Cambridge Assessment International Education

Cambridge Pre-U

CANDIDATE NAME									
CENTRE NUMBER						CANDIDATE NUMBER			

0254390540

CHEMISTRY **9791/03**

Paper 3 Part B Written **May/June 2022**

2 hours 15 minutes

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This syllabus is regulated for use in England, Wales and Northern Ireland as a Cambridge International Level 3 Pre-U Certificate.

This document has **16** pages. Any blank pages are indicated.

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1 Liquid methyl methanoate reacts slowly with water in the presence of an acid catalyst.

$$HCOOCH_3 + H_2O \xrightarrow{H^+} HCOOH + CH_3OH$$

A series of experiments is carried out to investigate the kinetics of the reaction.

expt	volume of $HCOOCH_3$ / cm^3	volume of 2.00 mol dm^{-3} HCl(aq) / cm^3	volume of H_2O / cm^3	rate / mol dm^{-3} s^{-1}
1	5.00	10.00	5.00	9.37×10^{-3}
2	5.00	15.00	0.00	1.41×10^{-2}
3	10.00	10.00	0.00	1.87×10^{-2}
4	5.00	5.00	10.00	4.69×10^{-3}

(a) State the type of reaction occurring.

..... [1]

(b) It was found that the order of reaction with respect to water is zero.

Deduce the rate equation for the reaction.
Explain your working, clearly indicating the experiments compared.

rate equation .....

explanation .....

.....

.....

.....

..... [3]

(c) The density of methyl methanoate is 0.974 g cm^{-3}.
Calculate the rate constant for the reaction, using data from experiment 1.
Include units in your answer.
Show your working.

k = ...

units = ...
[3]

(d) State **one** condition that needs to be kept constant for all experiments in order for data in the table to be used to determine the rate constant.

..... [1]

(e) Suggest a two-step mechanism for the reaction which would be consistent with the rate equation you deduced in **(b)**.

step 1 ..... $\xrightarrow{\text{slow}}$ .....

step 2 ..... $\xrightarrow{\text{fast}}$ .....

[2]

(f) A similar series of experiments were carried out to investigate the kinetics of the reaction between $HCOOCH_3(aq)$ and NaOH(aq).

(i) Give the ionic equation for the reaction between $HCOOCH_3(aq)$ and NaOH(aq).

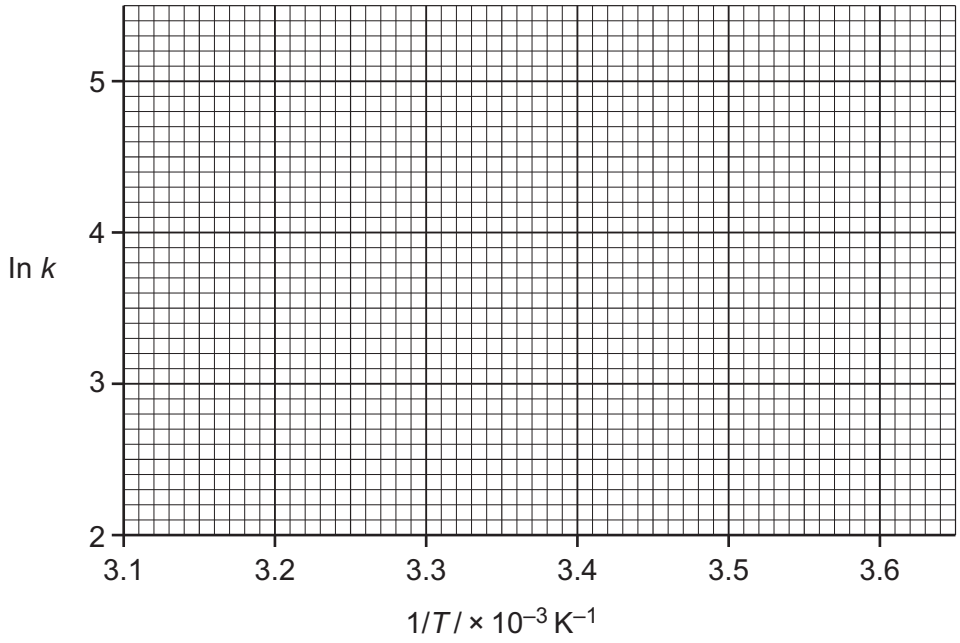
..... [1]

(ii) Equal volumes of $0.200\,mol\,dm^{-3}$ $HCOOCH_3$ and $0.400\,mol\,dm^{-3}$ NaOH solutions were mixed and the initial rate at different temperatures was recorded. From these values the following data was obtained.

T/K	$1/T$ / $\times 10^{-3}\,K^{-1}$	initial rate of reaction / $mol\,dm^{-3}\,s^{-1}$	k / $dm^3\,mol^{-1}\,s^{-1}$	ln k
280	3.57	0.234	11.7	2.46
290	3.45	0.425	21.3	3.06
300	3.33	0.741	37.1	3.61
310	3.23	1.595	79.8	4.38
320	3.13	2.030	102	4.62

Draw a graph of ln k against $1/T$.

Use the relevant equation from the *Data Booklet* to calculate the activation energy, E_a, for this reaction.
Show your working.



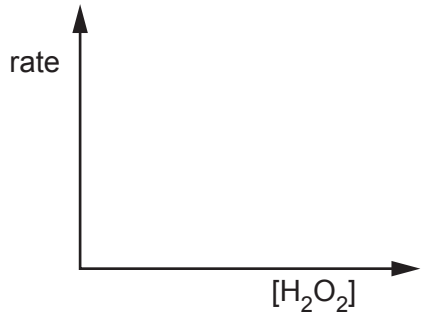
E_a = ... kJ mol^{-1} [4]

(g) The decomposition of hydrogen peroxide, H_2O_2, is catalysed by iodide ions.

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g) \qquad \text{rate} = k[H_2O_2][I^-]$$

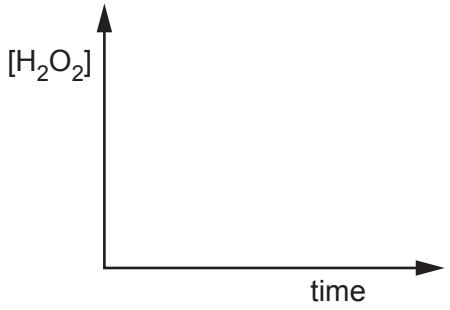
Sketch the shapes of the following graphs for the decomposition of hydrogen peroxide, H_2O_2, catalysed by iodide ions.

(i) Rate against $[H_2O_2]$, assuming an excess of iodide at the start of the reaction.



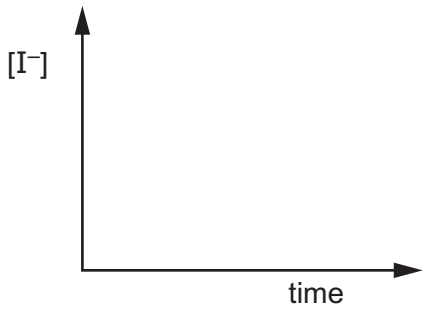
[1]

(ii) $[H_2O_2]$ against time, assuming equimolar amounts of H_2O_2 and I^- at the start of the reaction.



[1]

(iii) $[I^-]$ against time, assuming an excess of H_2O_2 at the start of the reaction.



[1]

[Total: 18]

2 Solid potassium carbonate, K_2CO_3, can be prepared by thermally decomposing potassium hydrogen carbonate, $KHCO_3$.

$$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O \qquad \Delta_r H^{\ominus} = +96.1\,kJ\,mol^{-1}, \quad \Delta_r S^{\ominus} = +208.0\,J\,K^{-1}\,mol^{-1}$$

(a) Standard entropy values for the products are given in the table.

species	$S^{\ominus}$ (298 K) / $J\,K^{-1}\,mol^{-1}$
K_2CO_3	155.5
CO_2	213.6
H_2O	69.9

(i) State why CO_2 has a higher $S^{\ominus}$ than K_2CO_3.

.....

..... [1]

(ii) Suggest why H_2O has a lower $S^{\ominus}$ than K_2CO_3.

.....

.....

..... [1]

(iii) Calculate $S^{\ominus}(KHCO_3)$.
Show your working.

$S^{\ominus}(KHCO_3)$ = ... $J\,K^{-1}\,mol^{-1}$ [2]

(iv) Calculate the minimum temperature, in °C, at which $KHCO_3$ decomposes.
Give your answer to **three** significant figures.
Show your working.

$KHCO_3$ decomposes at ..... °C [3]

(v) Use the relevant equation from the *Data Booklet* to calculate the equilibrium constant, *K*, for the reaction at 250 °C.
Comment on the position of equilibrium at this temperature.
Show your working.

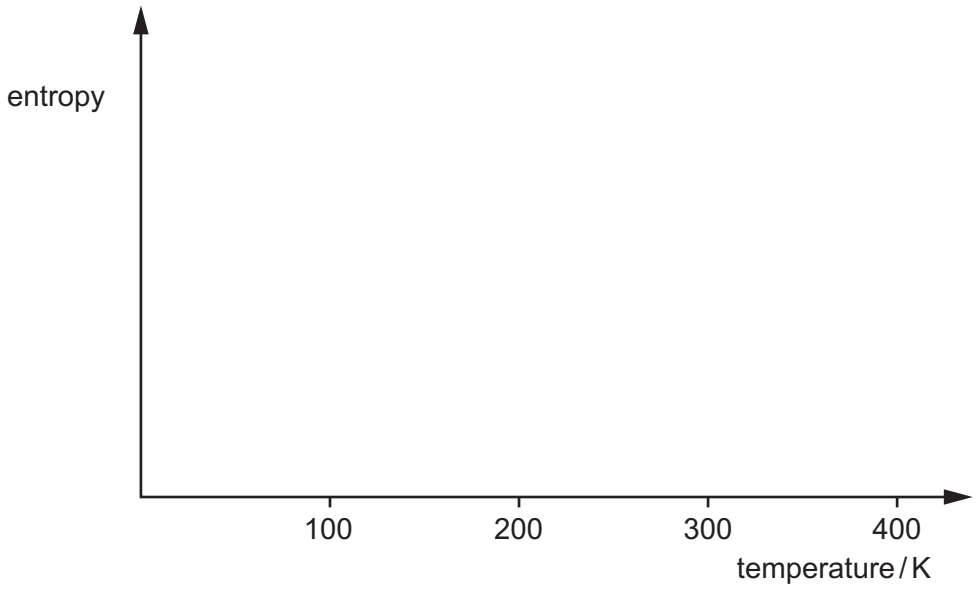
K (250 °C) = ...

Comment .....

.....

.....
[3]

(b) Entropy changes with temperature. Sketch the graph for the entropy of H_2O against temperature on the axes below.



[3]

(c) In a solution of saturated aqueous K_2CO_3 the potassium ion concentration, $[K^+]$, is $1.62\,mol\,dm^{-3}$ at room temperature.

(i) Write an equation to show K_2CO_3 dissolving in water.

..... [1]

(ii) Calculate the solubility of K_2CO_3 in $g\,dm^{-3}$ at room temperature.
Show your working.

solubility of K_2CO_3 = ... $g\,dm^{-3}$ [2]

(iii) Write the expression for $K_{sp}(K_2CO_3)$ and hence calculate $K_{sp}(K_2CO_3)$ at room temperature.
Show your working.

K_{sp} =

K_{sp} = ...
[3]

(iv) Saturated aqueous K_2CO_3 is added dropwise to saturated aqueous potassium chloride, KC*l*.
KC*l* is much less soluble than K_2CO_3.
Suggest what would be observed. Explain your answer.

.....

.....

..... [2]

[Total: 21]

3 Benzene, C_6H_6, is a colourless liquid.

(a) Describe all the bonding in a molecule of benzene.

.....

.....

.....

.....

..... [4]

(b) Benzene was originally thought to have the Kekulé structure, cyclohexa-1,3,5-triene.
Give three pieces of evidence that suggest this is **not** the case, and explain each.

1 .....

.....

.....

.....

2 .....

.....

.....

.....

3 .....

.....

.....

..... [6]

(c) Nitrobenzene, $C_6H_5NO_2$, can be synthesised from benzene.

(i) Draw the mechanism for the reaction.
Include all relevant lone pairs of electrons, dipoles and curly arrows.
Include the role of the catalyst in this mechanism.

[5]

(ii) State the overall equation for this reaction.

..... [1]

(iii) Nitrobenzene is less readily chlorinated than benzene.
Explain why.

.....

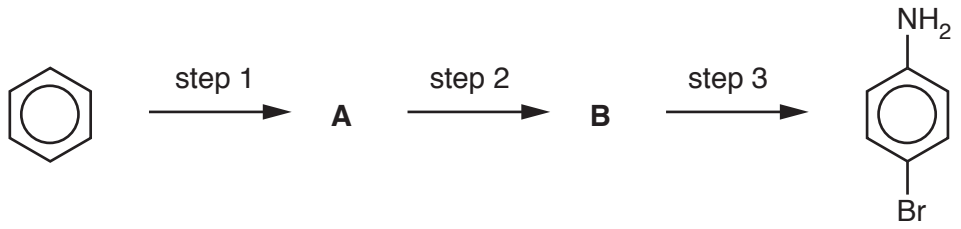
.....

.....

.....

..... [3]

(d) 4-bromophenylamine can be synthesised from benzene in 3 steps. Neither **A** nor **B** is nitrobenzene, $C_6H_5NO_2$.



(i) Suggest structures for compounds **A** and **B**.

A	**B**

[2]

(ii) Suggest reagents for step 1 and step 3.

step 1 .....

step 3 ..... [2]

(iii) Describe the ^1H NMR spectrum of 4-bromophenylamine. Indicate any signals that would disappear following addition of D_2O. You may wish to draw a diagram to help your answer.

.....

.....

.....

..... [3]

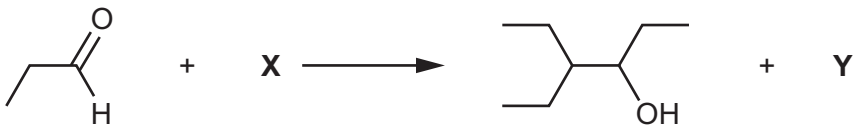
(iv) Deduce the number of peaks that would be seen in the ^{13}C NMR spectrum of 4-bromophenylamine.

..... [1]

[Total: 27]

4 Grignard reagents are useful in organic synthesis for forming C-C bonds.

(a) A Grignard reagent, **X**, is used to synthesise 4-ethylhexan-3-ol from propanal.



(i) Draw the structure of **X**.

[1]

(ii) State the formula of **Y**.

..... [1]

(b) 4-ethylhexan-3-ol has a chiral centre.

(i) Explain why 4-ethylhexan-3-ol has a chiral centre.

.....

..... [1]

(ii) Draw three-dimensional diagrams showing the structures of the enantiomers of 4-ethylhexan-3-ol.

[2]

(iii) The enantiomers of 4-ethylhexan-3-ol are made in this synthesis in equal amounts. State the effect of the product on plane-polarised light, if any.
Explain your answer.

.....

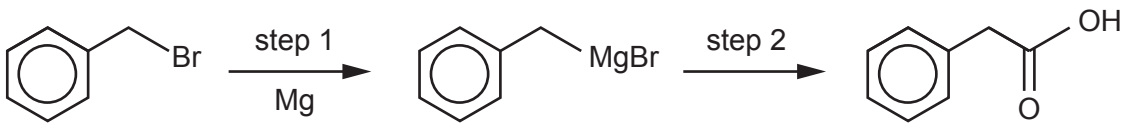
..... [1]

(iv) Explain why the enantiomers of 4-ethylhexan-3-ol in this synthesis are made in equal amounts.

.....

..... [2]

(c) Phenylethanoic acid can be synthesised from (bromomethyl)benzene by forming a Grignard reagent.



(i) State the reagents for step 2 in the order in which they are added.

1 .....

2 ..... [2]

(ii) Phenylethanoic acid can be reduced to 2-phenylethan-1-ol.
Suggest a suitable reducing agent.

..... [1]

(iii) Write an equation for the reduction of phenylethanoic acid to 2-phenylethan-1-ol.
Represent a hydrogen atom from the reducing agent as [H].

..... [2]

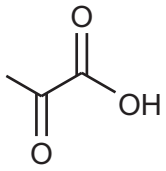
(iv) During this reduction, phenylethanal is converted to 2-phenylethan-1-ol.
Suggest the mechanism for this conversion.
Include all relevant lone pairs of electrons, dipoles and curly arrows.
Use H^- as the reducing agent.

[4]

[Total: 17]

5 Pyruvic acid, $CH_3COCOOH$, is metabolised from glucose in the body.

pyruvic acid



$pK_a = 2.55$

(a) Pyruvic acid is a weak acid.

(i) Calculate the value for K_a.

K_a = ... [1]

(ii) Write an equation to show the dissociation of pyruvic acid and give the expression for K_a.

equation .....

K_a =

[2]

(iii) The pK_a of propanoic acid is 4.88.
Suggest why the pK_a of pyruvic acid is smaller and comment on the relative acidity of the two compounds.

.....

.....

.....

.....

..... [3]

(b) Pyruvic acid reacts with sulfuric acid.
Label the conjugate acid base pairs, indicating the acid and base in each pair.

$CH_3COCOOH$ + H_2SO_4 $\rightleftharpoons$ $CH_3COCOOH_2^+$ + HSO_4^-

.... [1]

(c) Solid sodium hydroxide is added to aqueous pyruvic acid to form a buffer solution.

(i) State what is meant by a *buffer solution*.

.....

..... [2]

(ii) Write the equation for the reaction of solid sodium hydroxide with aqueous pyruvic acid. Include state symbols.

..... [2]

(iii) Calculate the pH of the solution formed when 8.00 g of sodium hydroxide is added to 250 cm^3 of 2.00 mol dm^{-3} pyruvic acid.

pH = ... [6]

[Total: 17]