

Please check the examination details below before entering your candidate information

Candidate surname

Other names

Centre Number

Candidate Number

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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.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **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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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 . If you change your mind, put a line through the box and then mark your new answer with a cross .

- 1 Two ways of writing an equation for the reaction between nitrogen monoxide and oxygen are shown.



- (a) Which **pair** of rate equations could be correct for this reaction?

(1)

| | Equation 1 | Equation 2 |
|-----------------------------------|-------------------------------------|---|
| <input type="checkbox"/> A | rate = $k[\text{NO}]^2[\text{O}_2]$ | rate = $k[\text{NO}]^2[\text{O}_2]$ |
| <input type="checkbox"/> B | rate = $k[\text{NO}]^2[\text{O}_2]$ | rate = $k[\text{NO}][\text{O}_2]^{1/2}$ |
| <input type="checkbox"/> C | rate = $k[\text{NO}_2]^2$ | rate = $k[\text{NO}_2]^2$ |
| <input type="checkbox"/> D | rate = $k[\text{NO}_2]^2$ | rate = $k[\text{NO}_2]$ |

- (b) Which two methods can be used for **continuous** monitoring of the progress of this reaction?

(1)

- A** colorimetry and titration
- B** colorimetry and volume change
- C** mass change and volume change
- D** mass change and titration

(Total for Question 1 = 2 marks)

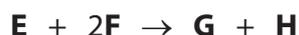
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- 2 The half-life of a first order chemical reaction is
- A half the time taken for the reaction to be complete
 - B the time taken for the value of the rate constant to halve
 - C the time taken for the concentration of a reactant to halve
 - D the time taken for the concentration of a product to double

(Total for Question 2 = 1 mark)

- 3 Two chemicals, **E** and **F**, react to form products **G** and **H**.



The mechanism for the reaction occurs in two steps via the formation of an intermediate **J**.



What is the rate equation for the reaction?

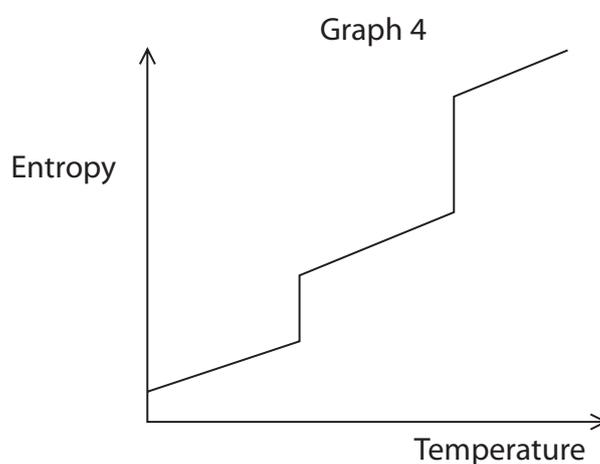
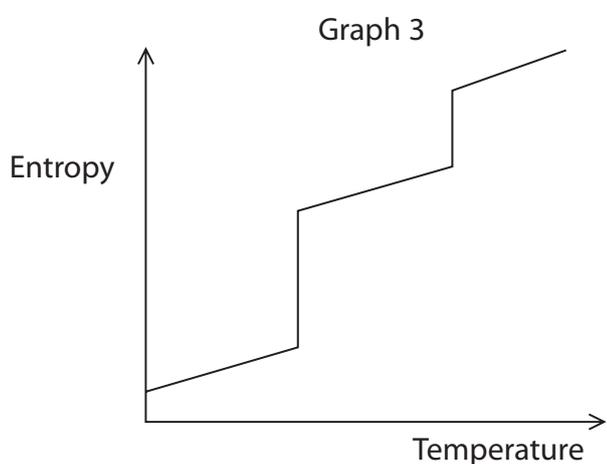
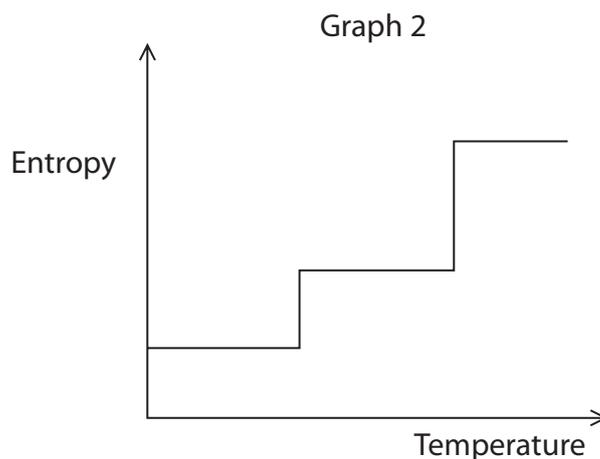
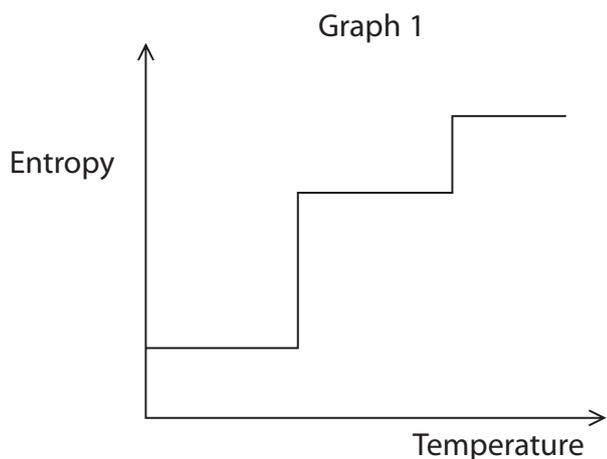
- A rate = $k[\text{E}][\text{F}]$
- B rate = $k[\text{E}][\text{F}]^2$
- C rate = $k[\text{F}][\text{J}]$
- D rate = $k[\text{E}][\text{F}]^2[\text{J}]$

(Total for Question 3 = 1 mark)

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4 Which graph shows the entropy of a substance as it changes state from solid to liquid to gas?



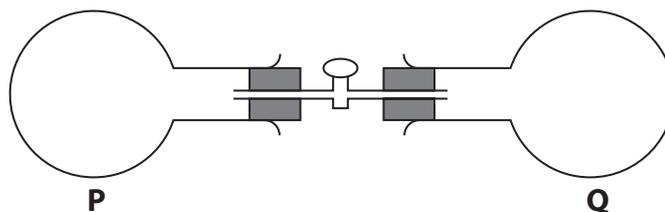
- A Graph 1
- B Graph 2
- C Graph 3
- D Graph 4

(Total for Question 4 = 1 mark)

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- 5 Two flasks, **P** and **Q**, are connected by a tube fitted with a tap.



Flask **P** contains argon gas and flask **Q** is in vacuum.

Assume argon behaves as an ideal gas and therefore has no intermolecular forces between its atoms.

How do the entropy and energy of the system change when the tap is opened and the argon fills both flasks?

| | Entropy of the system | Energy of the system |
|-----------------------------------|-----------------------|----------------------|
| <input type="checkbox"/> A | increases | decreases |
| <input type="checkbox"/> B | decreases | decreases |
| <input type="checkbox"/> C | increases | unchanged |
| <input type="checkbox"/> D | decreases | unchanged |

(Total for Question 5 = 1 mark)

- 6 When hydrogen and oxygen are mixed in a flask, there is no reaction. When a platinum gauze is added to the flask, the mixture explodes.

It can be deduced that, in the absence of a platinum gauze, the mixture of hydrogen and oxygen is

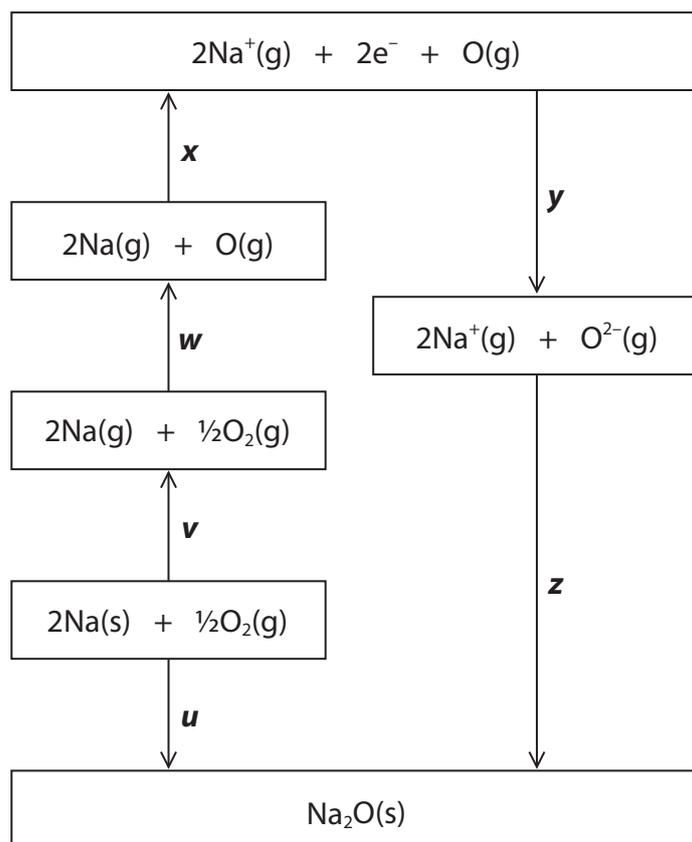
- A** kinetically stable and thermodynamically stable
- B** kinetically stable and thermodynamically unstable
- C** kinetically unstable and thermodynamically stable
- D** kinetically unstable and thermodynamically unstable

(Total for Question 6 = 1 mark)

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



7 The diagram shows the Born–Haber cycle for sodium oxide.



(a) Which energy change in the cycle does **y** represent?

(1)

- A** the first electron affinity of oxygen
- B** the second electron affinity of oxygen
- C** the sum of the first and second electron affinities of oxygen
- D** the sum of the enthalpy change of atomisation of oxygen and the first and second electron affinities of oxygen

(b) Which expression gives the enthalpy change of formation of sodium oxide, $\Delta_f H$?

(1)

- A** $\Delta_f H = v + w + x - y - z$
- B** $\Delta_f H = v + w + x + y - z$
- C** $\Delta_f H = v + w + x - y + z$
- D** $\Delta_f H = v + w + x + y + z$

(Total for Question 7 = 2 marks)



8 An ionic compound is found to have some degree of covalent bonding.

What will be the cause of the covalency and how will the lattice energy obtained from a Born–Haber cycle differ from the theoretical value obtained from electrostatic theory?

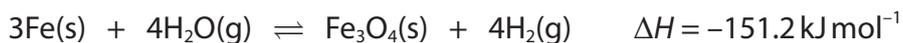
| | Cause of covalency | Born–Haber lattice energy compared with theoretical value |
|----------------------------|---------------------------|---|
| <input type="checkbox"/> A | cation polarised by anion | Born–Haber more exothermic |
| <input type="checkbox"/> B | anion polarised by cation | Born–Haber less exothermic |
| <input type="checkbox"/> C | cation polarised by anion | Born–Haber less exothermic |
| <input type="checkbox"/> D | anion polarised by cation | Born–Haber more exothermic |

(Total for Question 8 = 1 mark)

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



9 The equation for the reaction between iron and steam is shown.



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

(1)

A $K_c = \frac{[\text{Fe}_3\text{O}_4] \times [\text{H}_2]^4}{[\text{Fe}]^3 \times [\text{H}_2\text{O}]^4}$

B $K_c = \frac{[\text{Fe}_3\text{O}_4] \times [\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$

C $K_c = \frac{[\text{H}_2]^4}{[\text{Fe}]^3 \times [\text{H}_2\text{O}]^4}$

D $K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$

(b) What is the effect on the equilibrium constant for this reaction if small pieces of iron are replaced by iron powder and if the temperature is increased?

(1)

| | Iron powder used | Temperature increased |
|-----------------------------------|------------------|-----------------------|
| <input type="checkbox"/> A | K_c increases | K_c increases |
| <input type="checkbox"/> B | K_c unchanged | K_c increases |
| <input type="checkbox"/> C | K_c increases | K_c decreases |
| <input type="checkbox"/> D | K_c unchanged | K_c decreases |

(Total for Question 9 = 2 marks)

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



10 Equal amounts of ethanoic acid and methanoic acid are mixed.

[pK_a values: ethanoic acid = 4.8 methanoic acid = 3.8]

What are the conjugate acid-base pairs in the mixture?

| | acid 1 | base 1 | acid 2 | base 2 |
|----------------------------|----------------------|----------------------------------|--|----------------------------------|
| <input type="checkbox"/> A | HCOOH | HCOO ⁻ | CH ₃ COOH ₂ ⁺ | CH ₃ COOH |
| <input type="checkbox"/> B | CH ₃ COOH | CH ₃ COO ⁻ | HCOOH ₂ ⁺ | HCOOH |
| <input type="checkbox"/> C | HCOOH | CH ₃ COOH | CH ₃ COOH ₂ ⁺ | HCOO ⁻ |
| <input type="checkbox"/> D | CH ₃ COOH | HCOOH | HCOOH ₂ ⁺ | CH ₃ COO ⁻ |

(Total for Question 10 = 1 mark)

11 A 1 mol dm⁻³ solution of ethanoic acid is gradually diluted by the addition of distilled water.

What happens to the degree of dissociation of the acid and the pH of the solution as the distilled water is added?

| | Degree of dissociation | pH |
|----------------------------|------------------------|-----------|
| <input type="checkbox"/> A | increases | increases |
| <input type="checkbox"/> B | increases | decreases |
| <input type="checkbox"/> C | decreases | increases |
| <input type="checkbox"/> D | decreases | decreases |

(Total for Question 11 = 1 mark)

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12 The solubility of magnesium hydroxide is $1.1 \times 10^{-4} \text{ mol dm}^{-3}$ at 25°C and $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ at 100°C .

$[K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 25°C $K_w = 5.5 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 100°C]

(a) What is the pH of a saturated solution of magnesium hydroxide at 25°C ? (1)

- A 9.7
- B 10.0
- C 10.3
- D 12.0

(b) Saturated solutions of magnesium hydroxide at 25°C and 100°C are compared.

How do the concentrations of hydroxide ions and the pH values of these solutions differ? (1)

| | Concentration of hydroxide ions at 100°C | pH at 100°C |
|----------------------------|--|---------------------------|
| <input type="checkbox"/> A | higher | lower |
| <input type="checkbox"/> B | higher | higher |
| <input type="checkbox"/> C | lower | higher |
| <input type="checkbox"/> D | lower | lower |

(Total for Question 12 = 2 marks)

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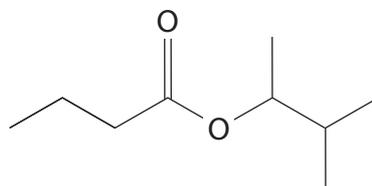
13 Propanal has a much higher boiling temperature than butane even though both compounds have the same molar mass.

The main reason for the difference in boiling temperature is that in the liquid state

- A propanal forms much stronger London forces than butane
- B propanal forms permanent dipole-permanent dipole forces
- C propanal forms hydrogen bonds
- D propanal forms hydrogen bonds and permanent dipole-permanent dipole forces

(Total for Question 13 = 1 mark)

14 The structure of an ester is shown.



Which two compounds react to form this ester?

- A butanoyl chloride and 2-methylbutan-2-ol
- B butanoyl chloride and 3-methylbutan-2-ol
- C propanoyl chloride and 2-methylbutan-2-ol
- D propanoyl chloride and 3-methylbutan-2-ol

(Total for Question 14 = 1 mark)

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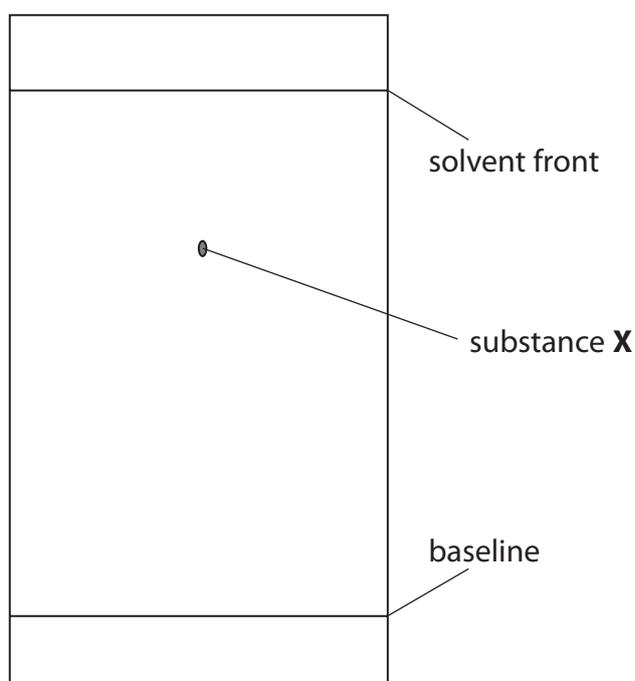
15 Samples of ethanal and propanone are added to separate test tubes containing iodine dissolved in aqueous potassium hydroxide and the mixtures are heated gently.

A pale yellow precipitate will be formed with

- A ethanal and propanone
- B ethanal only
- C propanone only
- D neither ethanal nor propanone

(Total for Question 15 = 1 mark)

16 The chromatogram of a substance X is shown.



What is the R_f value for substance X?

- A 0.28
- B 0.62
- C 0.70
- D 0.86

(Total for Question 16 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS



(ii) The student's results are shown.

| Run | [H ₂ O ₂ (aq)] / mol dm ⁻³ | [I ⁻ (aq)] / mol dm ⁻³ | [H ⁺ (aq)] / mol dm ⁻³ | Rate / mol dm ⁻³ s ⁻¹ |
|-----|---|--|--|---|
| 1 | 0.0210 | 0.0198 | 0.00105 | 0.00181 |
| 2 | 0.0105 | 0.0400 | 0.00105 | 0.00181 |
| 3 | 0.0105 | 0.0797 | 0.00099 | 0.00364 |
| 4 | 0.0210 | 0.0801 | 0.00201 | 0.00730 |

Deduce the rate equation for this reaction.

(3)

(iii) Calculate the rate constant for this reaction at 293 K, using the results from Run 1. Include units with your answer.

(3)



- (b) The student carried out a second series of experiments with this reaction at 313 K. The rate of reaction was found to be 4.45 times faster at 313 K than at 293 K.

Calculate the activation energy, E_a , for this reaction, using the Arrhenius equation. Give your answer to an appropriate number of significant figures and include units.

$$\ln k = -\frac{E_a}{RT} + \text{constant} \quad (4)$$

(Total for Question 17 = 13 marks)



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(b) Poly(lactic acid) is a polyester derived from lactic acid as the **only** monomer. Poly(lactic acid), which is often referred to as PLA, may be obtained from renewable resources and is also biodegradable.

(i) Draw the structure of a section of PLA showing **two** repeat units.

(2)

(ii) Lactic acid is converted into compound **X** which is then polymerised to form PLA.

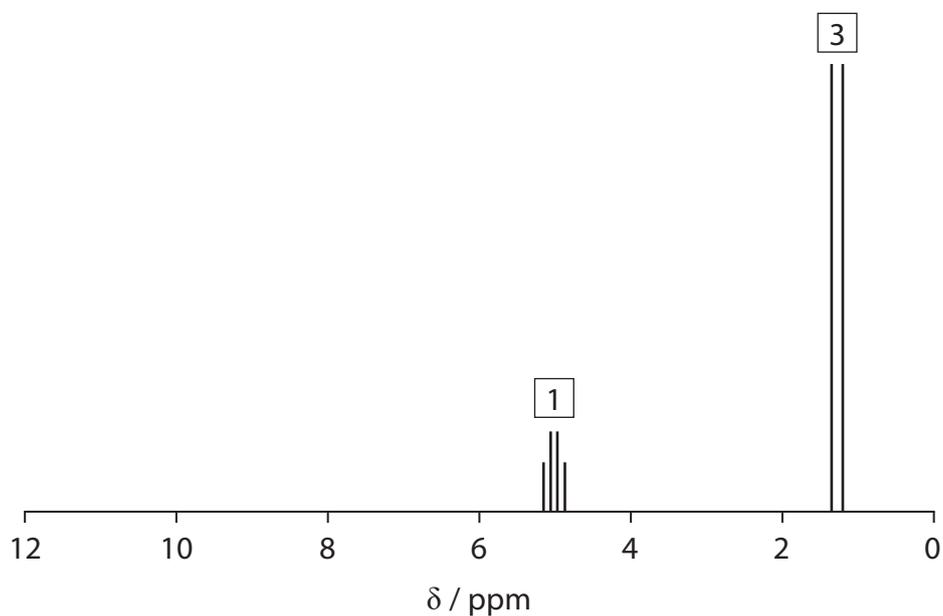
The empirical formula of **X** is $C_3H_4O_2$ and its molar mass is 144 g mol^{-1} .

Determine the molecular formula of **X**.

(1)



- (iii) A simplified high resolution proton NMR spectrum of **X** is shown.
The numbers above the peaks are the relative peak areas.
Note that the chemical shifts for **X** are different from the general values in the Data Booklet.



State what the number of peaks, their relative peak areas and splitting patterns show about the structure of **X**.

(3)

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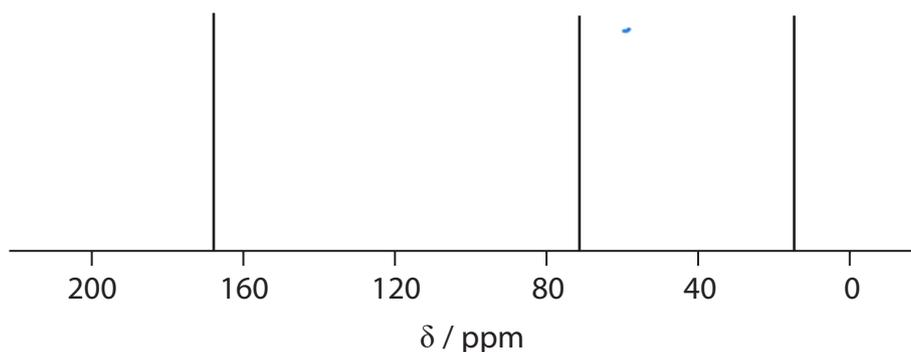
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(iv) A simplified carbon-13 NMR spectrum of **X** is shown.



State what additional information about the structure of **X** is given by this spectrum.

(2)

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.....

(v) Draw the structure of **X** using the information from (b)(ii) to (b)(iv).

(1)

(Total for Question 18 = 15 marks)



19 Carbonyl compounds are usually reduced in the laboratory using complex metal hydrides such as lithium tetrahydridoaluminate(III), LiAlH_4 .

The metal hydrides react by supplying hydride ions, H^- , which then react with the carbonyl group to form an intermediate.

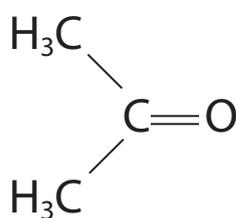
The addition of a strong acid in aqueous solution to the intermediate produces the reduction product.

(a) State the essential condition for using LiAlH_4 .

(1)

(b) Complete the mechanism for the reduction of propanone with LiAlH_4 , showing the structure of the intermediate **and** of the final product. Include curly arrows, and relevant lone pairs and dipoles.

(4)



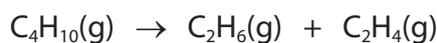
(c) Explain why LiAlH_4 reduces carbonyl compounds but not alkenes, even though both types of compound have π bonds.

(3)

(Total for Question 19 = 8 marks)



20 Cracking reactions are used to obtain more useful compounds from the alkanes found in crude oil. An equation for the cracking of butane is shown.



Thermodynamic data for the compounds in this reaction are given in the table.

| | $\text{C}_4\text{H}_{10}(\text{g})$ | $\text{C}_2\text{H}_6(\text{g})$ | $\text{C}_2\text{H}_4(\text{g})$ |
|---|-------------------------------------|----------------------------------|----------------------------------|
| Standard molar entropy $S^\ominus / \text{JK}^{-1} \text{mol}^{-1}$ | 310.1 | 229.5 | 219.5 |
| Standard molar enthalpy change of formation $\Delta_f H^\ominus / \text{kJ mol}^{-1}$ | -126.5 | -84.7 | +52.2 |

- (a) (i) Calculate the entropy change in the system, $\Delta S_{\text{system}}^\ominus$, for the cracking of butane.
Include a sign and units with your answer.

(2)

- (ii) Calculate the enthalpy change of reaction, $\Delta_r H^\ominus$, for the cracking of butane.
Include a sign and units with your answer.

(2)



(iii) Calculate the entropy change in the surroundings, $\Delta S_{\text{surroundings}}^{\ominus}$, at 298 K for the cracking of butane, using your answer to (a)(ii).
Include a sign and units with your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S_{\text{total}}^{\ominus}$, at 298 K for the cracking of butane, using your answers to (a)(i) and (a)(iii).
Include a sign and units with your answer.

(1)

(v) Calculate the temperature at which the cracking reaction becomes feasible.

(2)

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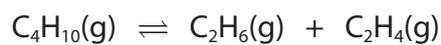
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- (b) 5 mol of butane is cracked at 750 K. At equilibrium, 4.45 mol of ethene is formed and the total pressure is 1.20 atm.



- (i) Give the expression for the equilibrium constant, K_p , for this reaction. (1)

- (ii) Calculate the value of K_p , including units if required. (5)

(Total for Question 20 = 15 marks)

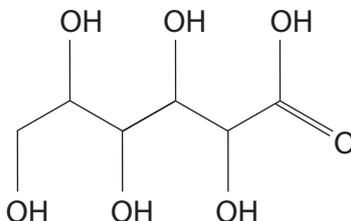
TOTAL FOR SECTION B = 51 MARKS



SECTION C

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

- 21 Gluconic acid is a weak acid which occurs in fruit and honey and is widely used as a food additive.



gluconic acid

- (a) A solution of gluconic acid was prepared by dissolving 4.75 g of the solid in water and making the solution up to 250.0 cm³ in a volumetric flask.

- (i) Write the equation for the acid dissociation constant, K_a , of gluconic acid. Use RCOOH for gluconic acid.

(1)

- (ii) Calculate the pH of the solution of gluconic acid.

$$[M_r(\text{gluconic acid}) = 196 \quad K_a(\text{gluconic acid}) = 1.38 \times 10^{-4} \text{ mol dm}^{-3}]$$

(4)

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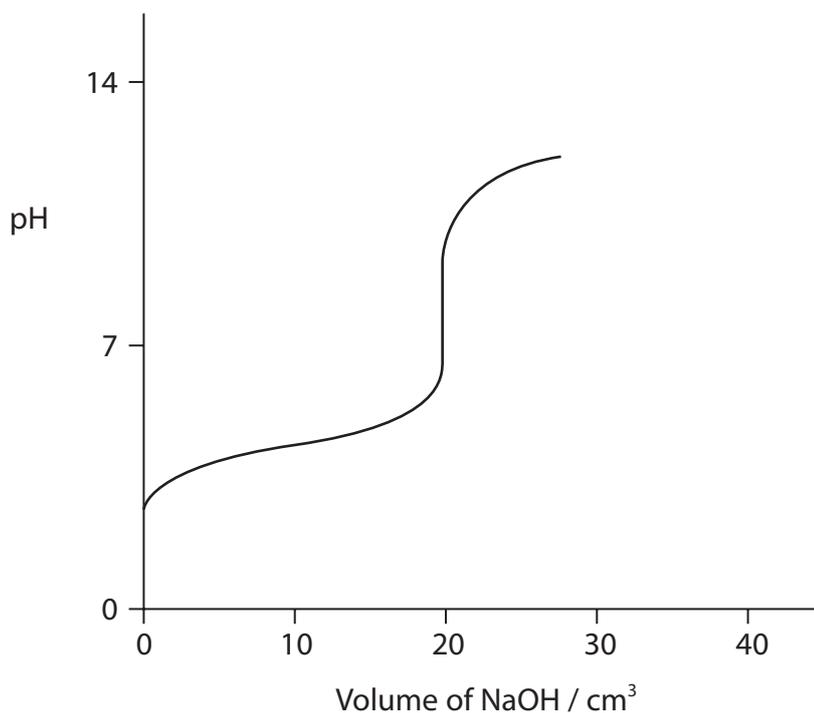
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(b) A solution of $0.105 \text{ mol dm}^{-3}$ sodium hydroxide was titrated against 25.0 cm^3 of the gluconic acid solution prepared in (a).

The titration curve is shown. The curve is **not** to scale.



(i) Explain why phenol red is an appropriate indicator for this titration. Refer to the titration curve and the Data Booklet.

(2)



(ii) Calculate the pH of the titration mixture after the addition of 35.0 cm^3 of sodium hydroxide solution.

The value required **cannot** be obtained from the titration curve in (b).

(5)

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(ii) The concentration of a solution of gluconic acid is 1.55 mol dm^{-3} .

Calculate the number of moles of sodium gluconate that must be added to 1.00 dm^3 of this solution to give a buffer with $\text{pH} = 3.71$.

Assume that the volume of the solution is unchanged.

(3)

(Total for Question 21 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS

TOTAL FOR PAPER = 90 MARKS

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