Centre No.						Paper Reference							Surname	Initial(s)
Candidate No.						6	C	H	0	4	/	1	Signature	

Paper Reference(s)

6CH04/1

Edexcel GCE

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rate, Equilibria and Further Organic Chemistry (including synoptic assessment)

Sample Assessment Material

Time: 1 hour 40 minutes

Materials required for examination
Data Booklet

Items included with question papers
Nil

Examiner's use only

Team Leader's use only

Question Number	Leave Blank
1	
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20	
Total	

Instructions to Candidates

In the boxes above, write your centre number, candidate number, your surname, initial(s) and signature. Check that you have the correct question paper. Answer ALL the questions. Write your answers in the spaces provided in this question paper.
Some questions must be answered with a cross in a box (☒). If you change your mind, put a line through the box (☒) and then mark your new answer with a cross (☒).
Do not use pencil. Use black or blue ink.

Information for Candidates

The marks for individual questions and the parts of questions are shown in round brackets: e.g. **(2)**.
There are 20 questions in this question paper. The total mark for this paper is 90.
There are 32 pages in this question paper. Any blank pages are indicated.
Candidates may use a calculator.

Advice to Candidates

Quality of written communication will be taken into account in the marking of your responses to Questions 16(d), 17(b), 18(c)(ii), 19, 20(b)(i) and 20(b)(iii). These questions are indicated with an asterisk. Quality of written communication includes clarity of expression, the structure and presentation of ideas and grammar, punctuation and spelling.

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SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 30 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. This question involves the following techniques which can be used to follow chemical reactions in order to investigate their kinetics.

A collecting and measuring the volume of a gas

B colorimetry

C measuring the electrical conductivity

D titration with standard acid solution

Select, from A to D, the technique **most** appropriate to investigate:

(a) the hydrolysis of 1-bromobutane using hydroxide ions

$$C_4H_9Br(l) + OH^-(aq) \rightarrow C_4H_9OH(l) + Br^-(aq)$$

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(b) the decomposition of the benzenediazonium ion

$$C_6H_5N_2^+(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + H^+(aq)$$

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

Leave blank

(c) the reaction of acidified potassium manganate(VII) with propan-2-ol to give propanone and manganese(II) sulfate.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(d) the catalytic decomposition of hydrogen peroxide.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

Q1

(Total 4 mark)

Leave blank

2. 1,2-dibromoethane reacts with potassium iodide dissolved in methanol according to the equation:

$$C_2H_4Br_2 + 2KI \rightarrow C_2H_4 + 2KBr + I_2$$

The rate equation for this reaction is

☒ **A** rate = $k[KI]^2[C_2H_4Br_2]$

☒ **B** rate = $k[KI]^2$

☒ **C** rate = $k[C_2H_4Br_2]$

☒ **D** not possible to deduce from this information

Q2

(Total 1 mark)

3. For the reaction between sodium bromate(V) and sodium bromide in acidic solution, the rate equation is:

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

When the concentrations of all three reactants are doubled, the rate will increase by a factor of

☒ **A** 4

☒ **B** 6

☒ **C** 8

☒ **D** 16

Q3

(Total 1 mark)

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

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4. This question refers to the following reaction at 298 K:

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad \Delta H = +57.2 \text{ kJ mol}^{-1}$$

	S /J mol^{-1}K^{-1}
$N_2O_4(g)$	304.2
$NO_2(g)$	240.0

(a) Calculate ΔS_{system}, in J mol^{-1} K^{-1}, for this reaction.

☒ **A** –175.8

☒ **B** +175.8

☒ **C** –64.2

☒ **D** +64.2

(1)

(b) Calculate $\Delta S_{surroundings}$, in J mol^{-1} K^{-1}, for this reaction at 298 K.

☒ **A** –192

☒ **B** +192

☒ **C** –0.192

☒ **D** +0.192

(1) **Q4**

(Total 2 marks)

5. For the equilibrium,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Which is the correct expression for K_p?

☒ **A** $\dfrac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$

☒ **B** $\dfrac{P_{N_2(g)}P_{H_2(g)}}{P_{NH_3(g)}}$

☒ **C** $\dfrac{P^2_{NH_3(g)}}{P_{N_2(g)}P^3_{H_2(g)}}$

☒ **D** $\dfrac{P_{N_2(g)}P^3_{H_2(g)}}{P^2_{NH_3(g)}}$

Q5

(Total 1 mark)

Leave blank

6. The expression for K_c for the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is

$$K_c = \frac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$$

What are the units of K_c in this equilibrium expression?

- ☒ **A** $mol\ dm^{-3}$
- ☒ **B** $mol^2\ dm^{-6}$
- ☒ **C** $dm^3\ mol^{-1}$
- ☒ **D** atm^{-1}

Q6

(Total 1 mark)

7. For the equilibrium

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57.2\ kJ\ mol^{-1}$$

which one of the following changes would result in a different value of the equilibrium constant?

- ☒ **A** an increase in temperature
- ☒ **B** a decrease in pressure
- ☒ **C** an increase in pressure
- ☒ **D** an increase in the concentration of $NO_2(g)$

Q7

(Total 1 mark)

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

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8. Solutions of concentration 0.1 mol dm^{-3} of iron(II) ions and silver(I) ions were mixed at room temperature and allowed to reach equilibrium.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Which one of the following statements is true?

☒ **A** as the equilibrium position was approached, the forward reaction became slower until it stopped.

☒ **B** at the equilibrium position, no more Ag(s) reacted with $Fe^{3+}(aq)$.

☒ **C** at the equilibrium position, the rate of the forward reaction equalled the rate of the backward reaction.

☒ **D** no $Fe^{3+}(aq)$ reacted with Ag(s) until the equilibrium position was reached.

Q8

(Total 1 mark)

Leave blank

9. This question concerns four solutions, A to D. They were prepared by mixing equal volumes of 0.2 mol dm^{-3} solutions of two different substances. The substances were

A HCl(aq) and NaOH(aq)

B HCl(aq) and NaCl(aq)

C NH_3(aq) and NH_4Cl(aq)

D CH_3COOH(aq) and CH_3CO_2Na(aq)

Select, from A to D, the mixture which would:

(a) have the lowest concentration of hydrogen ions

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(b) act as a buffer of pH about 5

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(c) have a chloride ion concentration of 0.2 mol dm^{-3}.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1) **Q9**

(Total 3 marks)

Leave blank

10. This question concerns the titration of a solution of sodium hydroxide with a solution of hydrochloric acid. As the titration proceeds the pH of the mixture changes.

(a) What was the pH when 24.95 cm^3 of 1.00 mol dm^{-3} NaOH(aq) had been added to 25 cm^3 of 1.00 mol dm^{-3} HCl(aq)?

☒ **A** 3

☒ **B** 6

☒ **C** 8

☒ **D** 11

(1)

(b) What was the pH when 25.05 cm^3 of 1.00 mol dm^{-3} NaOH(aq) had been added to 25 cm^3 of 1.00 mol dm^{-3} HCl(aq)?

☒ **A** 3

☒ **B** 6

☒ **C** 8

☒ **D** 11

(1)

(c) Which one of the following indicators would be **most** suitable to use to determine the end point of this titration?

		pH range
☒ **A**	methyl violet	0–1.6
☒ **B**	universal indicator	3–11
☒ **C**	thymolphthalein	8.3–10.6
☒ **D**	alizarin yellow R	10.1–13.0

(1)

Q10

(Total 3 marks)

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

Leave blank

11. Which one of the following organic compounds does **not** exist?

☒ **A** an ester which is a structural isomer of a carboxylic acid $C_3H_6O_2$

☒ **B** a carboxylic acid which is a structural isomer of an ester $C_2H_4O_2$

☒ **C** an aldehyde which is a structural isomer of a ketone C_3H_6O

☒ **D** a ketone which is a structural isomer of an aldehyde C_2H_4O **Q11**

(Total 1 mark)

12. This question concerns a proposed two-stage synthetic route to prepare butanamide, $CH_3CH_2CH_2CONH_2$

$$\text{Carboxylic acid} \xrightarrow{} \text{Acyl chloride} \xrightarrow{NH_3} \text{butanamide}$$

(a) A suitable starting material for this preparation would have the formula

☒ **A** $CH_3CH_2CH_2COH$

☒ **B** $CH_3CH_2CH_2CH_2COOH$

☒ **C** $CH_3CH_2CH_2COOH$

☒ **D** $CH_3CH_2CH_2CH_2OOH$

(1)

(b) Each stage in the sequence produced a 50% yield of required product. What is the minimum number of moles of the carboxylic acid which should be used in order to produce one mole of butanamide?

☒ **A** 0.25

☒ **B** 2.00

☒ **C** 2.50

☒ **D** 4.00

(1)

(c) Which of the following reagents is needed to convert the carboxylic acid into the acyl chloride?

☒ **A** chlorine

☒ **B** phosphorus(V) chloride

☒ **C** hydrogen chloride

☒ **D** ethanoyl chloride

(1) **Q12**

(Total 3 marks)

Leave blank

13. This question concerns the following compounds containing four carbon atoms.

☒ **A** Butanoic acid, $CH_3CH_2CH_2COOH$

☒ **B** Butanone, $CH_3COCH_2CH_3$

☒ **C** Propyl methanoate, $HCOOCH_2CH_2CH_3$

☒ **D** Butanoyl chloride, $CH_3CH_2CH_2COCl$

Select, from A to D, the compound that

(a) can be made by the oxidation of a primary alcohol.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(b) would be expected to react most rapidly with ethanol.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1)

(c) would have 4 different chemical shifts in its nmr spectrum and a broad absorption between 2500–3300 cm^{-1} in its infrared spectrum.

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(1) **Q13**

(Total 3 marks)

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

Leave blank

14. This question concerns the nucleophilic addition reaction between a carbonyl compound and hydrogen cyanide, HCN.

(a) Which one of the following carbonyl compounds would produce a racemic mixture?

☒ **A** CH_3COCH_3

☒ **B** C_2H_5CHO

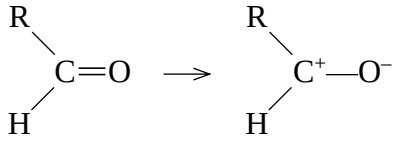
☒ **C** HCHO

☒ **D** $C_2H_5COC_2H_5$

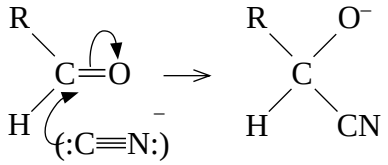
(1)

(b) Which of the following best represents the first step of the mechanism for this reaction with an aldehyde?

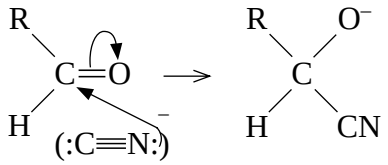
☒ **A**



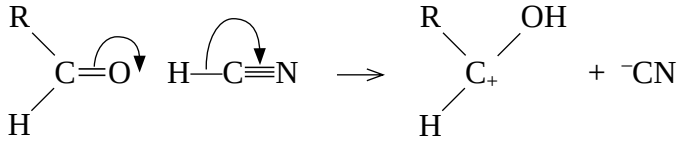
☒ **B**



☒ **C**



☒ **D**



(1) **Q14**

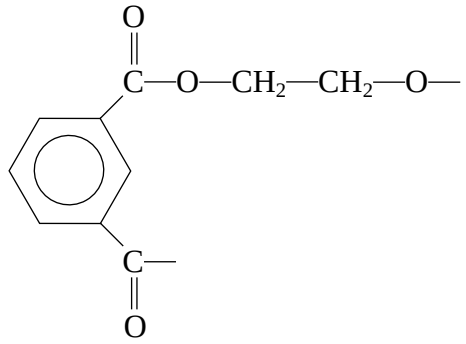
(Total 2 marks)

Leave blank

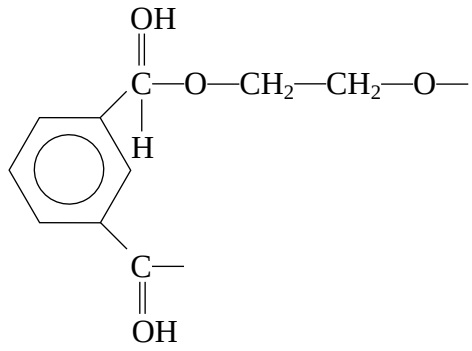
15. This question concerns the formation of a polymer.

(a) Which one of the following is a possible formula of the repeat unit of a polymer formed from ethane-1,2-diol and benzene-1,4-dicarboxylic acid.

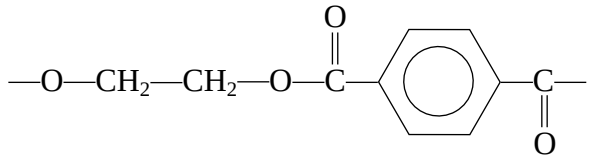
☒ **A**



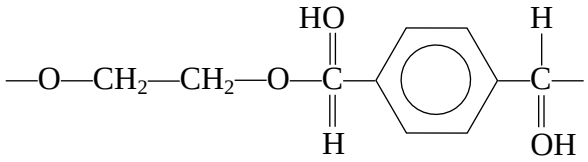
☒ **B**



☒ **C**



☒ **D**



(1)

(b) What type of reaction is this?

☒ **A** addition

☒ **B** condensation

☒ **C** dehydration

☒ **D** neutralisation

(1) **Q15**

(Total 2 marks)

TOTAL FOR SECTION A: 29 MARKS

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

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SECTION B

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

16. This question is about the pineapple flavouring used in sweets. It is an ester with the formula $C_3H_7COOCH_3$, which can be broken down into butanoic acid and methanol when mixed with hydrochloric acid.

The following equilibrium is set up:

$$C_3H_7COOCH_3(l) + H_2O(l) \rightleftharpoons C_3H_7COOH(l) + CH_3OH(l)$$

(a) Give the name of this ester.

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(1)

(b) Why does the ester have a comparatively low boiling point compared to the other three substances in the equation?

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(1)

(c) What is the name given to this type of reaction?

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(1)

Leave blank

*(d) Suggest the reasons why manufacturers choose to use the chemically manufactured pineapple flavouring rather than the natural product and why consumers might prefer to choose the natural product.

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(4)

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(e) In an experiment, 10.2 g (0.10 mol) of the ester was mixed with 18 cm^3 of 1.0 mol dm^{-3} hydrochloric acid and left until equilibrium had been reached. The hydrochloric acid acts as a catalyst and contains 18 g (1 mol) of water. At equilibrium, 4.4 g of butanoic acid was found to be present.

Molar mass of butanoic acid = 88 g; assume the total volume at equilibrium is 30 cm^3.

Give the expression for the equilibrium constant, K_c, for this equilibrium and calculate its value. Explain why it has no units.

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(5)

Q16

(Total 12 marks)

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17. Methane reacts with steam in an endothermic reaction.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

(a) State the effect on the value of the equilibrium constant of an increase in temperature.

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(1)

*(b) Use your answer to (a) to explain the effect of this change on the position of equilibrium.

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(2)

Q17

(Total 3 marks)

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18. This question is about the reaction of magnesium with hydrochloric acid which takes place rapidly at room temperature.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g) \qquad \Delta H = -467 \text{ kJ mol}^{-1}$$

(a) Rewrite the equation omitting spectator ions.

(1)

(b) Suggest the sign of the following entropy changes for this reaction. Justify each of your answers.

(i) ΔS_{system}

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(2)

(ii) $\Delta S_{surroundings}$

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(2)

(iii) ΔS_{total}

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(1)

Leave blank

(c) A student carried out this experiment at five different temperatures in order to calculate the activation energy of the reaction. The student's laboratory record is shown below.

Method

Clean a strip of magnesium weighing 0.100 g with sand paper. Measure the temperature of 20 cm^3 of 1.00 mol dm^{-3} hydrochloric acid in a 100 cm^3 beaker. Add the magnesium ribbon, stir continuously, and time how long it takes for the magnesium to disappear. Repeat the experiment at four other temperatures.

Assumption: the initial rate of reaction is proportional to 1/time.

Results

Temperature /^0C	Temperature /K	1/T /K^{-1}	time /s	1/time /s^{-1}	ln 1/time
24	297	3.37×10^{-3}	45	0.0222	-3.81
33	306	3.27×10^{-3}	25	0.0400	-3.22
45	318	3.14×10^{-3}	11	0.0909	-2.40
56	329	3.04×10^{-3}	6	0.1667	-1.79
10	283	3.53×10^{-3}	122	0.0082	-4.80

The Arrhenius equation is $\ln k = -E_a/R \times (1/T) + \text{constant}$

ln 1/time is proportional to ln k and so a graph of ln 1/time will have the same gradient as that of the Arrhenius plot of ln k against 1/Temperature

The student plotted the graph of ln 1/time against 1/Temperature and from this the activation energy, E_A, was calculated as + 51.3 kJ mol^{-1}.

(i) Suggest the reason for cleaning the magnesium ribbon with sand paper.

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(1)

Leave blank

*(ii) Calculate the number of moles of hydrochloric acid used up when all the magnesium reacts in one experiment. Hence comment on whether the change in concentration during the reaction will have a significant effect on the validity of the assumption that the initial rate of reaction is proportional to 1/time. How would you overcome this potential error?

[Take the relative atomic mass of magnesium as 24 in this and subsequent calculations.]

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(5)

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(iii) Use the value of ΔH and other information given in the question to calculate the temperature change in an experiment assuming no energy is lost to the surroundings. Hence comment on whether this change in temperature will have a significant effect. How would you overcome this potential error?

[$\Delta H = -467$ kJ mol^{-1}.

heat produced = mass × specific heat capacity × change in temperature.

Assume that the specific heat capacity of the solution is 4.18 J K^{-1} g^{-1}]

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(4)

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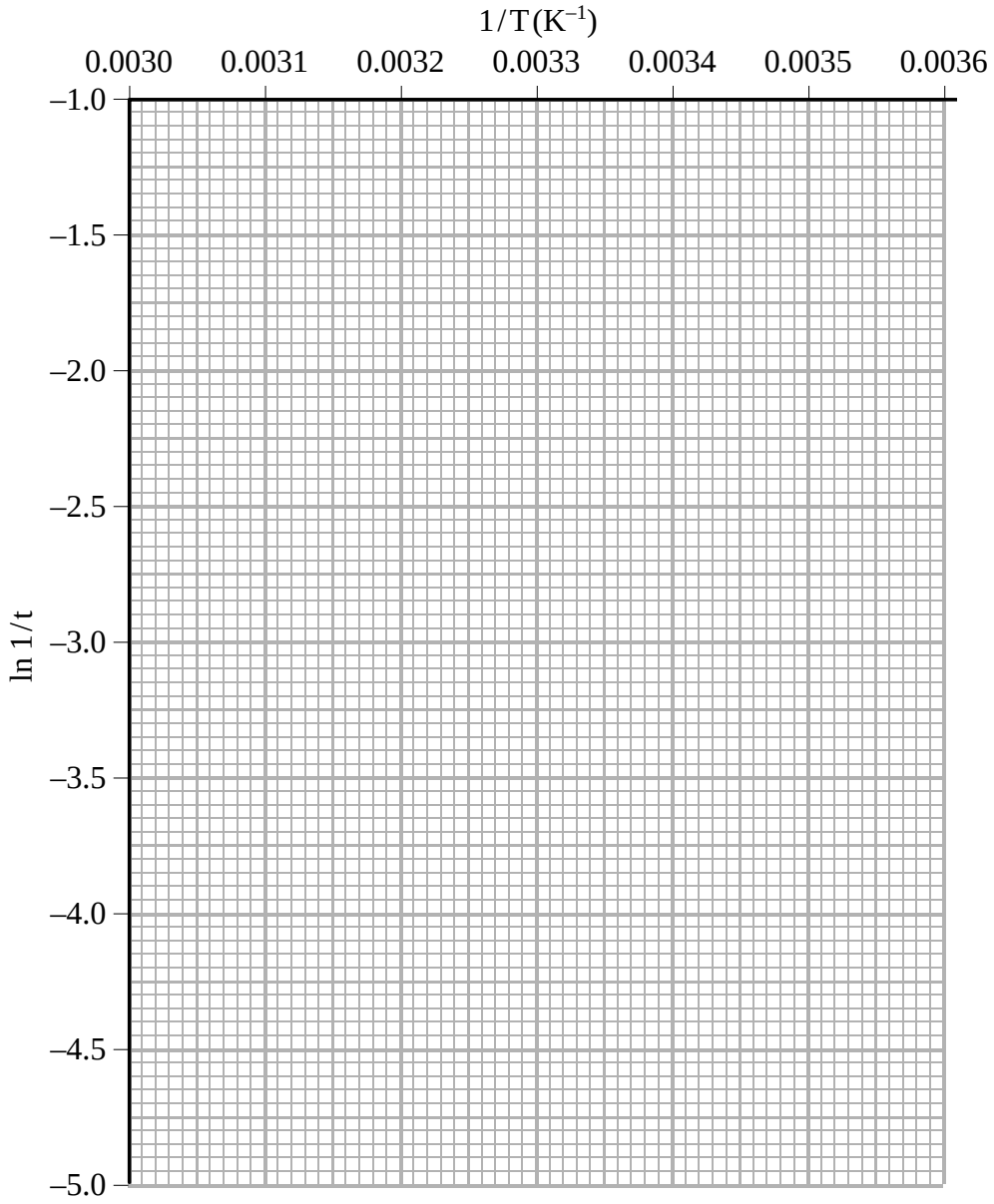
(iv) The most difficult thing to measure accurately is the time it takes for the magnesium to disappear and the time measured can be up to 2 seconds out. Assuming this error, calculate the shortest time at 56 °C **and** the longest time at 10 °C for this reaction.

Complete the table for these times. Plot the two points on the grid below and join them with a straight line. From the gradient, which equals $-E_A/R$, of this line calculate another value for the activation energy.

Temperature / °C	Temperature /K	1/T /K^{-1}	time /s	1/time /s^{-1}	ln 1/time
56	329	3.04×10^{-3}			
10	283	3.53×10^{-3}			



(4)

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(v) If the reaction mixture is not stirred, the magnesium tends to float on the surface of the acid.

Suggest how this would affect the measurements of the rate of the reaction.

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(1)

(vi) Suggest **two** other improvements the student could do to this experiment to improve the accuracy or validity of the results.

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(2)

(vii) If ethanoic acid of the same concentration and at the same temperature is used instead of hydrochloric acid, explain how the rate would differ.

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(1)

Q18

(Total 24 marks)

Leave blank

***19.** One step in the production of nitric acid is the oxidation of ammonia.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

This is carried out at 900 °C over a platinum-rhodium catalyst and is an example of heterogeneous catalysis.

Explain in terms of collision frequency and collision energy how the rate would change if the temperature were increased, and which of these causes the greater effect.

What is the difference between a heterogeneous and a homogeneous catalyst? Suggest **one** advantage of using a heterogeneous catalyst in processes such as this.

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Q19

(Total 6 marks)

TOTAL FOR SECTION B: 45 MARKS

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SECTION C

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

20. In moths a pheromone, **P**, acts as an attractant for the opposite sex. **P** has the molecular formula $C_7H_{12}O$.

What can be deduced about the structure of **P** from the following information?

(a) (i) 1 mole of **P** reacts with 1 mole of Br_2 molecules to form a compound with the formula $C_7H_{12}OBr_2$.

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(1)

(ii) When lithium tetrahydridoaluminate is reacted with **P** a compound with the formula $C_7H_{14}O$ is formed.

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(1)

(iii) **P** forms an orange precipitate with 2,4-dinitrophenylhydrazine.

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(1)

(iv) When **P** is heated with Fehling's or Benedict's solution, the solution remains blue.

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(1)

(v) **P** is a Z-isomer.

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(1)

Leave blank

(b) What does the following physical data tell you about the structure of **P**? Use your Data booklet where necessary.

*(i) The infrared spectrum of **P** has the following absorptions at wavenumbers above 1600 cm^{-1}.

3060 cm^{-1}

2920 cm^{-1}

1690 cm^{-1}

1660 cm^{-1}

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(3)

(ii) The nmr spectrum does **not** have a peak corresponding to a chemical shift, δ, of between 9 and 10.

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(1)

*(iii) The mass spectrum showed the presence of peaks at mass/charge ratios of 15 and 29, but no peak at 43.

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(3)

Leave blank

(c) Given that **P** has a straight chain of carbon atoms in its formula, use the information you have deduced above to suggest a displayed formula for the pheromone **P**.

(2)

(d) How could you use a purified sample of the orange precipitate in (a)(iii) to confirm the formula of **P**?

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(2)

Q20

(Total 16 marks)

TOTAL FOR SECTION C: 16 MARKS
TOTAL FOR PAPER: 90 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lathanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103