Cambridge International Examinations
Cambridge Pre-U Certificate

CANDIDATE NAME

CENTRE NUMBER | CANDIDATE NUMBER

CHEMISTRY (PRINCIPAL) **9791/03**

Paper 3 Part B Written **May/June 2017**

2 hours 15 minutes

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.
Electronic calculators may be used.
You may lose marks if you do not show your working, if you do not use appropriate units or if you do not give your answer to appropriate significant figures.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
Total	

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

This document consists of **19** printed pages and **1** blank page.

DC (NF/SG) 129367/4

CAMBRIDGE International Examinations

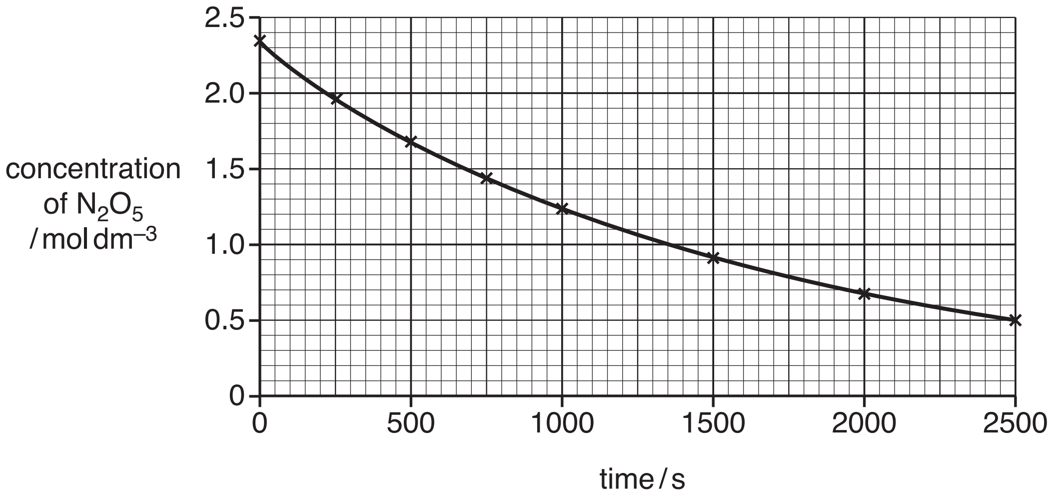
[Turn over

1 Nitrogen forms a wide range of oxides in which it exhibits oxidation states from +1 to +5.

(a) Nitrogen(V) oxide, N_2O_5, is a solid that sublimes just above room temperature. In the gaseous state, N_2O_5 decomposes into nitrogen(IV) oxide, NO_2, and oxygen.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

An investigation of the rate of this decomposition produced the graph shown.



(i) Use the graph to show that the reaction is first order.

You must show your working.

[2]

(ii) Give the rate equation for the reaction.

.... [1]

(iii) Use an appropriate equation from the *Data Booklet* to calculate the value of the rate constant, *k*.

Include the units of *k*.

k = ... [3]
value *units*

(iv) State what is meant by the term *rate-determining step*.

....

.... [1]

(v) A suggested three-step mechanism for the decomposition is shown.

step 1 $N_2O_5 \rightarrow NO_2 + NO_3$

step 2 $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$

step 3 $NO + N_2O_5 \rightarrow 3NO_2$

Show how this is consistent with the equation for the overall reaction.

[1]

(b) Nitrogen(I) oxide, N_2O, commonly called laughing gas, can be prepared by a reaction between hydrogen and nitrogen(II) oxide, NO.

$$H_2(g) + 2NO(g) \rightarrow N_2O(g) + H_2O(l)$$

A rate investigation of this reaction gave the data shown in the table.

$[H_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
0.100	0.500	to be calculated
0.200	0.300	1.84×10^{-6}
0.100	0.300	9.22×10^{-7}
0.200	0.600	7.37×10^{-6}

(i) What is the order of reaction with respect to hydrogen?

order = ... [1]

(ii) What is the order of reaction with respect to nitrogen(II) oxide, NO?

order = ... [1]

(iii) Calculate the missing initial rate in the table.

initial rate = ... mol dm^{-3} s^{-1} [2]

(iv) Give the rate equation for the reaction between H_2 and NO.

.... [1]

(v) Calculate the value of the rate constant, *k*, and give its units.

k = ... [2]
value *units*

[Total: 15]

PLEASE TURN OVER.

2 The hydrogen halides, HF, HCl, HBr and HI all behave as Brønsted-Lowry acids in aqueous solution.

(a) **(i)** State what is meant by the term *Brønsted-Lowry acid*.

....

.... [1]

(ii) Write an equation showing the reaction of HF with water and use your equation to show the acid-base pairs.

....

.... [2]

(b) Two solutions are prepared.

P is made by mixing 50.0 cm^3 of 2.00×10^{-3} mol dm^{-3} HCl(aq) with 50.0 cm^3 of 2.00×10^{-3} mol dm^{-3} NaCl(aq) and has a pH of 3.00. If 1.0 cm^3 of 1.00 mol dm^{-3} HNO_3(aq) is added to **P**, the pH changes to 1.96.

Q is made by mixing 50.0 cm^3 of 0.100 mol dm^{-3} HF(aq) with 50.0 cm^3 of 0.100 mol dm^{-3} NaF(aq) and has a pH of 3.20. If 1.0 cm^3 of 1.00 mol dm^{-3} HNO_3(aq) is added to **Q**, the pH changes to 3.02.

(i) Use the data about **P** to prove that HCl(aq) is a strong acid.

Show your working.

....

....

.... [3]

(ii) Write the expression for the acid dissociation constant, K_a, for hydrofluoric acid, HF(aq).

[1]

(iii) Use the data given about **Q** to calculate the K_a value for hydrofluoric acid and explain qualitatively how **Q** is able to resist change in pH on addition of an acid to a much greater extent than **P**.

Show your working.

....

....

.... [4]

(iv) Use your K_a value for hydrofluoric acid from **(iii)** to calculate the pH of a 0.100 mol dm^{-3} solution of hydrofluoric acid.

If you were unable to calculate a value for K_a you should use a value of 8.20×10^{-4} in this calculation. This is **not** the correct value.

pH = ... [2]

(v) Explain the different acid strengths of HF and HCl in terms of the H–F and H–Cl bond strengths.

....

....

....

.... [2]

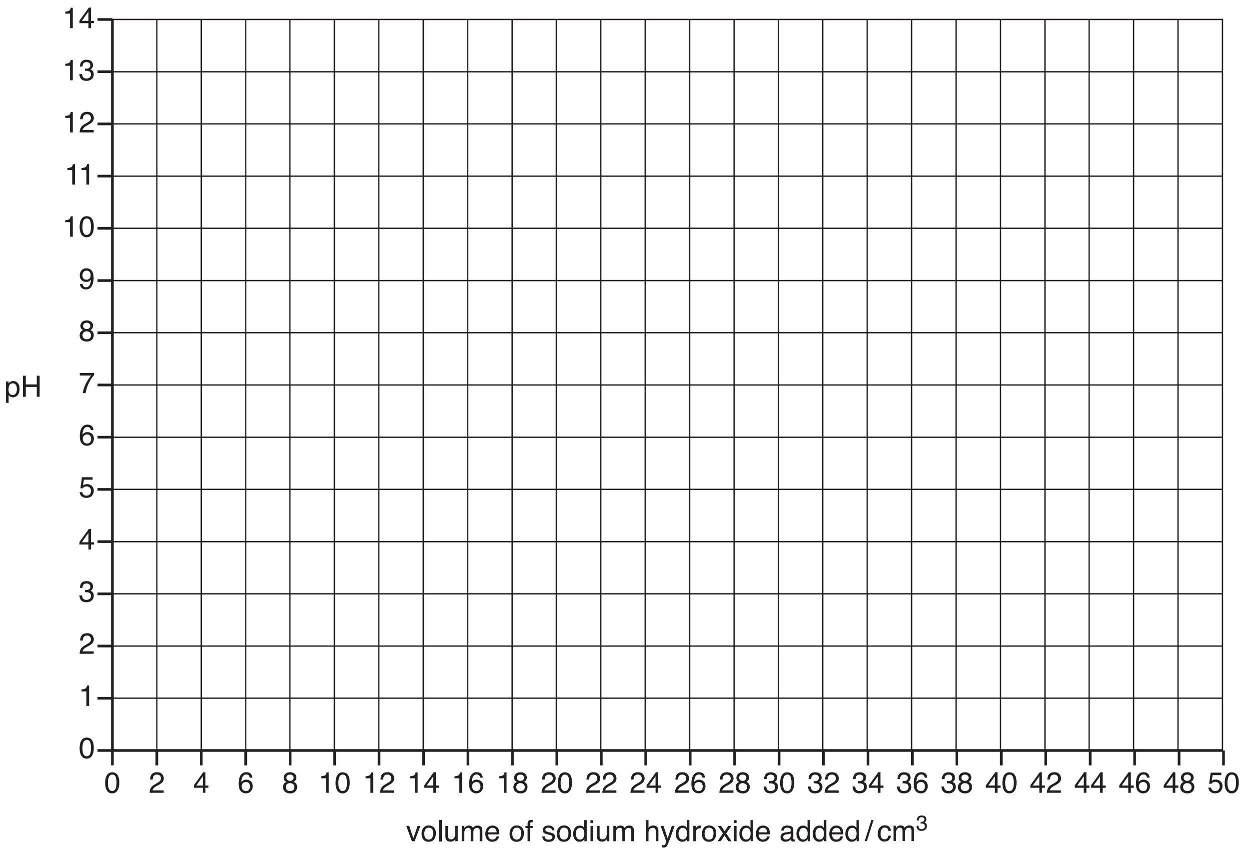
(c) A 0.0500 mol dm^{-3} sodium hydroxide solution is added from a burette to 15.0 cm^3 of a 0.100 mol dm^{-3} solution of hydrofluoric acid until the sodium hydroxide is in excess.

(i) On the axes below sketch the titration curve to represent how the pH changes during the addition of the sodium hydroxide solution to the hydrofluoric acid.

You should ensure that your sketch shows

- the value of the pH at the start,
- the value of the pH at half-equivalence, when half of the HF has been neutralised,
- the volume of NaOH added at half-equivalence,
- the volume of NaOH added at the equivalence point.

You should use appropriate data and any relevant answers from **(b)**.



[5]

(ii) Use the data in the table to choose the most appropriate indicator to identify when the reaction between sodium hydroxide and hydrofluoric acid is complete.

Explain your choice.

indicator	pK_a
malachite green	1.0
bromophenol blue	4.0
phenol red	7.9
alizarin yellow	12.5

....

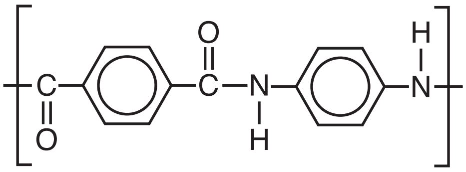
....

....

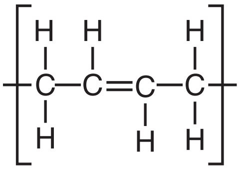
.... [2]

[Total: 22]

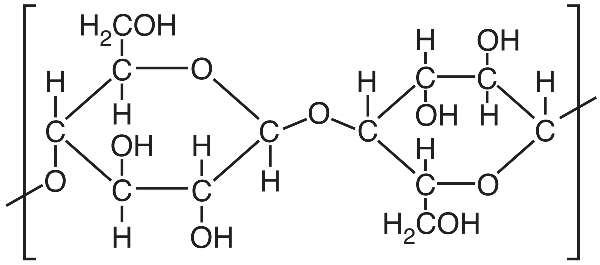
3 **(a)** The structures of three polymers, **A**, **B** and **C**, are shown.



A



B



C

(i) State the type of polymerisation involved in the formation of each of these polymers.

polymer	type of polymerisation
A	
B	
C	

[3]

(ii) State the type of link involved in the formation of polymer **A** and polymer **C**.

polymer	type of link
A	
C	

[2]

(iii) Give the structures of two monomers that could be used to form polymer **A**.

[2]

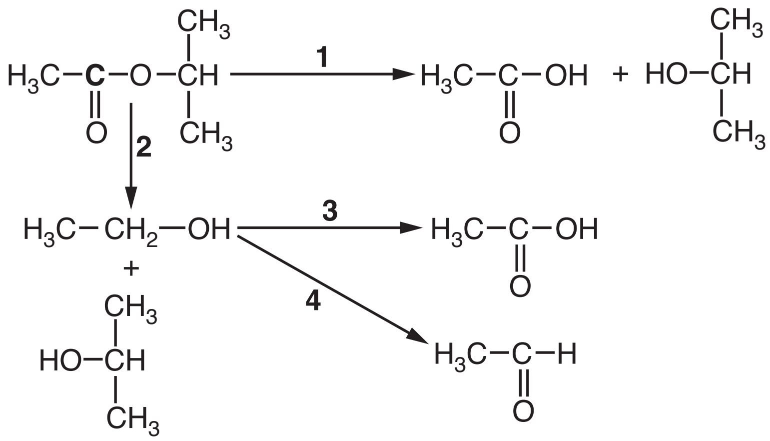
(iv) Polymer **B** is formed by the polymerisation of buta-1,3-diene, $CH_2{=}CHCH{=}CH_2$.

Buta-1,3-diene can also be used to make a synthetic rubber polymer, known as SBR, by 1:1 polymerisation with phenylethene (styrene), $C_6H_5CH{=}CH_2$.

Draw part of the structure of SBR, showing **two** repeat units.

[2]

(b) A series of reactions starting from an ester is shown.



(i) For each of reactions **1** and **2**, identify the change, if any, in the functional group level (FGL) of the carbon atom shown in bold.

Name the reaction types and suggest the reagent(s) needed.

Reaction **1**

change in FGL ....

reaction type ....

reagent(s) ....

Reaction **2**

change in FGL ....

reaction type ....

reagent(s) .... [6]

(ii) Reactions **3** and **4** are both oxidation reactions.

Suggest a suitable oxidising agent that could be used for **both** of these reactions.

.... [1]

(iii) Write an equation for reaction **3**, using [O] to represent the oxidising agent.

.... [2]

(iv) Reaction **3** has a different experimental set up from reaction **4**.

Describe the set up needed for each reaction and explain why a different set up is required.

....

....

....

....

....

.... [3]

[Total: 21]

PLEASE TURN OVER.

4 Copper forms compounds in which it exhibits oxidation states of +1 and +2.

(a) The table shows the lattice energies, LE, of some copper(I) and some copper(II) halides.

copper halide	LE / $kJ\,mol^{-1}$
CuF	–
CuF_2	–3082
CuC*l*	–996
$CuCl_2$	–2811
CuBr	–979
$CuBr_2$	–2763
CuI	–966
CuI_2	–

(i) Explain the trends shown by these lattice energies.

....

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.... [4]

(ii) The actual lattice energy for CuF_2, as calculated from a Born-Haber cycle, has only a small difference from the predicted value derived from the ionic model.

The actual lattice energy for $CuBr_2$, as calculated from a Born-Haber cycle, has a large difference from the predicted value derived from the ionic model.

Explain these observations.

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.... [3]

(b) The stability of copper in different oxidation states can be judged by reference to the electrochemical data shown.

$$2Cu^{+}(aq) \rightleftharpoons Cu(s) + Cu^{2+}(aq) \qquad E^{\ominus}_{cell}(298\,K) = +0.36\,V$$

$$Cu^{2+}(aq) + e^{-} \rightleftharpoons Cu^{+}(aq) \qquad E^{\ominus}(298\,K) = +0.15\,V$$

$$Cu^{2+}(aq) + I^{-} + e^{-} \rightleftharpoons CuI(s) \qquad E^{\ominus}(298\,K) = +0.87\,V$$

(i) Use the electrochemical data to calculate the standard electrode potential, $E^{\ominus}(298\,K)$, for the $Cu^{+}(aq)|Cu(s)$ half-cell. Include a sign in your answer.

$E^{\ominus}(298\,K)$ = ... V [2]

(ii) What would you expect to observe if copper(I) sulfate was added to water?

....

.... [2]

(iii) Using relevant equations in the *Data Booklet*, calculate the equilibrium constant, K_c, at 298 K for the reaction

$$Cu^{2+}(aq) + 2I^{-} \rightleftharpoons CuI(s) + ½I_2(aq)$$

given

$$½I_2(aq) + e^{-} \rightleftharpoons I^{-}(aq) \qquad E^{\ominus}(298\,K) = +0.54\,V$$

K_c = ... [3]

(iv) Suggest one observation you would make if an aqueous solution of iodide ions was added to an aqueous solution of copper(II) ions.

.... [1]

(c) Heating copper(II) carbonate produces a black solid, **W**, with the evolution of carbon dioxide gas.

On heating above 800 °C, **W** decomposes to form a red solid, **X**.

W reacts readily with dilute sulfuric acid, forming a blue solution containing the complex ion **Y**.

A solution containing **Y** reacts with potassium iodide to produce two products, one of which is a white solid containing copper.

Adding concentrated hydrochloric acid to the solution containing **Y** produces a green/yellow solution containing the complex ion **Z**.

- Identify **W**, **X**, **Y** and **Z**.
- Write an equation for each reaction described.
- State the shapes of the complex ions **Y** and **Z**.

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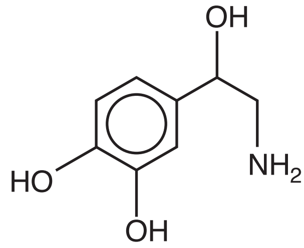
.... [10]

[Total: 25]

5 *R*-(–)-Norepinephrine is produced from the amino acid tyrosine and released into the bloodstream as a hormone as part of the 'fight-or-flight' response to a stressful event. Its structure is shown.



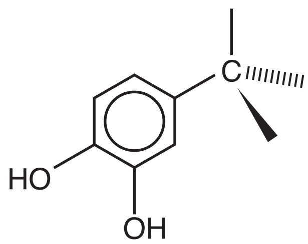
norepinephrine

(a) **(i)** Explain the meaning of the prefix '(–)'.

....

.... [1]

(ii) Complete the 3D structure of *R*-(–)-norepinephrine and explain why it is the '*R*' form.



....

....

....

.... [3]

(b) Proton NMR can be used as an aid to determine the structure of organic compounds.

(i) What property of a ^{1}H nucleus allows it to give rise to an NMR signal?

.... [1]

(ii) Explain how shielding arises and how it affects the position of an NMR signal on the delta chemical shift scale, δ.

....

....

.... [2]

(c) In mammals, norepinephrine is rapidly metabolised to produce a variety of compounds. One of these is known as MHPG. This compound

- is closely related to norepinephrine,
- has the molecular formula $C_9H_{12}O_4$,
- has a tri-substituted benzene ring in which no two substituents are the same,
- reacts in a 1:3 mole ratio with CH_3COCl,
- reacts in a 1:1 mole ratio with NaOH to form a salt but does not react with sodium carbonate,
- has a proton NMR spectrum with signals as described in the table.

signal identifier	integration value	splitting pattern	comments
signals A, B and C	1 each	singlets	disappear on shaking with D_2O
signal D	1	triplet	
signal E	2	doublet	
signal F	3	singlet	
signal G	3	complex	due to the 3 protons on the substituted benzene ring

Use the information given to suggest a structure for MHPG and explain your reasoning.

Explain the origins of the NMR signals A to F, with reference to your suggested structure.

Include equations for the reactions with CH_3COCl and NaOH.

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....

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.... [10]

[Total: 17]

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