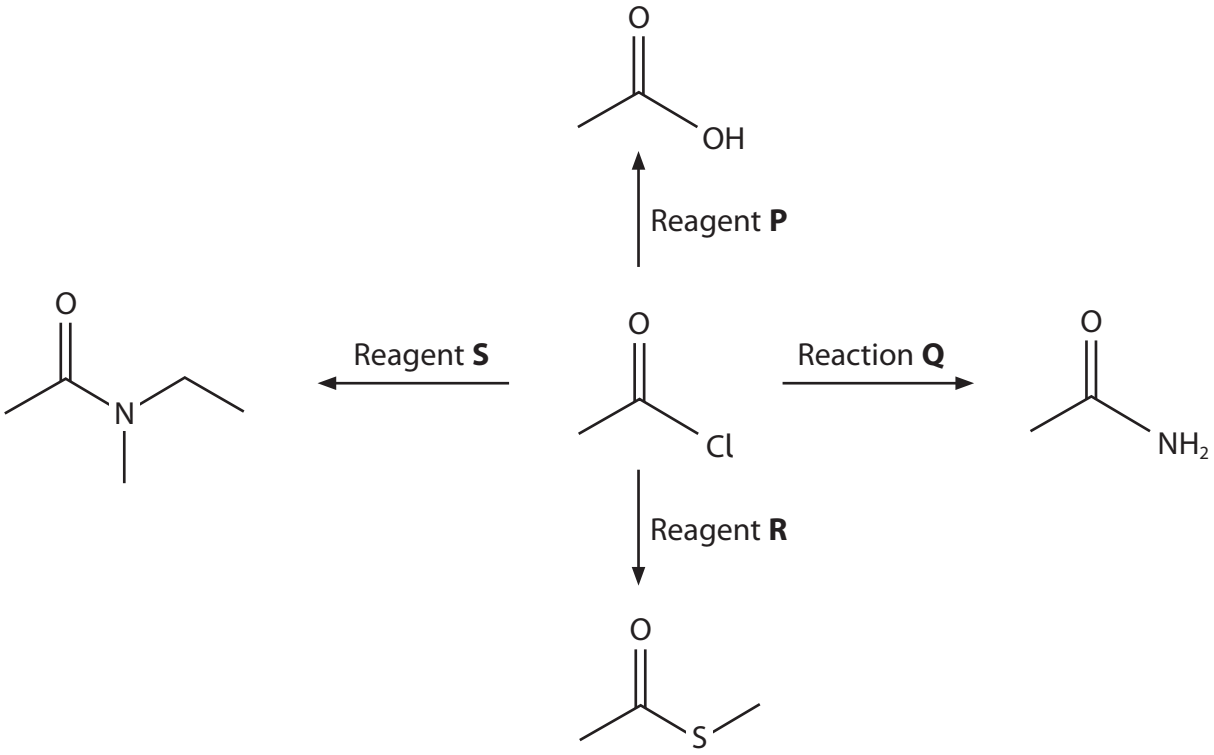
(c) Some reactions of ethanoyl chloride, CH_3COCl, are shown.



(i) Identify Reagent **P**, by name or formula.

(1)

.....

(ii) Write a balanced equation for Reaction **Q**.
State symbols are **not** required.

(2)

(iii) Suggest the structural formula of Reagent **R**.

(1)

.....

(iv) Draw the **skeletal** formula of Reagent **S**.

(1)

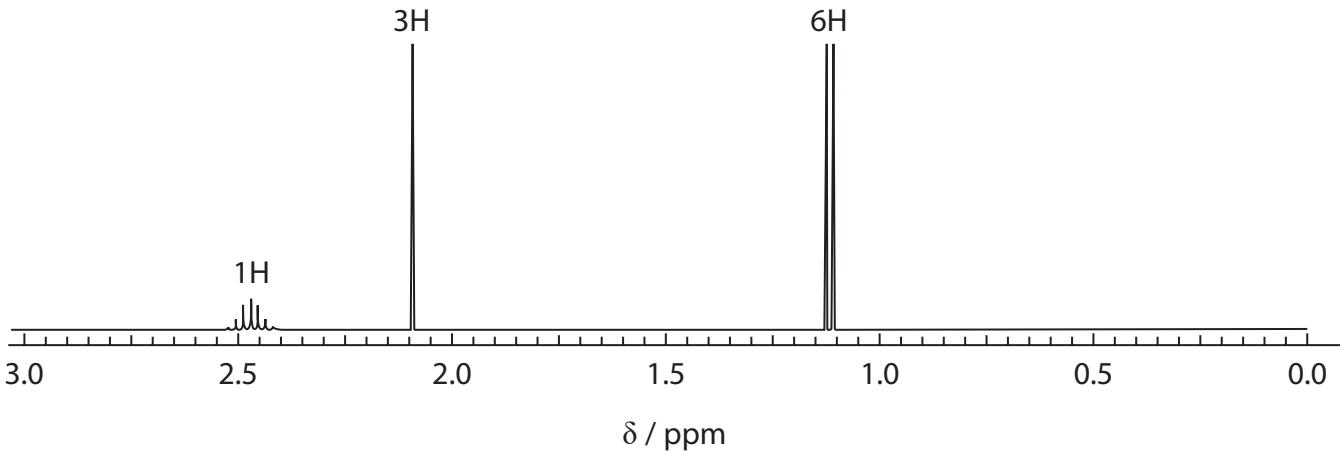
*(d) Sodium ethanoate, CH_3COONa, reacts with 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$, to form organic compound **Z** and sodium chloride, NaCl.

The molecular ion peak in the mass spectrum of **Z** is at $m/z = 130$.

The infrared spectrum of **Z** has peaks at 1820 cm^{-1} and 1754 cm^{-1}.

The carbon-13 NMR spectrum of **Z** has **five** peaks.

A simplified high resolution proton NMR spectrum of **Z** is shown.
The number of protons in each environment is indicated on the spectrum.



Deduce the structure of **Z**, showing how your answer is consistent with **all** the information provided.

(6)

(Total for Question 17 = 20 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

18 This question is about the homogeneous system

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

(a) Write the expression for the equilibrium constant, K_c, of this system.

(1)

(b) Chemist **A** carried out an experiment to determine K_c.

0.00500 mol of H_2 and 0.0100 mol of I_2 were heated in a sealed container of volume 1.00 dm^3.
At equilibrium, the mixture was found to contain 0.00968 mol of HI.

Calculate K_c, using these data and your expression from (a).
Include units, if any.
Give your answer to an appropriate number of significant figures.

(4)

(c) Chemist **B** determined the value of K_c at five different temperatures.

Temperature, T / K	$1 / T$ (K^{-1})	K_c	ln K_c
523		122	4.80
577	0.00173	99.2	
620	0.00161	86.5	4.46
669	0.00149	75.6	4.33
721	0.00139	66.8	4.20

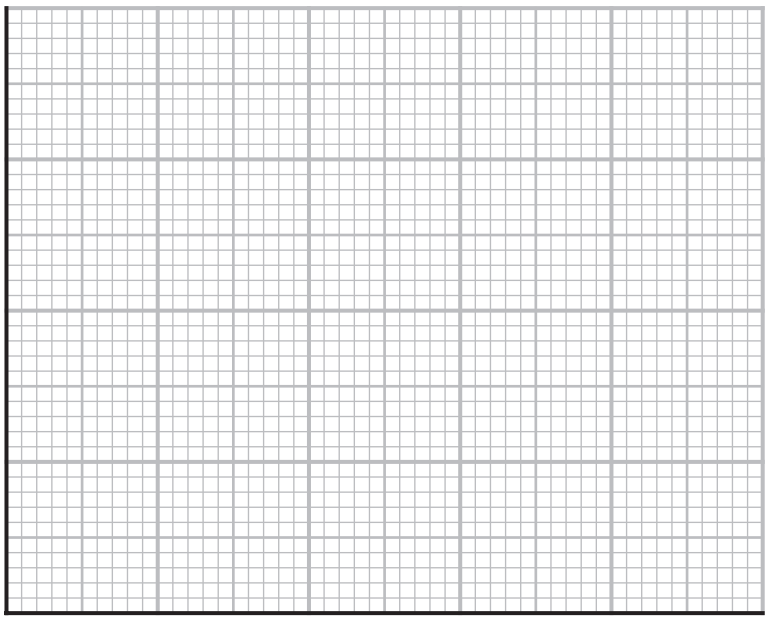
(i) Complete the table of data.

(2)

(ii) Plot a graph of ln K_c against $1 / T$.
Include a line of best fit.

(3)

ln K_c



$1 / T$ (K^{-1})

(iii) Determine the gradient of your graph.
You **must** show your working on the graph.

(1)

(iv) The gradient of the graph from (c)(iii) is related to the enthalpy change of the reaction, ΔH.

$$\text{gradient} = -\frac{\Delta H}{R}$$

Calculate ΔH, in $J\,mol^{-1}$, using your value for the gradient.

(2)

(v) The free energy change for the reaction, ΔG, is related to entropy and can be calculated from K_c.

$$\Delta G = -RT \ln K_c$$

Calculate ΔG at **620 K**, using this equation and data from the table.
Include units.

(2)

(vi) The equation relating ΔG, ΔH and ΔS_{system} is shown.

$$\Delta G = \Delta H - T\Delta S_{system}$$

Calculate ΔS_{system} at 620 K, using your answers to (c)(iv) and (c)(v).

(2)

(d) Explain, in terms of the total entropy change, ΔS_{total}, why this reaction is feasible at any temperature.
Assume that both ΔH and ΔS_{system} are independent of temperature.

(3)

(Total for Question 18 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS