

Please check the examination details below before entering your candidate information

Candidate surname		Other names	
Pearson Edexcel		Centre Number	Candidate Number
International			
Advanced Level			
Tuesday 30 October 2018			
Morning (Time: 1 hour 40 minutes)		Paper Reference WCH04/01	
Chemistry Advanced Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)			
You must have: Data Booklet Scientific calculator 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.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
– *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- 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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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 For a zero order reaction, the units of the rate constant, k , are

- ☐ A no units
☐ B s^{-1}
☐ C $\text{mol dm}^{-3} s^{-1}$
☐ D $\text{dm}^3 \text{mol}^{-1} s^{-1}$

(Total for Question 1 = 1 mark)

2 Which reaction could have its progress continuously monitored by measuring the change in pressure?

- ☐ A $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$
☐ B $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
☐ C $\text{CH}_3\text{Br}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{CH}_3\text{OH}(\text{aq}) + \text{NaBr}(\text{aq})$
☐ D $\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{I}_2(\text{aq})$

(Total for Question 2 = 1 mark)

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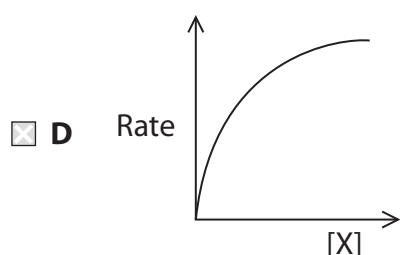
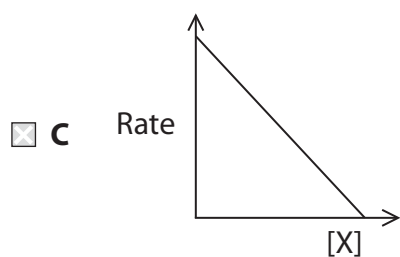
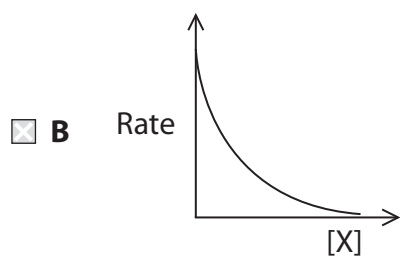
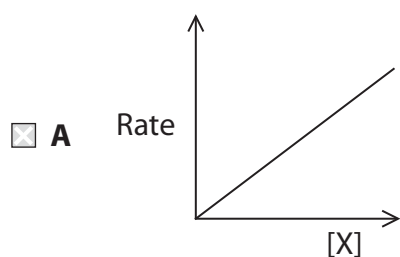
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3 The rate of decomposition of compound **X** is first order. The correct graph is

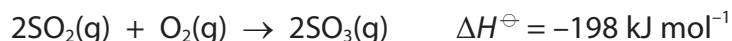


(Total for Question 3 = 1 mark)

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- 4 The oxidation of sulfur dioxide is a reaction in the manufacture of sulfuric acid:



What are the signs of the entropy change of the system (ΔS_{system}) and the entropy change of the surroundings ($\Delta S_{\text{surroundings}}$) for this reaction?

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

(Total for Question 4 = 1 mark)

- 5 The molar entropy of a perfect crystal is zero

- ☐ A in a vacuum.
- ☐ B at absolute zero, 0 K.
- ☐ C in its standard state at 1 atmosphere and 298 K.
- ☐ D at the 'triple point' when the gas, liquid and solid states of a substance are in equilibrium.

(Total for Question 5 = 1 mark)

- 6 When a gas jar containing pure oxygen is inverted over a gas jar containing pure nitrogen, the gases mix spontaneously. What is the **best** explanation for this?

- ☐ A Oxygen is denser than nitrogen.
- ☐ B The standard molar entropy of oxygen ($102.5 \text{ J K}^{-1} \text{ mol}^{-1}$) is greater than that of nitrogen ($95.8 \text{ J K}^{-1} \text{ mol}^{-1}$).
- ☐ C The mixing of the gases decreases the energy of the system.
- ☐ D The mixing of the gases increases the entropy of the system.

(Total for Question 6 = 1 mark)

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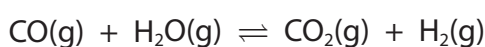


7 Which equation shows the relationship between the equilibrium constant and the entropy for a reaction?

- ☐ A $R \ln K = \Delta S_{\text{system}}$
- ☐ B $R \ln K = \Delta S_{\text{surroundings}}$
- ☐ C $R \ln K = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$
- ☐ D $R \ln K = \Delta S_{\text{system}} - \Delta S_{\text{surroundings}}$

(Total for Question 7 = 1 mark)

8 The reaction between carbon monoxide and steam is used in the industrial production of hydrogen.



The equilibrium constant, K_p , for this reaction is given by the expression

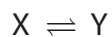
- ☐ A $K_p = \frac{p(\text{CO}_2\text{(g)}) \times p(\text{H}_2\text{(g)})}{p(\text{CO(g)})}$
- ☐ B $K_p = \frac{p(\text{CO(g)})}{p(\text{CO}_2\text{(g)}) \times p(\text{H}_2\text{(g)})}$
- ☐ C $K_p = \frac{p(\text{CO}_2\text{(g)}) \times p(\text{H}_2\text{(g)})}{p(\text{CO(g)}) \times p(\text{H}_2\text{O(g)})}$
- ☐ D $K_p = \frac{p(\text{CO(g)}) \times p(\text{H}_2\text{O(g)})}{p(\text{CO}_2\text{(g)}) \times p(\text{H}_2\text{(g)})}$

(Total for Question 8 = 1 mark)

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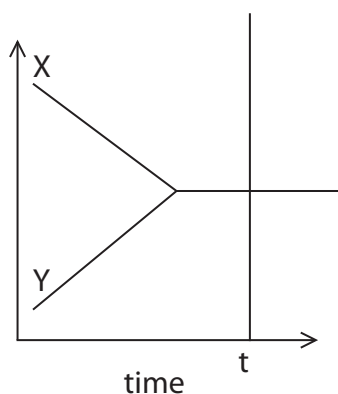


- 9 A substance, X, forms a new substance, Y, in an equilibrium reaction.

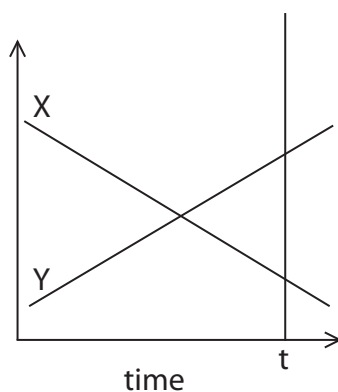


In an experiment, X and Y are mixed and react, reaching equilibrium at time t. Which diagram represents the variation in the concentrations of X and Y with time?

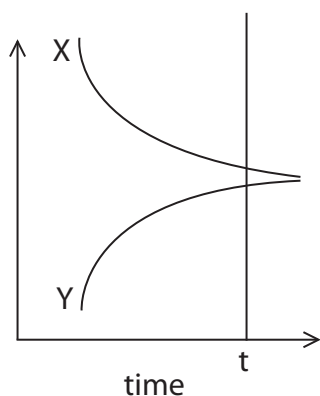
- ☐ A concentration



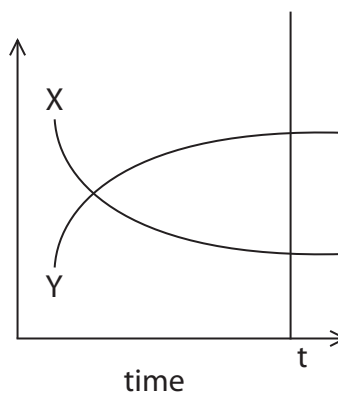
- ☐ B concentration



- ☐ C concentration



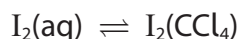
- ☐ D concentration



(Total for Question 9 = 1 mark)



- 10 Water and tetrachloromethane, CCl_4 , are immiscible liquids. When an aqueous solution of iodine is shaken with an equal volume of tetrachloromethane, an equilibrium is established:



Data on this equilibrium system:

$$K_c = 86.0 \quad \text{Densities: } \text{H}_2\text{O} = 1.00 \text{ g cm}^{-3} \quad \text{CCl}_4 = 1.59 \text{ g cm}^{-3}$$

At equilibrium

- ☐ A water will be the upper layer and have the smaller iodine concentration.
- ☐ B water will be the upper layer and have the larger iodine concentration.
- ☐ C water will be the lower layer and have the smaller iodine concentration.
- ☐ D water will be the lower layer and have the larger iodine concentration.

(Total for Question 10 = 1 mark)

- 11 The following equilibrium occurs in liquid ammonia.



What is/are the Brønsted-Lowry acid(s) in this system?

- ☐ A NH_3 and NH_4^+
- ☐ B NH_3 and NH_2^-
- ☐ C NH_4^+ and NH_2^-
- ☐ D Only NH_4^+

(Total for Question 11 = 1 mark)

- 12 At 18°C , the ionic product of water, K_w , is $6.4 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$.

At this temperature, water is

- ☐ A neutral with a pH of 7.0
- ☐ B neutral with a pH of 7.1
- ☐ C alkaline with a pH of 7.1
- ☐ D alkaline with a pH of 7.2

(Total for Question 12 = 1 mark)



- 13** A solution of the weak acid ethanoic acid ($pK_a = 4.76$) is diluted from 0.1 mol dm^{-3} to 0.01 mol dm^{-3} .

What happens to the pH of the solution and to the proportion of ethanoic acid molecules that are dissociated?

	pH	Proportion of ethanoic acid molecules dissociated
☐ A	increases	decreases
☐ B	increases	increases
☐ C	decreases	decreases
☐ D	decreases	increases

(Total for Question 13 = 1 mark)

- 14** What is the pH of a 0.10 mol dm^{-3} solution of barium hydroxide?

$$pK_w = 14.0$$

- ☐ **A** 13.0
☐ **B** 13.3
☐ **C** 13.8
☐ **D** 13.9

(Total for Question 14 = 1 mark)

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15 Propanone has a much higher boiling temperature than butane.

The **main** reason for this is

- ☐ A propanone has permanent dipole-dipole interactions between its molecules while butane does not.
- ☐ B propanone forms hydrogen bonds between its molecules while butane does not.
- ☐ C propanone has stronger London forces between its molecules than butane.
- ☐ D the carbon-oxygen double bond in propanone is very strong.

(Total for Question 15 = 1 mark)

16 When ethanal is warmed with either Fehling's solution or Benedict's solution, a red precipitate is formed.

What are the red precipitate and the organic product of the reaction?

	Red precipitate	Organic product
☐ A	copper	sodium ethanoate
☐ B	copper(I) oxide	sodium ethanoate
☐ C	copper	ethanol
☐ D	copper(I) oxide	ethanol

(Total for Question 16 = 1 mark)

17 Ethanal may be prepared by

- ☐ A heating ethanoic acid with lithium tetrahydridoaluminate(III) in dry ether.
- ☐ B refluxing a mixture of bromoethane and aqueous sodium hydroxide.
- ☐ C refluxing a mixture of ethanol and acidified potassium dichromate(VI).
- ☐ D distilling from a mixture of ethanol and acidified potassium dichromate(VI).

(Total for Question 17 = 1 mark)

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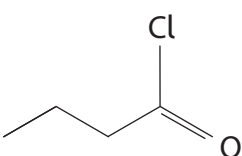
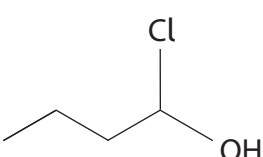
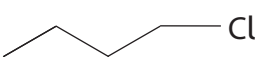
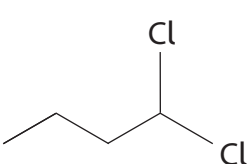


18 Which pair of compounds can **both** be separately hydrolysed in acidic conditions to form propanoic acid?

- ☐ A Propyl methanoate and ethanenitrile.
- ☐ B Propyl methanoate and propanenitrile.
- ☐ C Methyl propanoate and ethanenitrile.
- ☐ D Methyl propanoate and propanenitrile.

(Total for Question 18 = 1 mark)

19 What is the organic product of the reaction between butanoic acid and phosphorus(V) chloride?

- ☐ A 
- ☐ B 
- ☐ C 
- ☐ D 

(Total for Question 19 = 1 mark)

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20 Which radiation can be used to initiate some organic reactions?

- ☐ **A** Both radio waves and ultraviolet radiation.
- ☐ **B** Radio waves but not ultraviolet radiation.
- ☐ **C** Ultraviolet radiation but not radio waves.
- ☐ **D** Neither radio waves nor ultraviolet radiation.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

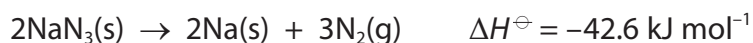


SECTION B

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

- 21 An airbag is a safety device fitted to modern cars. It is designed to inflate extremely rapidly in the event of a collision, in order to cushion the occupants of the car from the effects of the impact, and then quickly deflate.

The inflation of airbags depends on a sequence of reactions producing nitrogen gas. The first of these reactions is the decomposition of sodium azide, NaN_3 .



- (a) Predict the sign of the entropy change of the system, ΔS_{system} , for the decomposition of sodium azide. Justify your answer.

(1)

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- (b) Calculate the entropy change of the system, ΔS_{system} , for the decomposition of **two** moles of sodium azide. Give a sign and units with your answer.

Use data from page 2 of the Data Booklet (noting that the values are per mole of **atoms**) and

standard molar entropy of sodium azide $S_{298}^\ominus = 70.5 \text{ J K}^{-1} \text{ mol}^{-1}$

(3)

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- (c) Calculate the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, for the decomposition of **two** moles of sodium azide at 298 K.

(2)

- (d) Use your answers to (b) and (c) to calculate the total entropy change, ΔS_{total} , for the decomposition of **two** moles of sodium azide.

(2)

- *(e) When an airbag is deployed, the chemical reactions produce a rapid rise in temperature to about 300 °C.

By considering the molar entropies of the substances involved, explain the effect, if any, that this higher temperature will have on the entropy change of the system, ΔS_{system} , for the decomposition of sodium azide.

(3)

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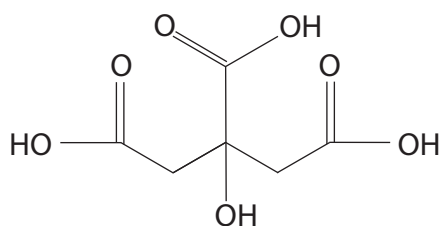
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(Total for Question 21 = 11 marks)



- 22 Citric acid occurs in significant amounts in most fruits and vegetables, and in particularly high concentrations in citrus fruits such as oranges, lemons and limes. It is used as a flavouring and preservative in food and beverages. The structure of citric acid is shown below.



Citric acid is a weak triprotic acid which means that it has three protons that can be ionised in aqueous solution and therefore three acid dissociation constants. The pK_a values for these are

$$pK_{a1} = 3.13 \quad pK_{a2} = 4.76 \quad pK_{a3} = 6.39$$

- (a) (i) When citric acid is dissolved in water, only one proton per molecule ionises significantly. Give **two** reasons for this.

(2)

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- (ii) Write the equation for the **first** dissociation of citric acid, using H_3A to represent citric acid. State symbols are not required.

(1)



- (iii) The pH of a solution of citric acid was 1.98. Calculate the concentration, in mol dm^{-3} , of this solution. Assume that the acidity is only due to the first dissociation of citric acid.

(3)

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P 5 5 4 5 0 A 0 1 5 3 2

(b) The concentration of citric acid in lemon juice was determined by a class of students, each using the following procedure.

Step 1 Squeeze three lemons and sieve the lemon juice to remove any pulp.

Step 2 Measure 25.0 cm^3 of lemon juice into a 250.0 cm^3 volumetric flask, using a pipette. Make up the volume to the mark with distilled water and mix the solution.

Step 3 Pipette 25.0 cm^3 of the diluted solution into a conical flask and add a few drops of indicator.

Step 4 Titrate the contents of the conical flask with a sodium hydroxide solution of concentration about 0.1 mol dm^{-3} .

Step 5 Repeat the titration until concordant results are obtained.

The equation for the titration reaction is



(i) Give a reason for removing pulp from the lemon juice.

(1)

(ii) Name a suitable indicator for this titration.

Use the data on page 19 of the Data Booklet to justify your choice.

(2)



- * (iii) One student carried out this titration using sodium hydroxide with a concentration of $0.095 \text{ mol dm}^{-3}$ and obtained a mean titre of 19.65 cm^3 . Calculate the concentration, in g dm^{-3} , of the citric acid in the **original** lemon juice.

(5)

- (iv) When the students compared the concentrations of citric acid from their experiments, they found that the variation was greater than expected from the uncertainties in the experiment. Suggest a reason for this.

(1)

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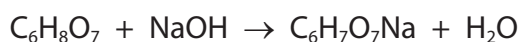
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- (c) Sodium dihydrogen citrate is formed when one mole of citric acid reacts with one mole of sodium hydroxide.



Solutions containing both citric acid and sodium dihydrogen citrate are buffers.

- (i) State the meaning of the term buffer.

(2)

- (ii) State the pH of a buffer solution containing equal numbers of moles of citric acid and sodium dihydrogen citrate.

(1)

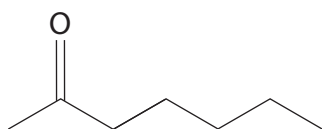
- *(iii) Explain how a solution containing citric acid and sodium dihydrogen citrate acts as a buffer.

(3)

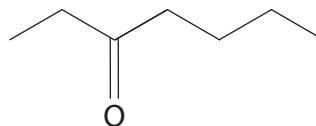
(Total for Question 22 = 21 marks)



23 Heptan-2-one and heptan-3-one are isomers. Both are colourless liquids.



heptan-2-one



heptan-3-one

Heptan-2-one occurs naturally in a variety of foods including bread, butter and some cheeses; it has a banana-like smell. Honey bees produce heptan-2-one when they bite pests invading the colony. The compound acts as an anaesthetic, enabling the honey bee to stun the pest and eject it from the hive.

Heptan-3-one, which is used as a fragrance and a solvent, does not occur naturally.

- (a) Name a reagent that could be used to show that heptan-2-one and heptan-3-one both contain a carbonyl group. State what would be observed.

(2)

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- (b) Describe a chemical test that could be used to distinguish heptan-2-one from heptan-3-one. Give the result of the test for both compounds.

(3)

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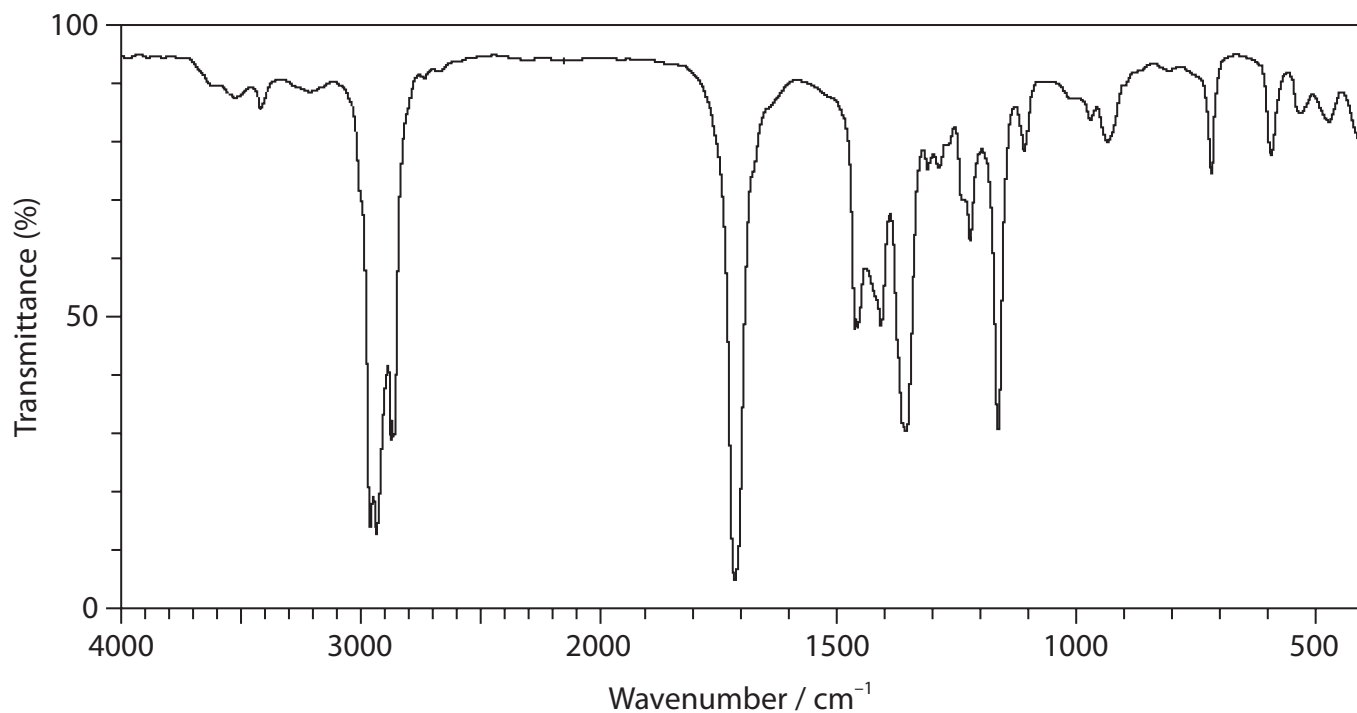
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(c) The infrared spectrum of heptan-2-one is shown below.



- (i) Circle the peak in the spectrum that you would expect to find in the infrared spectrum of any ketone but not in an alkane.

Identify the bond responsible for the stretching vibration giving this peak.

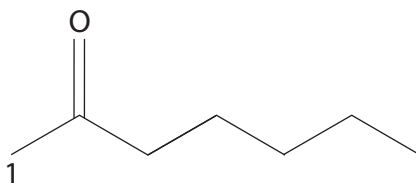
(2)

- (ii) State whether or not their infrared spectra could be used to distinguish between samples of heptan-2-one and heptan-3-one. Justify your answer.

(1)



- (d) The structure of heptan-2-one is given again below. On the diagram the first proton environment has been labelled '1'.



- (i) On the diagram, complete the labelling of the proton environments of heptan-2-one in sequence 1, 2, 3 etc. (1)
- (ii) Complete the table, giving the relative peak areas and their expected splitting patterns in the high resolution proton nmr spectrum of heptan-2-one. (3)

Proton environment	Relative peak area	Splitting pattern
1	3	



(e) Heptan-2-one reacts with hydrogen cyanide in the presence of cyanide ions to form a cyanohydrin.

- (i) Draw the mechanism for this reaction, using curly arrows to represent the movement of electrons. Represent heptan-2-one as RCOCH_3 .

(4)

- (ii) Explain why the cyanohydrin formed in (e)(i) has no effect on the plane of plane-polarised light.

(3)

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(Total for Question 23 = 19 marks)

TOTAL FOR SECTION B = 51 MARKS



SECTION C

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

24

Hydrogen Peroxide

Hydrogen peroxide is a pale blue liquid, slightly more viscous than water, which is miscible in all proportions with water, forming colourless solutions. Unlike water, hydrogen peroxide is unstable, decomposing to form water and oxygen:



This reaction is catalysed by a number of substances including platinum, iron(III) ions, manganese(IV) oxide and the enzyme catalase.

Hydrogen peroxide is used in the defence system of the bombardier beetle. A sequence of exothermic enzyme catalysed reactions occurs resulting in a boiling, pungent mixture of chemicals being sprayed from an abdominal gland. The spray is powered by the oxygen formed in the decomposition of hydrogen peroxide.

Hydrogen peroxide is seen as an environmentally safe alternative to chlorine-based bleaches and 60% of the world's production is used to bleach wood pulp and paper.

Data on hydrogen peroxide

Molar mass = 34.0 g mol^{-1}

Melting temperature = -0.43°C

Boiling temperature = 150.2°C

- (a) Draw a dot and cross diagram of a molecule of hydrogen peroxide, showing the outer shell electrons only.

(1)



- (b) Give **two** possible reasons why hydrogen peroxide has a higher boiling temperature than water.

(2)

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- (c) Suggest why hydrogen peroxide is much less stable than water.

(1)

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- (d) The rate of decomposition of hydrogen peroxide catalysed by Fe^{3+} ions was investigated.

100 cm^3 of a solution containing hydrogen peroxide of concentration 0.18 mol dm^{-3} and iron(III) nitrate of concentration $0.0025\text{ mol dm}^{-3}$ was used in one experiment. The concentration of hydrogen peroxide as the reaction proceeded was monitored by titrating samples of the mixture. The results of the experiment are shown in the table.

Time / s	Concentration of hydrogen peroxide / mol dm^{-3}
0	0.18
30	0.12
60	0.075
90	0.048
120	0.031
150	0.020

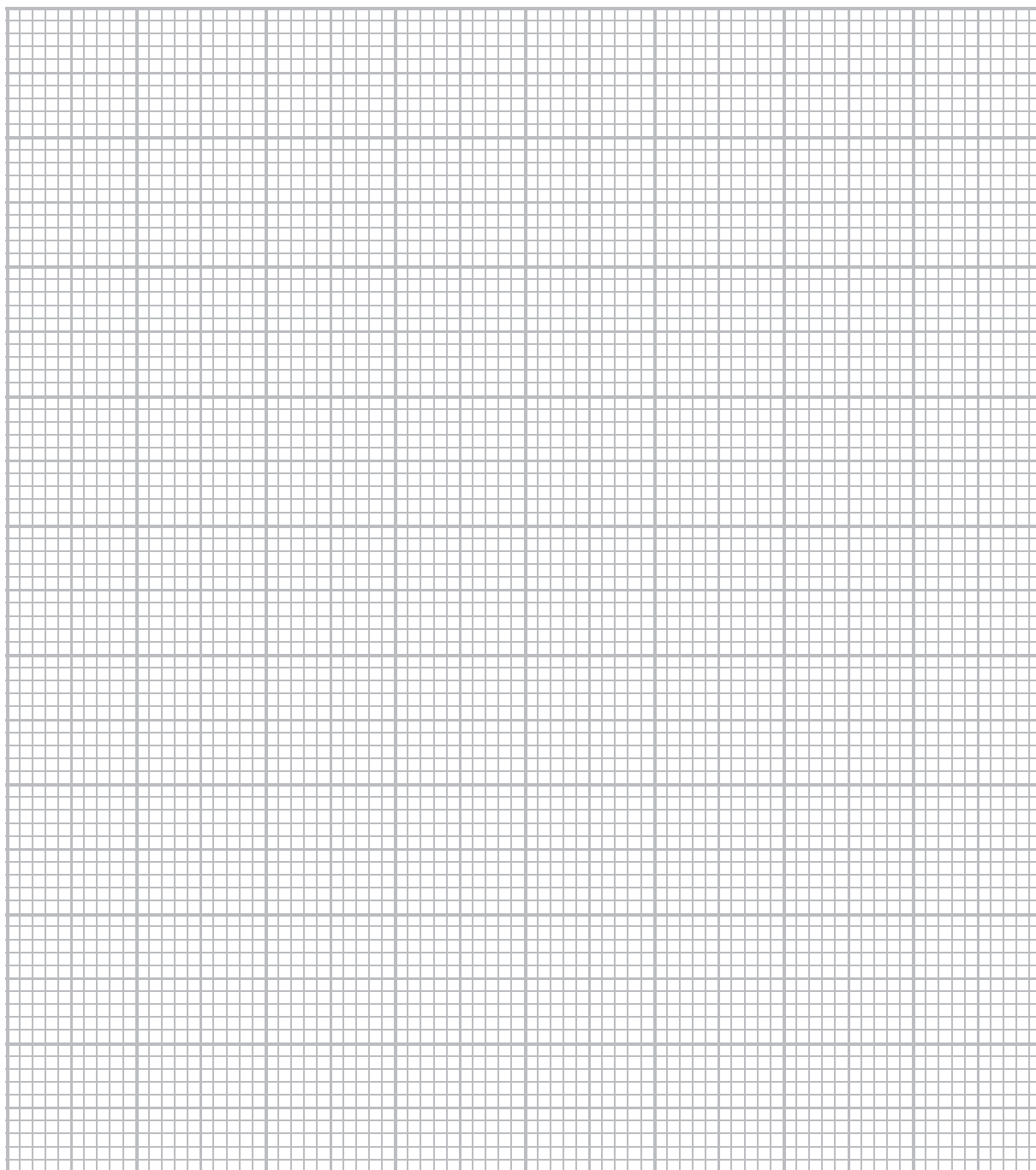


(i) Suggest how the samples from the mixture could be quenched.

(1)

(ii) Plot a graph of concentration of hydrogen peroxide (on the vertical axis) against time (on the horizontal axis). Use appropriate scales and label the axes of the graph.

(3)



(iii) From the graph, determine **two** successive half-lives of this reaction.

You **must** show your working on the graph.

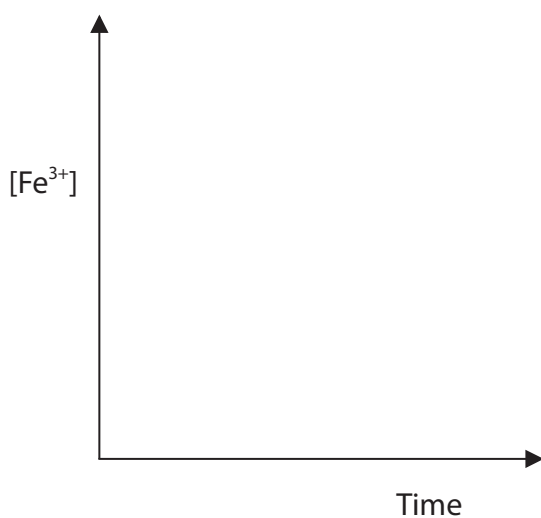
(1)

(iv) Using the half-lives that you have determined, deduce the order of the reaction with respect to hydrogen peroxide. Justify your answer.

(1)

(v) On the axes below, sketch the graph of concentration of Fe^{3+} ions with time as the reaction proceeds.

(1)



- (e) The experiment in (d) was repeated using different concentrations of Fe^{3+} ions and measuring the initial rate of reaction.

The results are shown in the table.

Concentration of hydrogen peroxide / mol dm^{-3}	Concentration of Fe^{3+} ions / mol dm^{-3}	Rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
0.18	0.00250	2.7×10^{-3}
0.18	0.00125	1.4×10^{-3}
0.18	0.00083	8.8×10^{-4}

- (i) Deduce the order of reaction with respect to Fe^{3+} ions. Justify your answer.

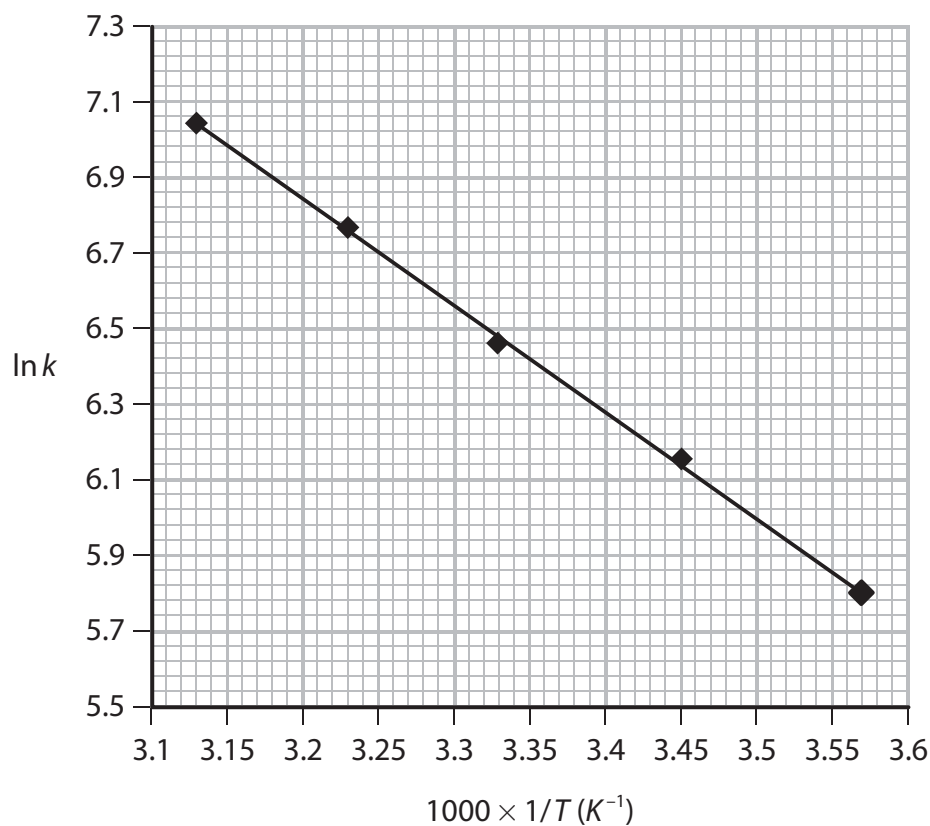
(1)

- (ii) Use your answers to (d)(iv) and (e)(i) to write the rate equation for the decomposition of hydrogen peroxide catalysed by Fe^{3+} ions.

(1)



- (f) In a further experiment, the rate constant, k , for the decomposition of hydrogen peroxide catalysed by the enzyme catalase was determined at a range of temperatures, T . A graph of $\ln k$ against $1000 \times 1/T$ was plotted.



- (i) Determine the gradient of the graph. Show your working.

(2)



- (ii) Use your answer from (f)(i) to calculate the activation energy, E_a , for the decomposition of hydrogen peroxide catalysed by the enzyme catalase. Give a sign and units with your answer. Use the equation

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

$$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

(3)

- (g) Give a reason why hydrogen peroxide is considered to be environmentally safe.

(1)

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(Total for Question 24 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS



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