Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

2165639790

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2021**

2 hours

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 document has **24** pages. Any blank pages are indicated.

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Answer **all** the questions in the spaces provided.

1 **(a)** An aqueous solution of chromium(III) contains the green $[Cr(H_2O)_6]^{3+}$ complex ion.

(i) Complete the electronic configuration of an isolated, gaseous Cr^{3+} ion.

$1s^2$ ..... [1]

(ii) Define the term *complex ion*.

.....

..... [1]

(b) $[Cr(H_2O)_6]^{3+}(aq)$ shows some similar chemical properties to $[Co(H_2O)_6]^{2+}(aq)$.

Samples of $[Cr(H_2O)_6]^{3+}$ are reacted separately with either NaOH(aq), $H_2O_2(aq)$, or excess $NH_3(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the chromium species formed. State the type of reaction taking place in each case.

reagent added to $[Cr(H_2O)_6]^{3+}(aq)$	formula of chromium species formed	type of reaction
NaOH(aq)		
$H_2O_2(aq)$		
an excess of $NH_3(aq)$		

[5]

(c) $[Cr(H_2O)_6]^{2+}$ and $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ are both complexes of chromium(II) and have different colours.

Explain why the colours of these complexes are different.

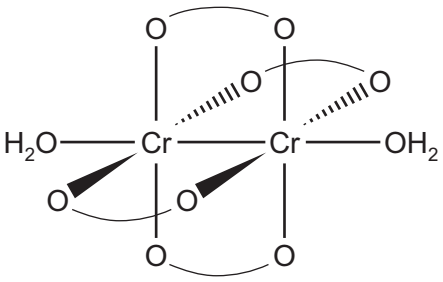
.....

.....

.....

..... [2]

(d) The structure of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ is shown. Ethanoate ions act as ligands in this complex. The ethanoate ligand, $CH_3CO_2^-$, is shown as .



(i) Water and ethanoate ions behave as different types of ligand in this complex.

Suggest an explanation for this statement.

.....

..... [1]

(ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number .....

geometry around Cr atom .....
[1]

(iii) State the type of bond between the two atoms in the Cr–Cr bond.

..... [1]

(e) The $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ complex reacts with aqueous acid to form $Cr^{2+}(aq)$ ions.

$Cr^{2+}(aq)$ ions react with $O_2(aq)$ under acidic conditions. $Cr^{3+}(aq)$ ions are formed.

Use the *Data Booklet* to answer the following questions.

(i) Construct an ionic equation for the reaction of $Cr^{2+}(aq)$ with $O_2(aq)$ under acidic conditions.

..... [2]

(ii) Calculate $E^{\ominus}_{cell}$ for the reaction in **(e)(i)**.

$E^{\ominus}_{cell}$ = ... V [1]

[Total: 15]

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[Turn over

2 **(a)** State and explain the trend observed in the thermal stability of the Group 2 nitrates.

.....

.....

.....

.....

..... [3]

(b) **(i)** Lead(II) nitrate, $Pb(NO_3)_2$, decomposes on heating in a similar manner to the Group 2 nitrates.

Write an equation for the decomposition of lead(II) nitrate.

..... [1]

(ii) Suggest how the ease of decomposition of $Pb(NO_3)_2$ would compare to that of $Ba(NO_3)_2$. Explain your answer. You may find it useful to refer to the *Data Booklet*.

.....

..... [1]

(c) **(i)** Barium ethanedioate, BaC_2O_4, decomposes on heating to produce barium oxide and a mixture of two different gases.

Construct an equation for the decomposition of barium ethanedioate.

..... [1]

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(ii) An impure sample of BaC_2O_4, of mass 0.500 g, is added to 50.0 cm^3 of 0.0200 mol dm^{-3} acidified $MnO_4^-(aq)$, an excess. A redox reaction takes place and all the BaC_2O_4 reacts.

The resulting solution, containing unreacted acidified MnO_4^-, is titrated with 0.0500 mol dm^{-3} $Fe^{2+}(aq)$.

The end-point is reached when 30.40 cm^3 of 0.0500 mol dm^{-3} $Fe^{2+}(aq)$ has been added.

$$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.
[M_r: BaC_2O_4, 225.3]

percentage by mass of BaC_2O_4 = ... [4]

(d) Barium hydroxide, $Ba(OH)_2$, is completely dissociated in aqueous solution.

Calculate the pH of 0.120 mol dm^{-3} $Ba(OH)_2(aq)$ at 298 K.

pH = ... [2]

[Total: 12]

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[Turn over

3 (a) (i) Define the term *standard electrode potential*.

.....

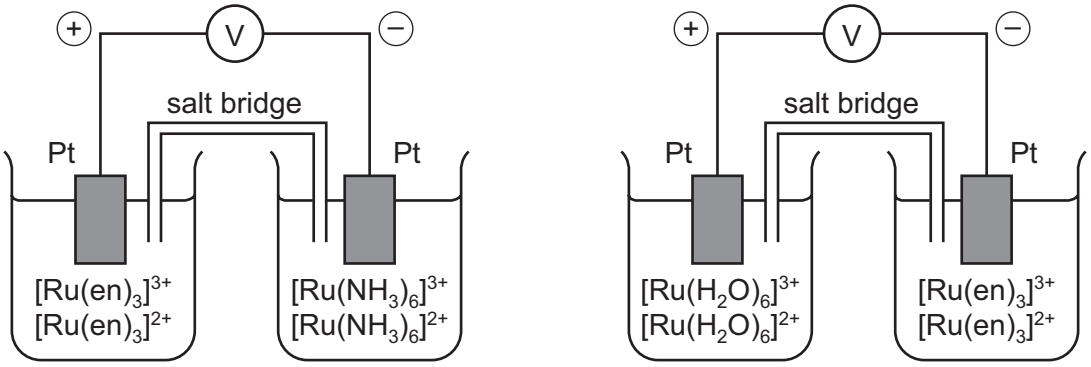
.....

..... [2]

Three redox systems, **A**, **B** and **C**, are shown. The ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is represented by en.

A	$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+}$
B	$[Ru(NH_3)_6]^{3+} + e^- \rightleftharpoons [Ru(NH_3)_6]^{2+}$
C	$[Ru(en)_3]^{3+} + e^- \rightleftharpoons [Ru(en)_3]^{2+}$

Two electrochemical cells are set up to compare the standard electrode potentials, $E^\ominus$, of three half-cells. The diagrams show the relative potential of each electrode.

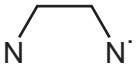


(ii) Use this information to complete the table by adding the labels **A**, **B** and **C** to deduce the order of $E^\ominus$ for the three half-cells.

$E^\ominus$	redox system
most negative	
↑	
least negative	

[1]

(iii) The complex $[Ru(en)_3]^{3+}$ shows stereoisomerism. The ligand en is bidentate.

Draw three-dimensional diagrams to show the two isomers of $[Ru(en)_3]^{3+}$. Represent the ligand en by using 

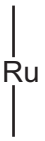
.

Name the type of stereoisomerism.

isomer 1



isomer 2



type of stereoisomerism .....

[3]

(b) (i) An electrochemical cell consists of a Br_2/Br^- half-cell and a Ag^+/Ag half-cell, under standard conditions.

Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$. Deduce the direction of electron flow in the wire through the voltmeter between these two half-cells.

$E^{\ominus}_{cell}$ = ... V

direction of electron flow from ..... to ..... [1]

(ii) Water is added to the Ag^+/Ag half-cell in **(b)(i)**.

Suggest the effect of this addition on the E_{cell}. Place a tick (✓) in the appropriate box.

less positive	no change	more positive

Explain your answer.

.....

.....

..... [2]

(c) Silver bromide, AgBr, dissolves in an aqueous solution of $S_2O_3^{2-}$ ions to form the complex ion $[Ag(S_2O_3)_2]^{3-}$. The $S_2O_3^{2-}$ ions act as monodentate ligands.

equilibrium 1 $AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

(i) Define the term *ligand*.

.....

..... [1]

(ii) Write an expression for the equilibrium constant, K_c, for equilibrium 1.

K_c =

[1]

(iii) Some additional data are given about the dissolution of AgBr in $S_2O_3^{2-}(aq)$.

equilibrium constant	numerical value
solubility product, K_{sp}, of AgBr	5.4×10^{-13}
stability constant, K_{stab}, of $[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

Use your answer to **(c)(ii)** and these data to calculate K_c for equilibrium 1. Include the units for K_c.

K_c = ... units ..... [2]

(d) The numerical values for the stability constants, K_{stab}, of two other silver(I) complexes are given.

silver(I) complex	numerical value of K_{stab}
$[Ag(CN)_2]^-$	5.3×10^{18}
$[Ag(NH_3)_2]^+$	1.6×10^7

An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of $CN^-(aq)$, $NH_3(aq)$ and $S_2O_3^{2-}(aq)$. The mixture is left to reach equilibrium.

Deduce the relative concentrations of $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer.

..... > ..... > .....

highest concentration lowest concentration

.....

..... [2]

[Total: 15]

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4 (a) (i) Define the term *lattice energy*.

.....

.....

..... [2]

(ii) Use the following data to calculate a value for the enthalpy change of solution of copper(II) chloride, $CuCl_2(s)$. You might find it helpful to construct an energy cycle.

enthalpy change of hydration of Cl^- = –378 kJ mol^{-1}
enthalpy change of hydration of Cu^{2+} = –2099 kJ mol^{-1}
lattice energy of $CuCl_2(s)$ = –2824 kJ mol^{-1}

enthalpy change of solution of $CuCl_2(s)$ = ... kJ mol^{-1} [2]

(iii) The enthalpy change of hydration of Ca^{2+} is –1579 kJ mol^{-1}.

Use the *Data Booklet* to suggest why there is a big difference in the values of ΔH_{hyd} for Ca^{2+} and Cu^{2+}.

.....

.....

..... [2]

(b) (i) Identify the substances formed at the anode and at the cathode during the electrolysis of saturated $CaCl_2(aq)$.

at the anode .....

at the cathode .....
[1]

(ii) Calcium can be produced by the electrolysis of molten calcium chloride, $CaCl_2(l)$.

Calculate the mass, in g, of Ca formed when a current of 0.75A passes through $CaCl_2(l)$ for 60 minutes.
[A_r: Ca, 40.1]

mass of Ca = ... g [2]

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(c) (i) Explain what is meant by the term *entropy of a system*.

.....

..... [1]

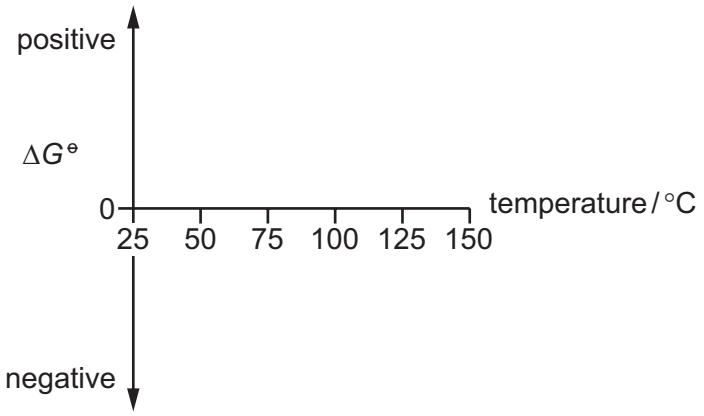
(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change, ΔS.

process	ΔS is negative	ΔS is zero	ΔS is positive
NaC*l* dissolving in water			
water solidifying to ice			

[1]

(iii) The evaporation of one mole of water has a standard Gibbs free energy change, $\Delta G^{\ominus}$, of +8.6 kJ at 25 °C.

Sketch a graph on the axes to show how $\Delta G^{\ominus}$ changes for this process between 25 °C and 150 °C at 101 kPa.



[2]

(d) The reaction between A and B is feasible at low temperatures but is **not** feasible at high temperatures.

$$A + B \rightleftharpoons C + D$$

Deduce the signs of ΔH and ΔS for this reaction and explain why the feasibility changes with temperature.

sign of ΔH = ... sign of ΔS = ...

.....

.....

.....

..... [2]

[Total: 15]

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5 **(a)** Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

..... > ..... > .....

most basic least basic

.....

.....

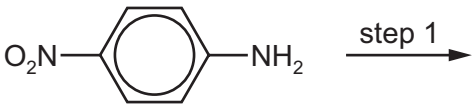
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.....

..... [4]

(b) The dye **R** can be synthesised from 4-nitrophenylamine in two steps.

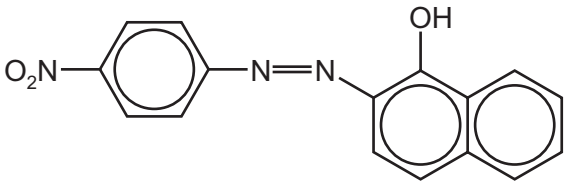
4-nitrophenylamine



Q

step 2

R



(i) Deduce and draw the structure of the organic salt **Q** in the box. [1]

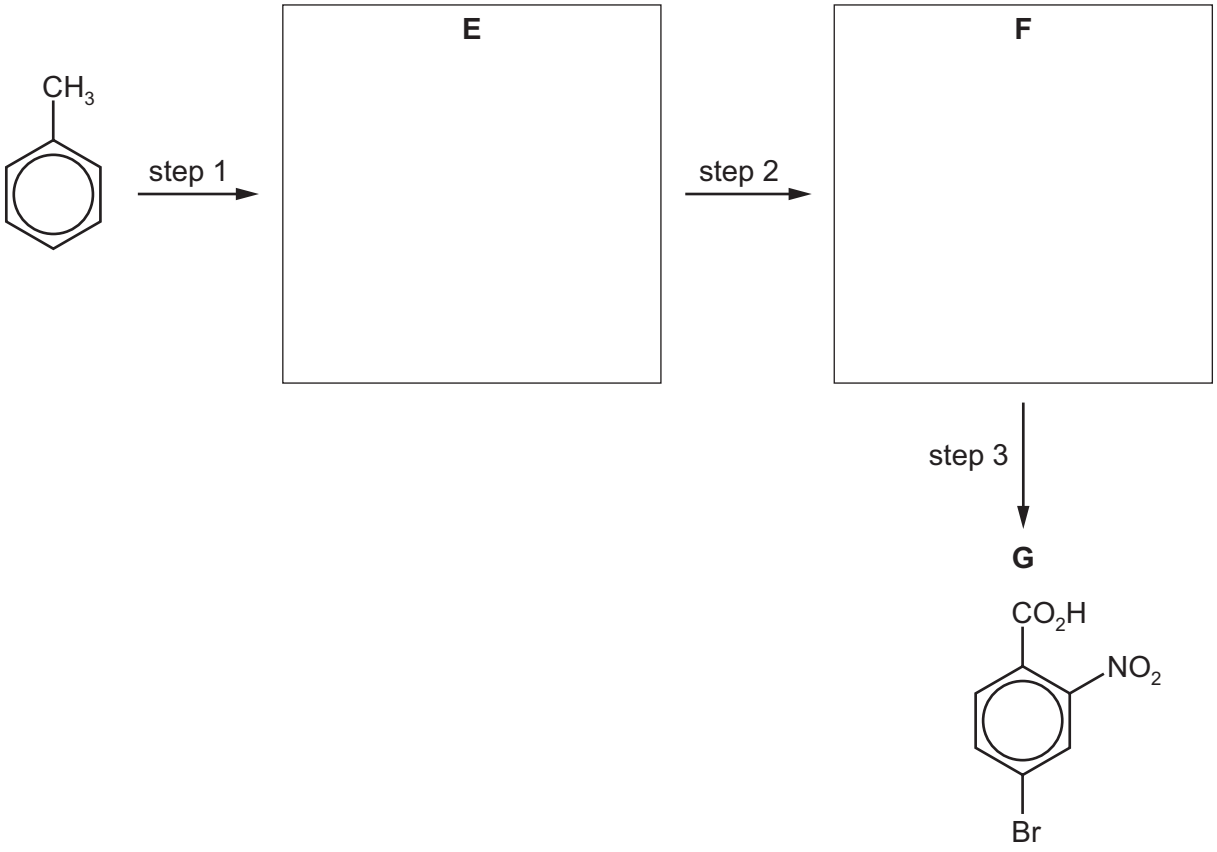
(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 .....

step 2 .....

[2]

(c) Compound **G** can be synthesised from methylbenzene in three steps.



(i) Give the systematic name of compound **G**.

..... [1]

(ii) Deduce the identities of **E** and **F** and draw their structures in the boxes. [2]

(iii) Suggest reagents and conditions for each of steps 1 to 3 in **(c)**.

step 1 .....

step 2 .....

step 3 .....

[3]

[Total: 13]

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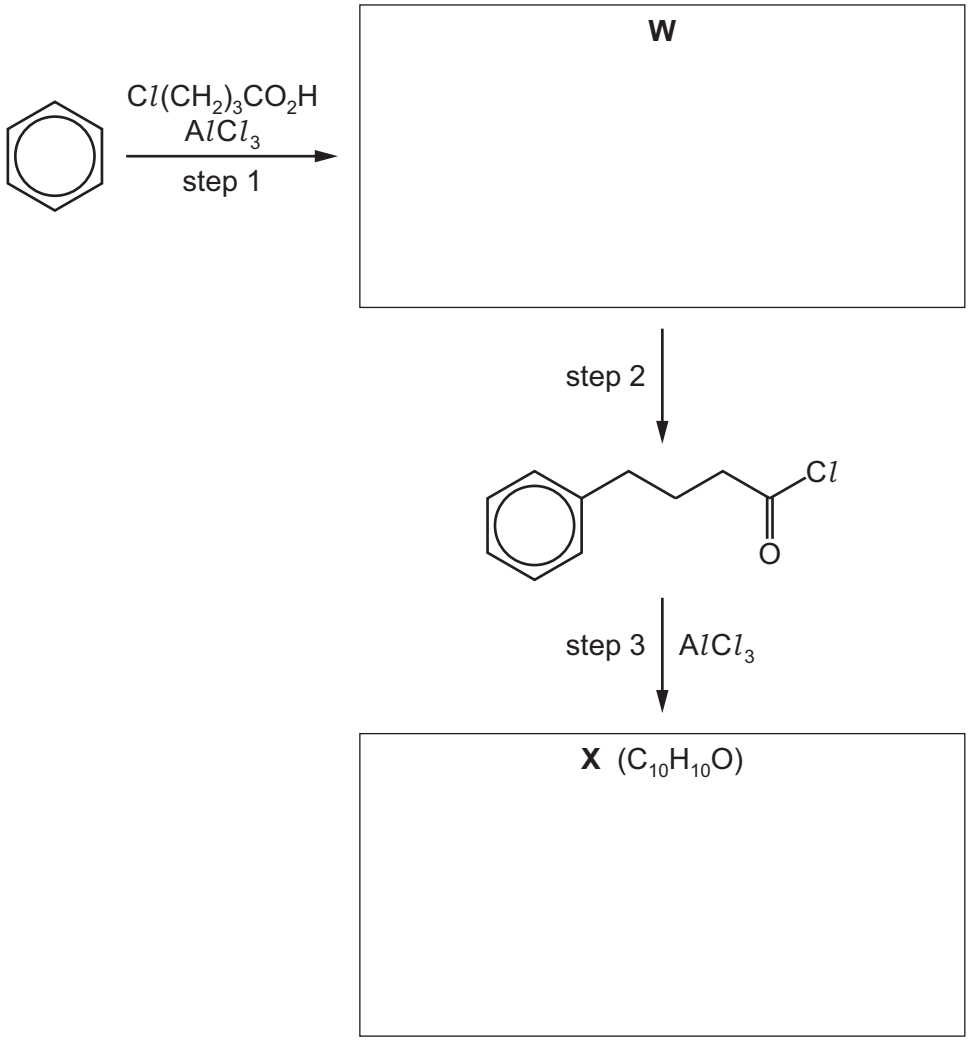
6 **(a)** There are four possible structural isomers of C_8H_{10} that contain a benzene ring.

Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

isomer 1 three peaks in ^{13}C NMR	isomer 2 four peaks in ^{13}C NMR
isomer 3 five peaks in ^{13}C NMR	isomer 4 six peaks in ^{13}C NMR

[4]

(b) A three-step synthesis of **X** ($C_{10}H_{10}O$) from benzene is suggested as shown.



(i) Step 1 is the alkylation of benzene by electrophilic substitution.
Use R–C*l* to represent $Cl(CH_2)_3CO_2H$.

Write an equation for the formation of an electrophile from R–C*l* and $AlCl_3$.

..... [1]

(ii) Deduce and draw the structures of **W** and **X** in the boxes. [2]

(iii) Suggest the reagents and conditions for step 2.

..... [1]

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(iv) Complete the mechanism for the reaction of benzene with the electrophile formed in **(b)(i)**.

Include all relevant charges and curly arrows showing the movement of electron pairs.

Draw the structure of the intermediate.



[3]

[Total: 11]

7 **(a)** In aqueous solution, chlorine dioxide, ClO_2, reacts with hydroxide ions as shown.

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

A series of experiments is carried out using different concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.020	0.030	7.20×10^{-4}
2	0.020	0.120	2.88×10^{-3}
3	0.050	0.030	4.50×10^{-3}

(i) Explain the term *order of reaction*.

.....

..... [1]

(ii) Use the data in the table to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning.

.....

.....

.....

.....

.....

..... [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction.

rate = ... [1]

(iv) Use your rate equation and the data from experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

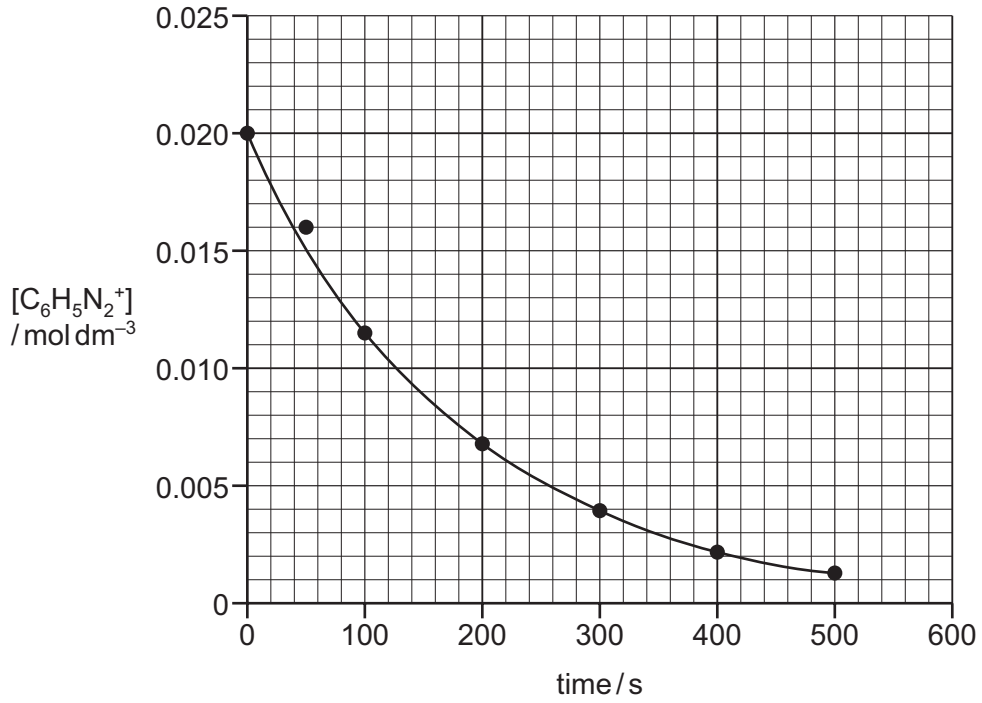
k = ... units ..... [2]

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Question 7 continues on the next page.

(b) The decomposition of benzenediazonium ions, $C_6H_5N_2^+$, using a large excess of water, is a first-order reaction.

The graph shows the results obtained.



(i) Draw the structure of the organic product formed in this reaction.

[1]

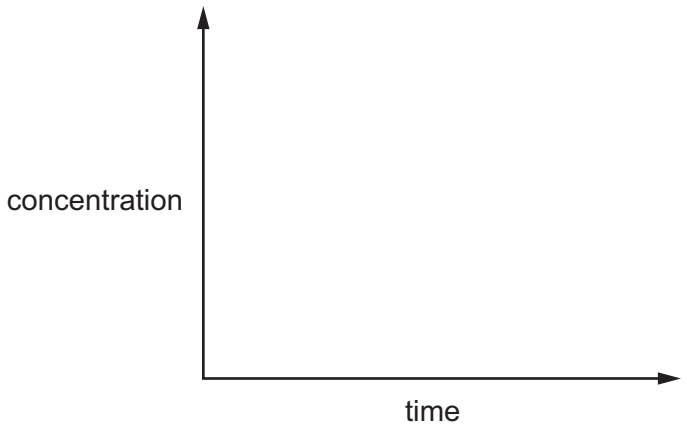
(ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

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

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(c) Sketch a concentration–time graph for a **zero-order** reaction.

Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (✓) in the appropriate box in the table.



successive half-lives decrease	no change in successive half-lives	successive half-lives increase

[1]

[Total: 9]

8 **(a)** State and explain the relative rate of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

..... > ..... > .....

fastest slowest

.....

.....

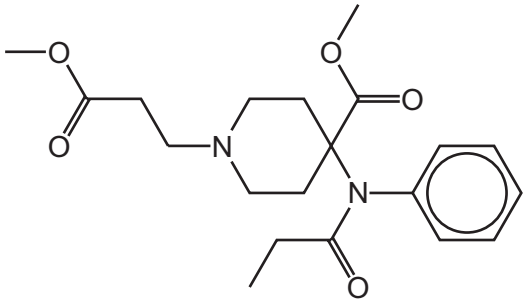
.....

.....

..... [3]

(b) The drug remifentanil is shown.

remifentanil

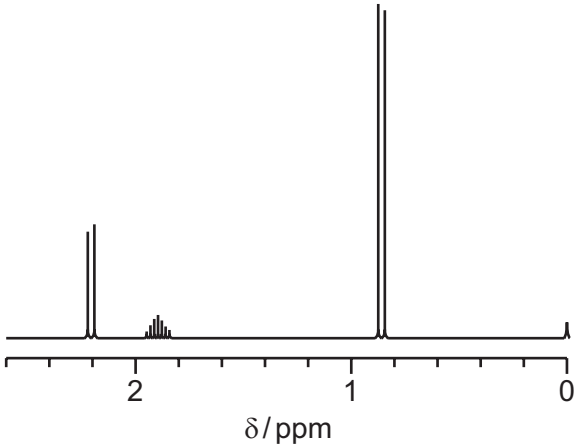


Remifentanil is **completely** hydrolysed under acidic conditions. Three different organic compounds are formed.

Draw the structures for these organic compounds in the boxes.

[3]

(c) Compound **Y**, $C_5H_{10}O_2$, reacts with Na_2CO_3(aq) to evolve bubbles of gas. The proton (^{1}H) NMR spectrum of compound **Y** in D_2O is shown.



(i) Use this information to suggest a structure for **Y**.

[1]

(ii) Use the *Data Booklet*, the proton (^{1}H) NMR spectrum and your answer to **(c)(i)** to complete the table.

chemical shift (δ)	environment of proton	splitting pattern	number of ^{1}H atoms responsible for the peak
0.95			
1.90			
2.20			

[3]

[Total: 10]

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