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 **black** 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.
- Check your answers if you have time at the end.

Turn over ▶

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P 6 7 1 3 0 A 0 1 2 8

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 The decomposition of ammonia is catalysed by tungsten metal.

$$2NH_3(g) \xrightarrow{\text{tungsten}} N_2(g) + 3H_2(g)$$

This reaction has zero order kinetics.

(a) What is the rate equation for this reaction?

(1)

☒ **A** rate = k

☒ **B** rate = $k[NH_3]$

☒ **C** rate = $k[NH_3]^2$

☒ **D** rate = $k[N_2][H_2]^3$

(b) What are the units of the rate constant, k, for this zero order reaction?

(1)

☒ **A** no units

☒ **B** s^{-1}

☒ **C** mol dm^{-3} s^{-1}

☒ **D** dm^3 mol^{-1} s^{-1}

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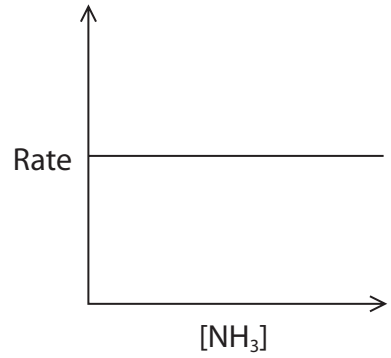
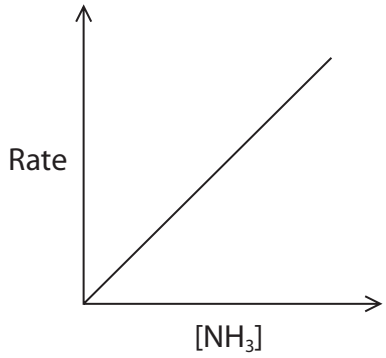
(c) Which of these graphs represents this zero order reaction?

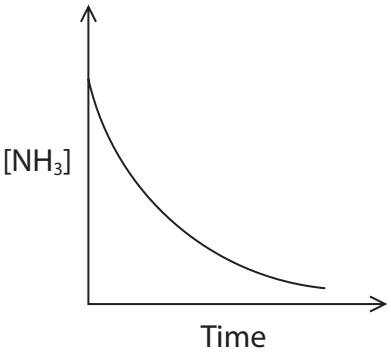
(1)



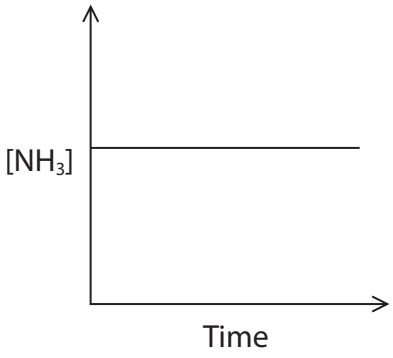
☒ **A**



☒ **B**



☒ **C**



☒ **D**

(Total for Question 1 = 3 marks)

2 What is the effect of increasing temperature on the average energy of the particles in a reaction and on the activation energy of the reaction?

	Effect on the average energy	Effect on the activation energy
☒ **A**	unchanged	decreased
☒ **B**	unchanged	unchanged
☒ **C**	increased	decreased
☒ **D**	increased	unchanged

(Total for Question 2 = 1 mark)

3 Ammonium nitrate is very soluble in water.

$$NH_4NO_3(s) + aq \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^{\ominus} = +25.8 \text{ kJ mol}^{-1}$$

What is the best explanation for this?

- ☒ **A** all ammonium salts are soluble in water
- ☒ **B** the activation energy of the reaction is very low
- ☒ **C** the enthalpies of hydration of the ions are very exothermic
- ☒ **D** the entropy change of the system, ΔS_{system}, is positive

(Total for Question 3 = 1 mark)

4 The decomposition of calcium carbonate is an important reaction in the manufacture of cement.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +178 \text{ kJ mol}^{-1}$$

What are the signs of the entropy change of the system, ΔS_{system}, and of the entropy change of the surroundings, $\Delta S_{surroundings}$?

	Sign of ΔS_{system}	Sign of $\Delta S_{surroundings}$
☒ **A**	positive	positive
☒ **B**	positive	negative
☒ **C**	negative	positive
☒ **D**	negative	negative

(Total for Question 4 = 1 mark)

5 The standard molar entropy, $S^{\ominus}$, of a substance

- ☒ **A** is not affected by changes of state or changes in temperature
- ☒ **B** only changes when the temperature changes
- ☒ **C** only changes when the substance changes state
- ☒ **D** changes when the temperature changes and when the substance changes state

(Total for Question 5 = 1 mark)

6 The water gas reaction is used in the manufacture of hydrogen.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H^{\ominus} = +131.2 \text{ kJ mol}^{-1}$$

(a) What is the equilibrium constant, K_c, for this reaction?

(1)

☒ **A** $K_c = [CO][H_2]$

☒ **B** $K_c = \dfrac{[CO][H_2]}{[C]}$

☒ **C** $K_c = \dfrac{[CO][H_2]}{[H_2O]}$

☒ **D** $K_c = \dfrac{[CO][H_2]}{[H_2O][C]}$

(b) What happens to the equilibrium constants of the forward and reverse reactions when the temperature is **increased**?

(1)

	K_c of forward reaction	K_c of reverse reaction
☒ **A**	increases	increases
☒ **B**	increases	decreases
☒ **C**	decreases	increases
☒ **D**	decreases	decreases

(Total for Question 6 = 2 marks)

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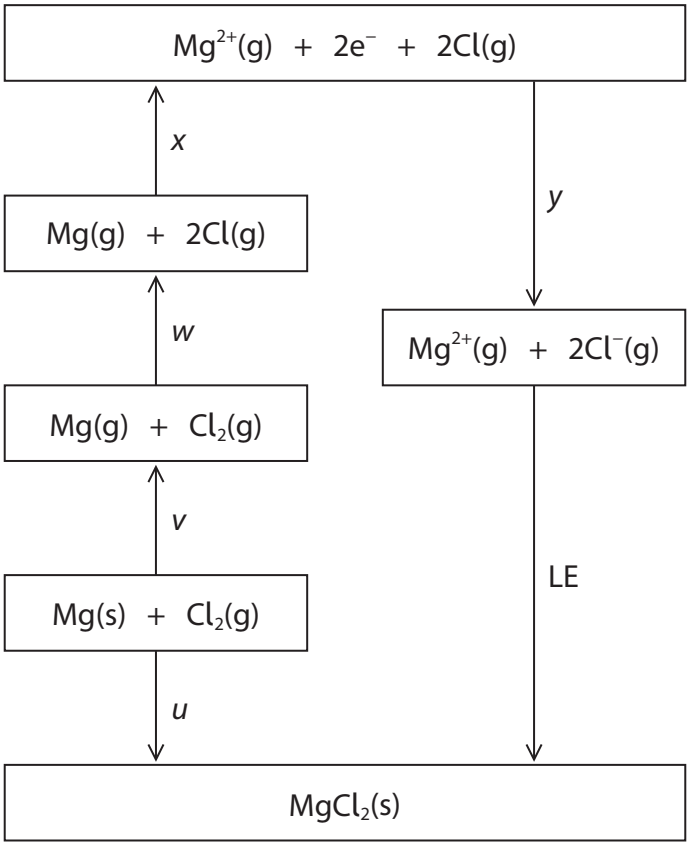
7 The diagram shows the Born-Haber cycle for magnesium chloride.



(a) Which of these is the electron affinity of chlorine?

(1)

- ☒ **A** y
- ☒ **B** $y/2$
- ☒ **C** $(w + y)$
- ☒ **D** $(w + y)/2$

(b) Which expression gives the lattice energy (LE) for magnesium chloride?

(1)

- ☒ **A** LE = $u - (v + w + x + y)$
- ☒ **B** LE = $v + w + x + y - u$
- ☒ **C** LE = $y - u - (v + w + x)$
- ☒ **D** LE = $v + w + x - y + u$

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(c) Which energy change in the cycle does *x* represent?

(1)

- ☒ **A** the first ionisation energy of magnesium
- ☒ **B** the second ionisation energy of magnesium
- ☒ **C** the sum of the first and second ionisation energies of magnesium
- ☒ **D** the sum of the enthalpy change of atomisation and the first and second ionisation energies of magnesium

(Total for Question 7 = 3 marks)

8 When ethanoic acid and chloroethanoic acid are mixed, an equilibrium is set up.

$$CH_3COOH + CH_2ClCOOH \rightleftharpoons CH_3COOH_2^+ + CH_2ClCOO^-$$

The Brønsted-Lowry acids in this equilibrium are

- ☒ **A** CH_3COOH and $CH_2ClCOOH$
- ☒ **B** CH_3COOH and $CH_3COOH_2^+$
- ☒ **C** $CH_2ClCOOH$ and $CH_3COOH_2^+$
- ☒ **D** $CH_3COOH_2^+$ and CH_2ClCOO^-

(Total for Question 8 = 1 mark)

9 What is the pH of 0.010 mol dm^{-3} aqueous calcium hydroxide, $Ca(OH)_2(aq)$?

[pK_w = 14]

- ☒ **A** 11.7
- ☒ **B** 12.0
- ☒ **C** 12.3
- ☒ **D** 13.3

(Total for Question 9 = 1 mark)

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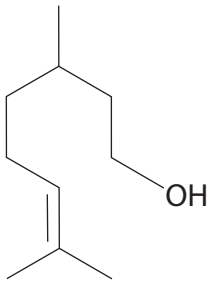
10 Citronellol is found in rose and geranium oils.



citronellol

The type(s) of stereoisomerism shown by citronellol is

☒ **A** optical and geometric isomerism

☒ **B** optical isomerism only

☒ **C** geometric isomerism only

☒ **D** neither optical nor geometric isomerism

(Total for Question 10 = 1 mark)

11 Ethanal and propane have the same molar mass but ethanal has a much higher boiling temperature.

Ethanal is fully miscible in water but propane is almost insoluble.

Which intermolecular forces of ethanal are mainly responsible for the differences in these properties?

	Higher boiling temperature	Greater solubility in water
☒ **A**	hydrogen bonds	hydrogen bonds
☒ **B**	permanent dipole forces	permanent dipole forces
☒ **C**	hydrogen bonds	permanent dipole forces
☒ **D**	permanent dipole forces	hydrogen bonds

(Total for Question 11 = 1 mark)

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

12 An unknown aldehyde may be identified by measuring the melting temperature of the purified precipitate formed in its reaction with

- ☒ **A** 2,4-dinitrophenylhydrazine
- ☒ **B** Fehling's solution
- ☒ **C** potassium dichromate and sulfuric acid
- ☒ **D** Tollens' reagent

(Total for Question 12 = 1 mark)

13 Butanoic acid may be prepared by the acid hydrolysis of

- ☒ **A** butyl ethanoate
- ☒ **B** 1-chlorobutane
- ☒ **C** ethyl butanoate
- ☒ **D** propanenitrile

(Total for Question 13 = 1 mark)

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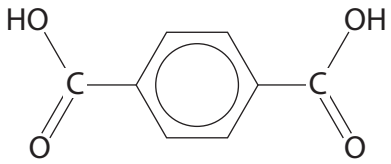
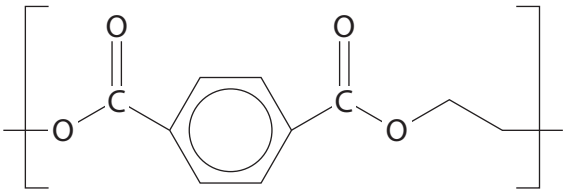
14 Terylene is a polyester derived from ethane-1,2-diol and terephthalic acid.



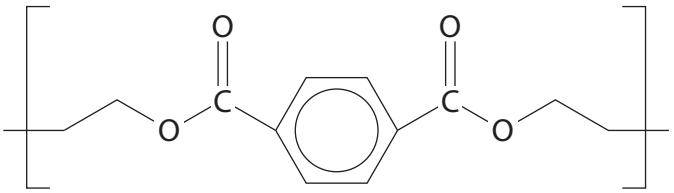
terephthalic acid

What is the structure of the repeat unit of terylene?

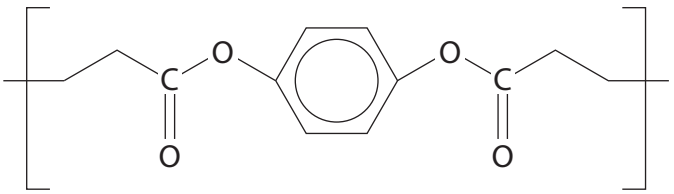
☒ **A**



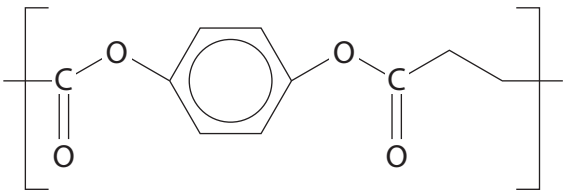
☒ **B**



☒ **C**



☒ **D**



(Total for Question 14 = 1 mark)

15 The formation of esters and the hydrolysis of esters are reactions that are slow under normal laboratory conditions.

What speeds up these reactions?

	Esterification	Hydrolysis
☒ **A**	acids only	acids only
☒ **B**	acids only	acids and bases
☒ **C**	bases only	bases only
☒ **D**	bases only	acids and bases

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

16 Compound **X** is used by mammals as an alternative energy source to sugars.
X is a compound of carbon, hydrogen and oxygen only.

(a) Complete combustion of a 2.50 g sample of **X** in dry oxygen produced 4.31 g of carbon dioxide and 1.32 g of water as the only products.

(i) Give a reason why the oxygen used must be dry.

(1)

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(ii) Show that the empirical formula of **X** is $C_4H_6O_3$. You **must** show your working.

(5)

(b) Compound **X** gave an orange precipitate with Brady's reagent (2,4-dinitrophenylhydrazine) but no reaction with Tollens' reagent.
When **X** was added to a solution of sodium hydrogencarbonate, effervescence occurred and the gas evolved turned limewater cloudy.

The carbon-13 NMR spectrum of **X** had only four peaks.

(i) Deduce the **two** possible structures of **X**, showing how this information supports your answer.

(6)

(ii) Give a **chemical** test which would allow you to distinguish between the two compounds you have given in (b)(i). Include the reagents required and the result for each of the compounds.

(3)

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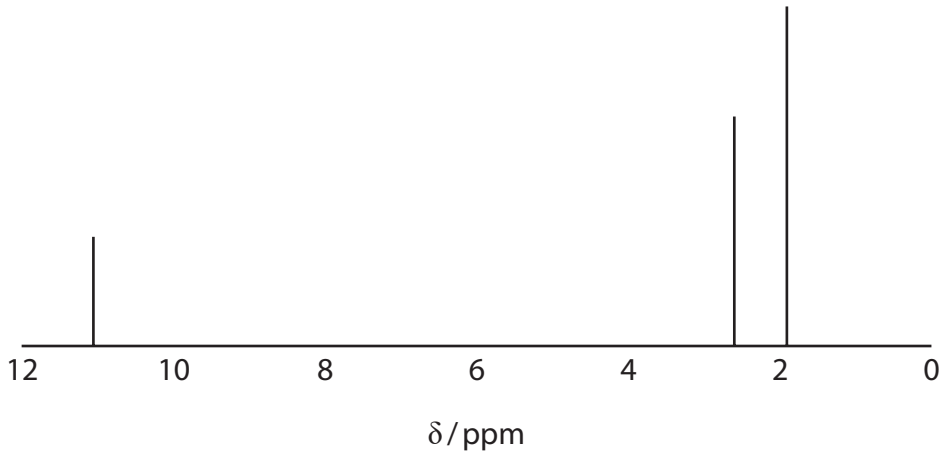
(c) A simplified **high** resolution proton (^{1}H) NMR spectrum of compound **X** is shown.



Explain how the number of peaks in the ^{1}H NMR spectrum, together with their relative heights, their chemical shifts and their splitting patterns, may be used to confirm the structure of **X**. Use the chemical shifts given in your Data Booklet.

(5)

(Total for Question 16 = 20 marks)

17 The decomposition of benzenediazonium chloride is a first order reaction.

$$C_6H_5N_2Cl + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

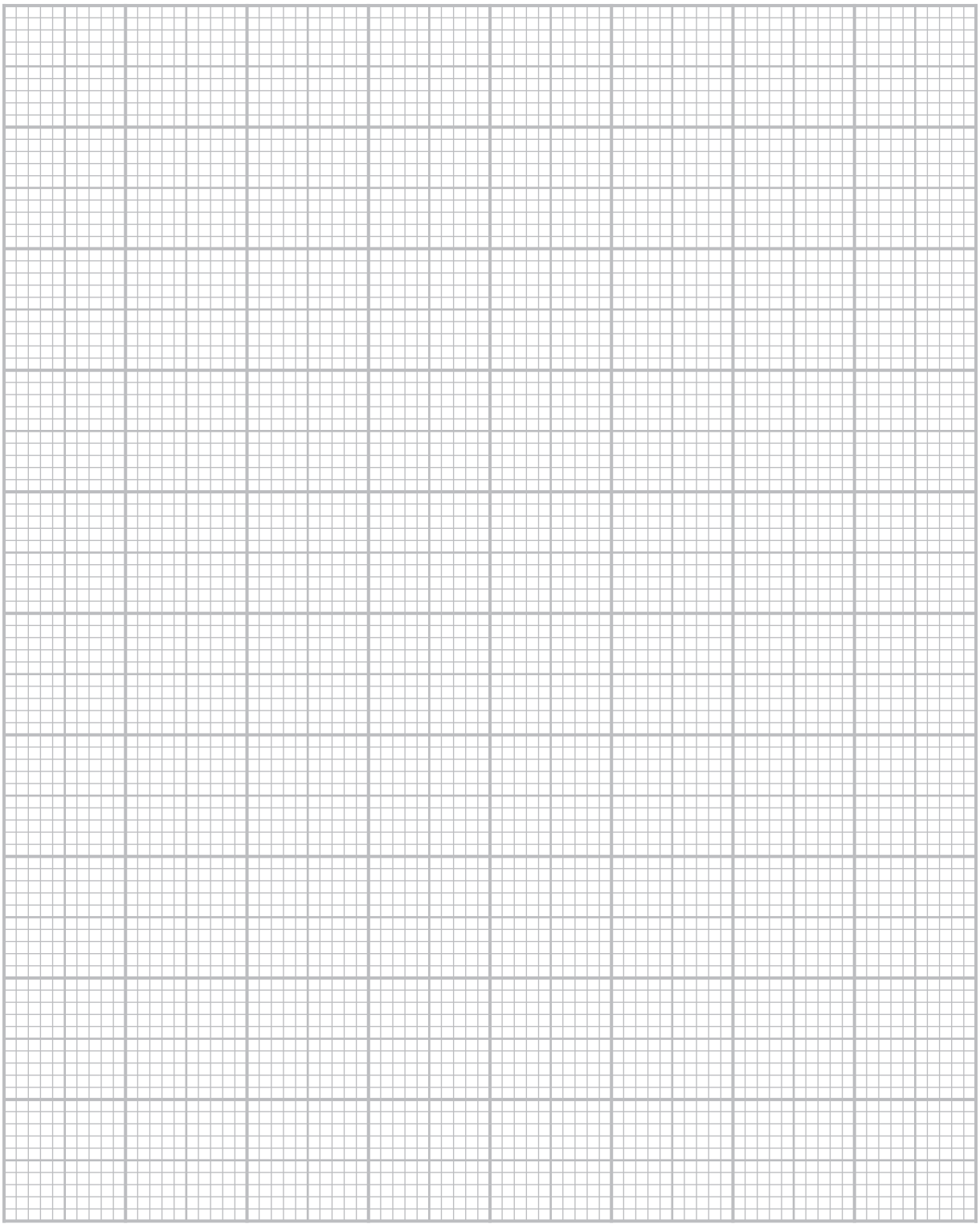
The activation energy of this reaction was determined by measuring the rate constant at various temperatures.

(a) In an experiment at 333 K, the concentration of a sample of benzenediazonium chloride was measured at various times during its decomposition. The results of this experiment are shown.

Time / s	$[C_6H_5N_2Cl]$ / mol dm^{-3}
0.0	0.500
40.0	0.410
100	0.285
200	0.165
280	0.100
350	0.070
400	0.050

(i) Plot a graph of concentration of benzenediazonium chloride against time.

(3)



(ii) Determine a value for the half-life, $t_{\frac{1}{2}}$, of this reaction.
You **must** show your working on the graph.

(1)

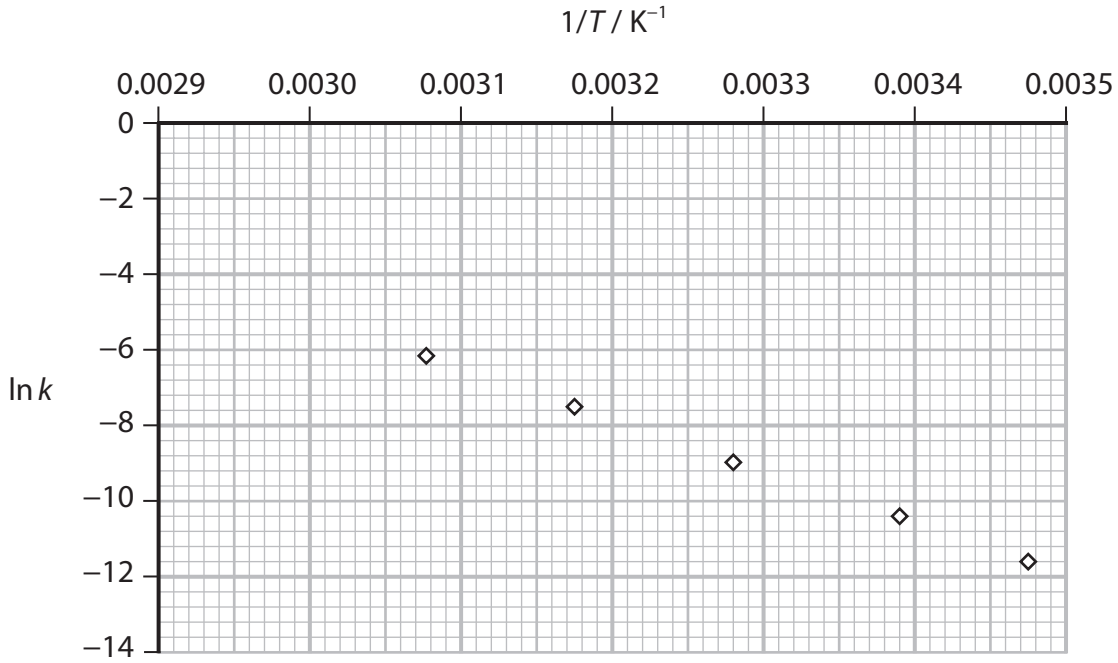
(iii) Calculate the rate constant, k, for the reaction at 333 K.
Include units in your answer.

Use the expression $\ln 2 = kt_{½}$

(2)

(b) The experiment described in (a) was repeated for five temperatures and the data used to plot a graph for the Arrhenius equation in the form

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$$



(i) Use the rate constant that you have calculated in (a)(iii) to obtain data for a point on the graph for 333 K.

(2)

(ii) Plot your data from (b)(i) on the graph.

(1)

(iii) Determine the gradient of the graph by drawing a best-fit line.
Include a sign and units in your answer.

(3)

(iv) Use the gradient determined in (b)(iii) to calculate the activation energy for the decomposition of benzenediazonium chloride.
Include a sign and units with your answer.

(3)

(Total for Question 17 = 15 marks)

***18** The hydrolysis of halogenoalkanes by alkali is a nucleophilic substitution reaction.

$$RX + OH^- \rightarrow ROH + X^-$$

The mechanism of this reaction for primary halogenoalkanes is different from the mechanism for tertiary halogenoalkanes.

Describe how knowledge of the rate equations for the hydrolysis of halogenoalkanes provides evidence for the mechanisms of these reactions.

Curly arrow mechanisms are **not** required.

(6)

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(Total for Question 18 = 6 marks)

19 Ethanol may be manufactured by the hydration of ethene.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g) \qquad \Delta H^{\ominus} = -45.3 \text{ kJ mol}^{-1}$$

(a) In a laboratory investigation of this reaction, 1.00 mol of ethene was mixed with 1.00 mol of steam at 150 °C. At equilibrium, when the total pressure of the system was 50.0 atm, 0.450 mol of ethanol had formed.

(i) Give the expression for the equilibrium constant, K_p, for the reaction.

(1)

(ii) Calculate the equilibrium constant, K_p, for the hydration of ethene at 150 °C. Include units with your answer.

(5)

(b) The manufacture of ethanol is carried out at 230 °C and 70 atm; the overall conversion into ethanol is 95 %.

Comment on these conditions in relation to their effect on the equilibrium and the overall yield of ethanol.

(3)

(Total for Question 19 = 9 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

20 Sodium hydrogensulfate is a widely used acid, with applications that include removing limescale and as a food additive. Sodium hydrogensulfate is a weak acid because of the presence of the hydrogensulfate ion, HSO_4^-.

(a) (i) Write the equation for the dissociation of the hydrogensulfate ion in aqueous solution. State symbols are not required.

(1)

(ii) A solution of sodium hydrogensulfate has pH = 1.13

Calculate the concentration of this solution, in g dm^{-3}.

[pK_a of HSO_4^- = 1.92]

(5)

(iii) State the assumptions you have used in (a)(ii).

(2)

(b) A solution containing sodium hydrogensulfate and sodium sulfate is a buffer that is used to preserve urine for steroid analysis.

(i) State what is meant by the term buffer.

(2)

(ii) Calculate the pH of the buffer prepared by dissolving 0.750 mol of sodium hydrogensulfate and 0.500 mol of sodium sulfate in distilled water to make 1.00 dm^3 of solution.

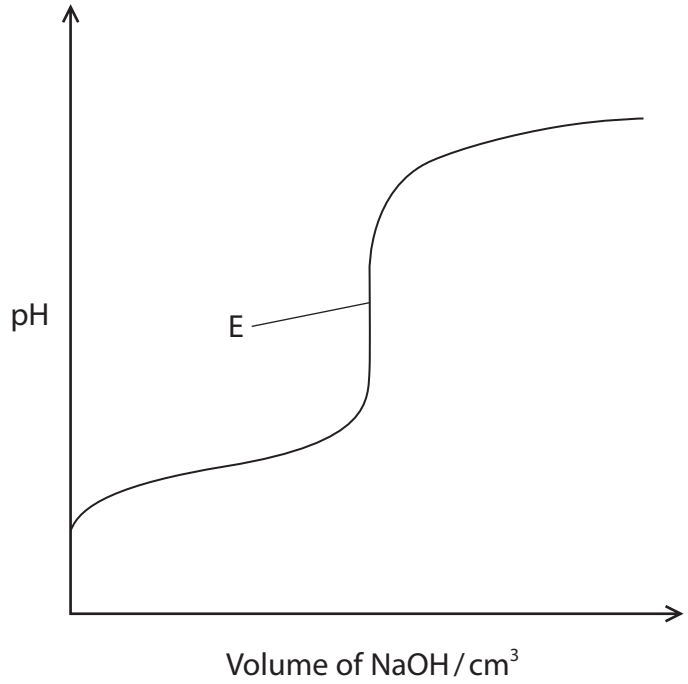
(3)

(iii) Separate samples of 0.00500 mol of hydrochloric acid are added to 1.00 dm^3 of distilled water and to the buffer in (b)(ii).

Calculate the pH **changes** that result in each case.
Assume that the volumes remain constant at 1.00 dm^3.

(4)

(c) The titration curve obtained from the addition of sodium hydroxide solution to a weak acid is shown. The equivalence point (E) of this titration occurred at pH = 8



Explain the observations that would be made if methyl orange (pK_{In} = 3.7) were used as the indicator for this titration.

(3)

(Total for Question 20 = 20 marks)

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