



# Cambridge International AS & A Level

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CENTRE  
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## 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.



## 2

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

1 (a) An aqueous solution of chromium(III) contains the green  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex ion.

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

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

(ii) Define the term *complex ion*.

.....  
 ..... [1]

(b)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  shows some similar chemical properties to  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ .

Samples of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  are reacted separately with either  $\text{NaOH}(\text{aq})$ ,  $\text{H}_2\text{O}_2(\text{aq})$ , or excess  $\text{NH}_3(\text{aq})$ .

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 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ | formula of chromium species formed | type of reaction |
|----------------------------------------------------------------------|------------------------------------|------------------|
| $\text{NaOH}(\text{aq})$                                             |                                    |                  |
| $\text{H}_2\text{O}_2(\text{aq})$                                    |                                    |                  |
| an excess of $\text{NH}_3(\text{aq})$                                |                                    |                  |

[5]

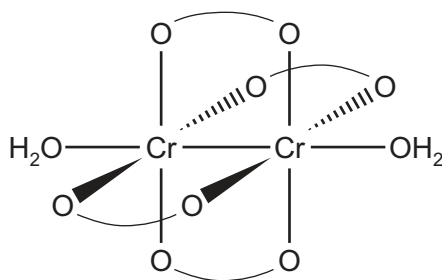
(c)  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$  are both complexes of chromium(II) and have different colours.

Explain why the colours of these complexes are different.

.....  
 .....  
 .....  
 ..... [2]

3

- (d) The structure of  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$  is shown. Ethanoate ions act as ligands in this complex. The ethanoate ligand,  $\text{CH}_3\text{CO}_2^-$ , is shown as  $\text{O} \text{---} \text{O}$ .



- (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  $[\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$  complex reacts with aqueous acid to form  $\text{Cr}^{2+}(\text{aq})$  ions.

$\text{Cr}^{2+}(\text{aq})$  ions react with  $\text{O}_2(\text{aq})$  under acidic conditions.  $\text{Cr}^{3+}(\text{aq})$  ions are formed.

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

- (i) Construct an ionic equation for the reaction of  $\text{Cr}^{2+}(\text{aq})$  with  $\text{O}_2(\text{aq})$  under acidic conditions.

..... [2]

- (ii) Calculate  $E_{\text{cell}}^\ominus$  for the reaction in (e)(i).

$E_{\text{cell}}^\ominus = \dots\dots\dots \text{V}$  [1]

[Total: 15]

4

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

.....

.....

.....

.....

..... [3]

- (b) (i) Lead(II) nitrate,  $\text{Pb}(\text{NO}_3)_2$ , 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  $\text{Pb}(\text{NO}_3)_2$  would compare to that of  $\text{Ba}(\text{NO}_3)_2$ . Explain your answer. You may find it useful to refer to the *Data Booklet*.

.....

..... [1]

- (c) (i) Barium ethanedioate,  $\text{BaC}_2\text{O}_4$ , decomposes on heating to produce barium oxide and a mixture of two different gases.

Construct an equation for the decomposition of barium ethanedioate.

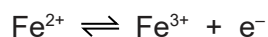
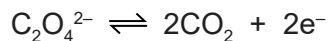
..... [1]

5

- (ii) An impure sample of  $\text{BaC}_2\text{O}_4$ , of mass 0.500 g, is added to  $50.0\text{ cm}^3$  of  $0.0200\text{ mol dm}^{-3}$  acidified  $\text{MnO}_4^-$ (aq), an excess. A redox reaction takes place and all the  $\text{BaC}_2\text{O}_4$  reacts.

The resulting solution, containing unreacted acidified  $\text{MnO}_4^-$ , is titrated with  $0.0500\text{ mol dm}^{-3}$   $\text{Fe}^{2+}$ (aq).

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



Calculate the percentage by mass of  $\text{BaC}_2\text{O}_4$  in the 0.500 g impure sample. Show your working.

[ $M_r$ :  $\text{BaC}_2\text{O}_4$ , 225.3]

percentage by mass of  $\text{BaC}_2\text{O}_4$  = ..... [4]

- (d) Barium hydroxide,  $\text{Ba}(\text{OH})_2$ , is completely dissociated in aqueous solution.

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

pH = ..... [2]

[Total: 12]

6

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

.....

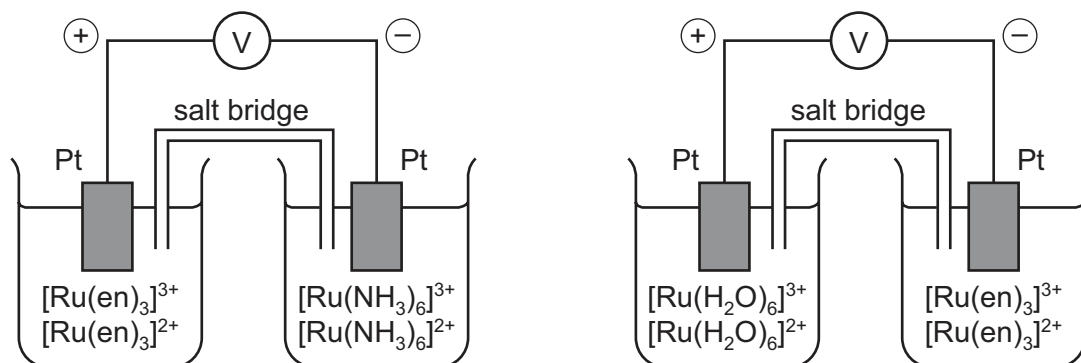
.....

..... [2]

Three redox systems, **A**, **B** and **C**, are shown. The ligand 1,2-diaminoethane,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ , is represented by en.

|          |                                                                                                                 |
|----------|-----------------------------------------------------------------------------------------------------------------|
| <b>A</b> | $[\text{Ru}(\text{H}_2\text{O})_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ |
| <b>B</b> | $[\text{Ru}(\text{NH}_3)_6]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{NH}_3)_6]^{2+}$               |
| <b>C</b> | $[\text{Ru}(\text{en})_3]^{3+} + \text{e}^- \rightleftharpoons [\text{Ru}(\text{en})_3]^{2+}$                   |

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



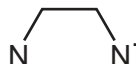
(ii) Use this information to complete the table by adding the labels **A**, **B** and **C** to deduce the order of  $E^\circ$  for the three half-cells.

| $E^\circ$      | redox system |
|----------------|--------------|
| most negative  |              |
| ↑              |              |
| least negative |              |

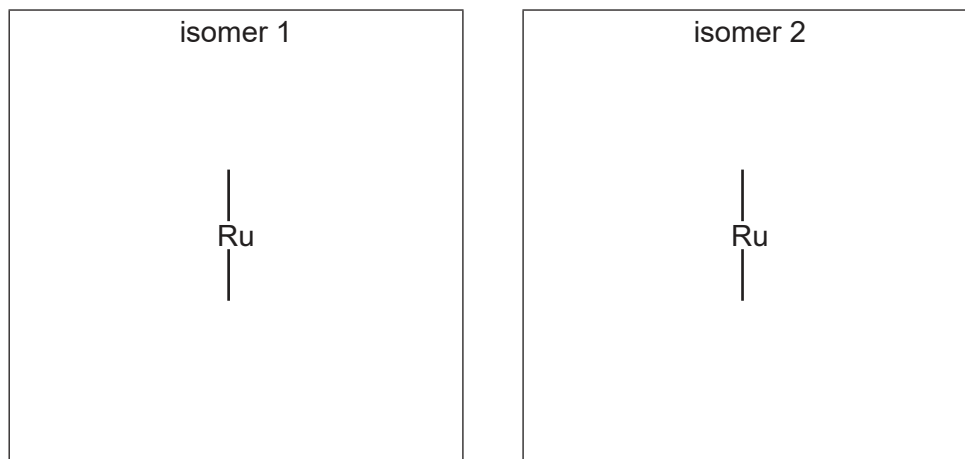
[1]

7

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

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

Name the type of stereoisomerism.



type of stereoisomerism ..... [3]

- (b) (i) An electrochemical cell consists of a  $\text{Br}_2/\text{Br}^-$  half-cell and a  $\text{Ag}^+/\text{Ag}$  half-cell, under standard conditions.

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

$E_{\text{cell}}^\ominus = \dots\dots\dots \text{ V}$

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

- (ii) Water is added to the  $\text{Ag}^+/\text{Ag}$  half-cell in (b)(i).

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

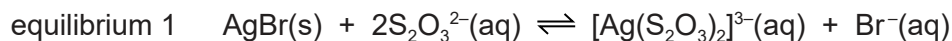
| less positive | no change | more positive |
|---------------|-----------|---------------|
|               |           |               |

Explain your answer.

.....  
 .....  
 ..... [2]

8

- (c) Silver bromide, AgBr, dissolves in an aqueous solution of  $\text{S}_2\text{O}_3^{2-}$  ions to form the complex ion  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ . The  $\text{S}_2\text{O}_3^{2-}$  ions act as monodentate ligands.



- (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  $\text{S}_2\text{O}_3^{2-}(\text{aq})$ .

| equilibrium constant                                                                  | numerical value       |
|---------------------------------------------------------------------------------------|-----------------------|
| solubility product, $K_{\text{sp}}$ , of AgBr                                         | $5.4 \times 10^{-13}$ |
| stability constant, $K_{\text{stab}}$ , of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ | $2.9 \times 10^{13}$  |

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

$$K_c = \text{..... units .....} [2]$$

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

| silver(I) complex                | numerical value of $K_{\text{stab}}$ |
|----------------------------------|--------------------------------------|
| $[\text{Ag}(\text{CN})_2]^{-}$   | $5.3 \times 10^{18}$                 |
| $[\text{Ag}(\text{NH}_3)_2]^{+}$ | $1.6 \times 10^7$                    |

An aqueous solution containing  $\text{Ag}^{+}$  is added to a solution containing equal concentrations of  $\text{CN}^{-}(\text{aq})$ ,  $\text{NH}_3(\text{aq})$  and  $\text{S}_2\text{O}_3^{2-}(\text{aq})$ . The mixture is left to reach equilibrium.

Deduce the relative concentrations of  $[\text{Ag}(\text{CN})_2]^{-}$ ,  $[\text{Ag}(\text{NH}_3)_2]^{+}$  and  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$  present in the resulting mixture. Explain your answer.

..... > ..... > .....  
 highest concentration lowest concentration

.....  
 ..... [2]

[Total: 15]

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,  $\text{CuCl}_2(\text{s})$ . You might find it helpful to construct an energy cycle.

enthalpy change of hydration of  $\text{Cl}^-$  =  $-378 \text{ kJ mol}^{-1}$   
 enthalpy change of hydration of  $\text{Cu}^{2+}$  =  $-2099 \text{ kJ mol}^{-1}$   
 lattice energy of  $\text{CuCl}_2(\text{s})$  =  $-2824 \text{ kJ mol}^{-1}$

enthalpy change of solution of  $\text{CuCl}_2(\text{s})$  = .....  $\text{kJ mol}^{-1}$  [2]

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

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

.....  
 .....  
 ..... [2]

(b) (i) Identify the substances formed at the anode and at the cathode during the electrolysis of saturated  $\text{CaCl}_2(\text{aq})$ .

at the anode .....  
 at the cathode ..... [1]

(ii) Calcium can be produced by the electrolysis of molten calcium chloride,  $\text{CaCl}_2(\text{l})$ .

Calculate the mass, in g, of Ca formed when a current of 0.75A passes through  $\text{CaCl}_2(\text{l})$  for 60 minutes.  
 [ $A_r$ : Ca, 40.1]

mass of Ca = ..... g [2]

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

.....  
 ..... [1]

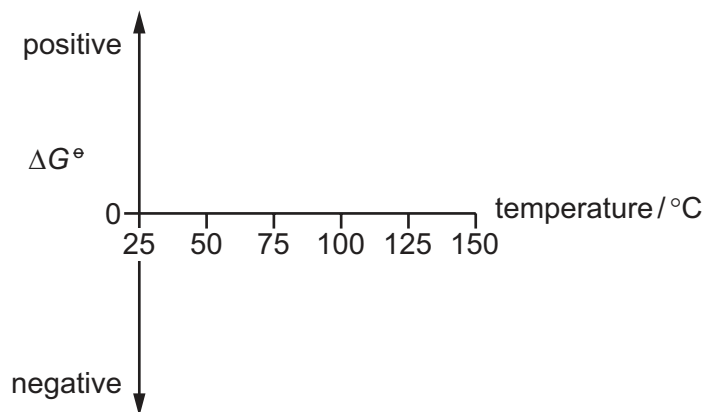
(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change,  $\Delta S$ .

| process                  | $\Delta S$ is negative | $\Delta S$ is zero | $\Delta S$ is positive |
|--------------------------|------------------------|--------------------|------------------------|
| NaCl dissolving in water |                        |                    |                        |
| water solidifying to ice |                        |                    |                        |

[1]

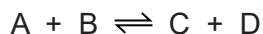
(iii) The evaporation of one mole of water has a standard Gibbs free energy change,  $\Delta G^\circ$ , of +8.6 kJ at 25 °C.

Sketch a graph on the axes to show how  $\Delta G^\circ$  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.



Deduce the signs of  $\Delta H$  and  $\Delta S$  for this reaction and explain why the feasibility changes with temperature.

sign of  $\Delta H$  = ..... sign of  $\Delta S$  = .....

.....  
 .....  
 .....  
 ..... [2]

[Total: 15]

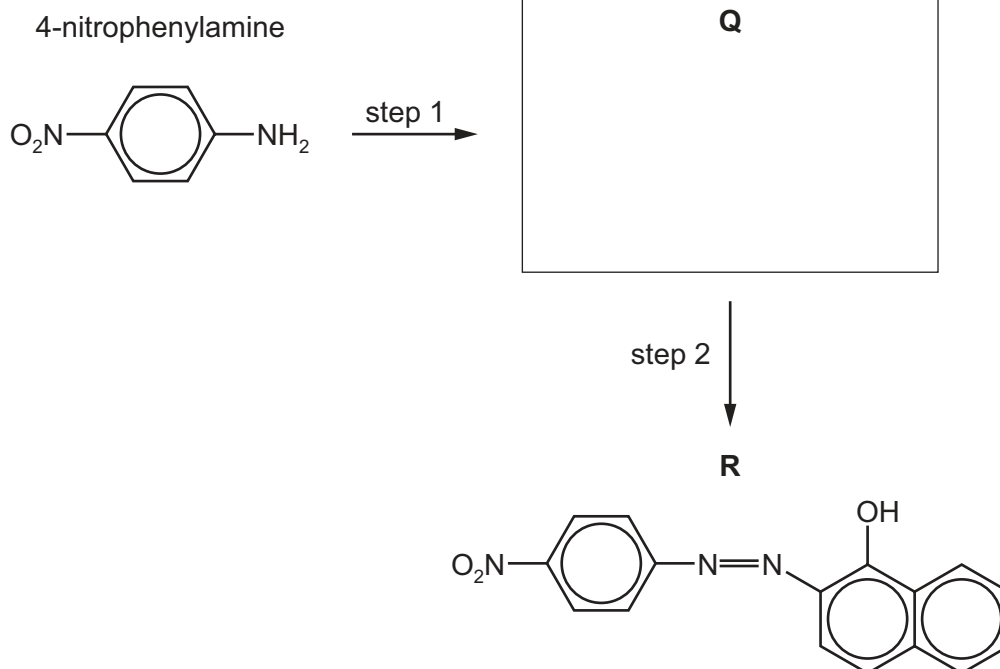
- 5 (a)** Describe and explain the relative basicities of phenylamine, ethylamine and 4-nitrophenylamine.

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

most basic                      least basic

..... [4]

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



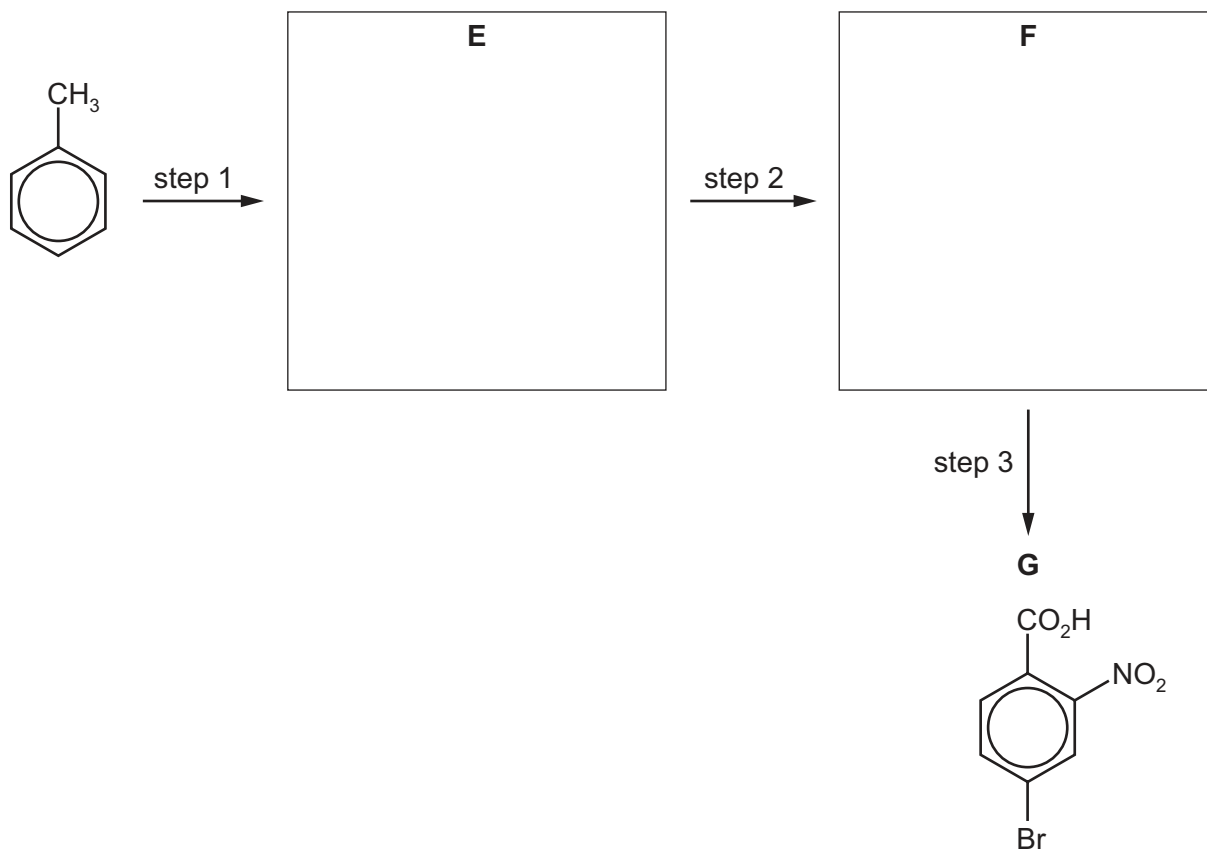
- (i) Deduce and draw the structure of the organic salt **Q** in the box. [1]
- (ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 .....

step 2 .....

12

(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]

13

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

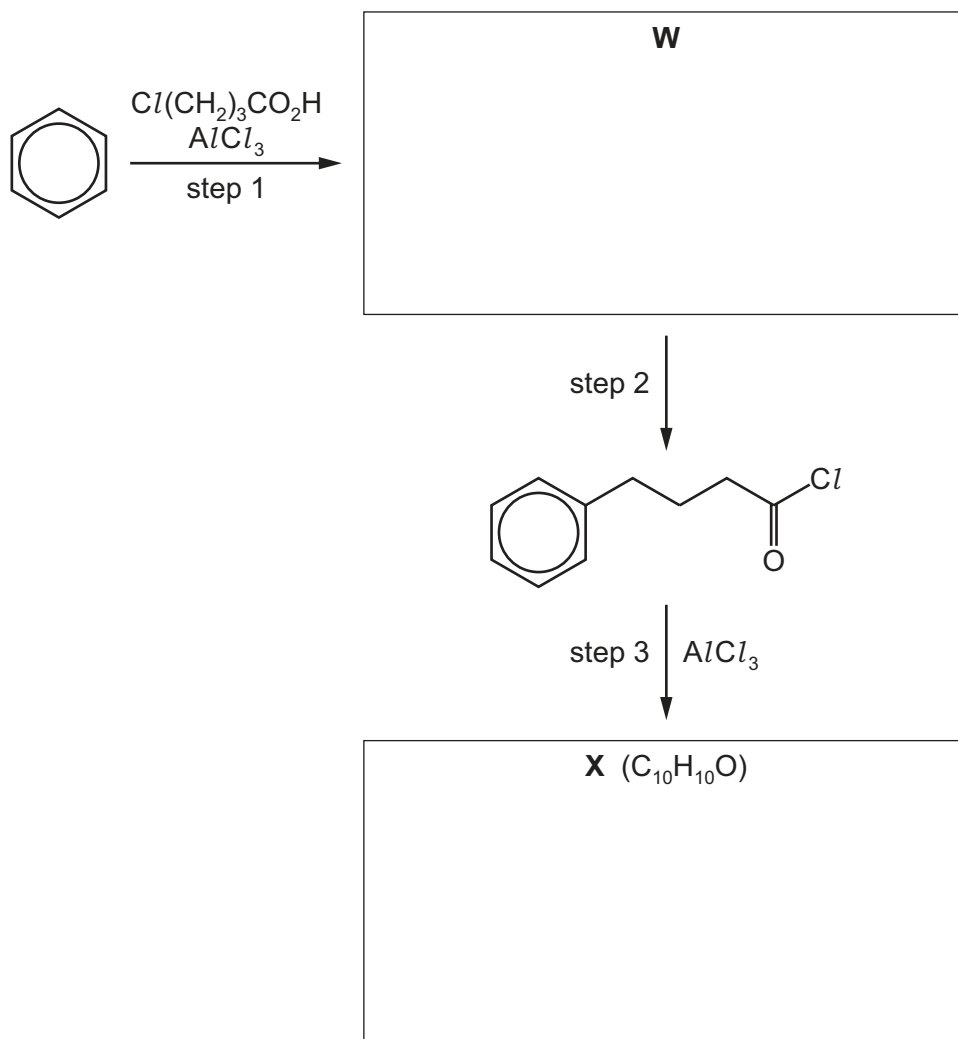
Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 ( $^{13}C$ ) NMR spectrum of each compound is given.

|                                                                             |                                                                            |
|-----------------------------------------------------------------------------|----------------------------------------------------------------------------|
| isomer 1<br><br><br><br><br><br><br><br><br><br>three peaks in $^{13}C$ NMR | isomer 2<br><br><br><br><br><br><br><br><br><br>four peaks in $^{13}C$ NMR |
| isomer 3<br><br><br><br><br><br><br><br><br><br>five peaks in $^{13}C$ NMR  | isomer 4<br><br><br><br><br><br><br><br><br><br>six peaks in $^{13}C$ NMR  |

[4]

14

(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  $R-Cl$  to represent  $Cl(CH_2)_3CO_2H$ .

Write an equation for the formation of an electrophile from  $R-Cl$  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.

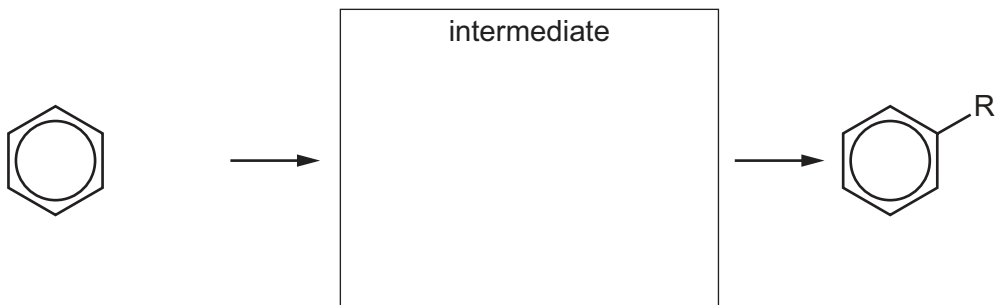
..... [1]

15

- (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,  $\text{ClO}_2$ , reacts with hydroxide ions as shown.



A series of experiments is carried out using different concentrations of  $\text{ClO}_2$  and  $\text{OH}^-$ . The table shows the results obtained.

| experiment | $[\text{ClO}_2]$<br>/ $\text{mol dm}^{-3}$ | $[\text{OH}^-]$<br>/ $\text{mol dm}^{-3}$ | initial rate<br>/ $\text{mol dm}^{-3} \text{min}^{-1}$ |
|------------|--------------------------------------------|-------------------------------------------|--------------------------------------------------------|
| 1          | 0.020                                      | 0.030                                     | $7.20 \times 10^{-4}$                                  |
| 2          | 0.020                                      | 0.120                                     | $2.88 \times 10^{-3}$                                  |
| 3          | 0.050                                      | 0.030                                     | $4.50 \times 10^{-3}$                                  |

- (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,  $\text{ClO}_2$  and  $\text{OH}^-$ .

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  $k$ .

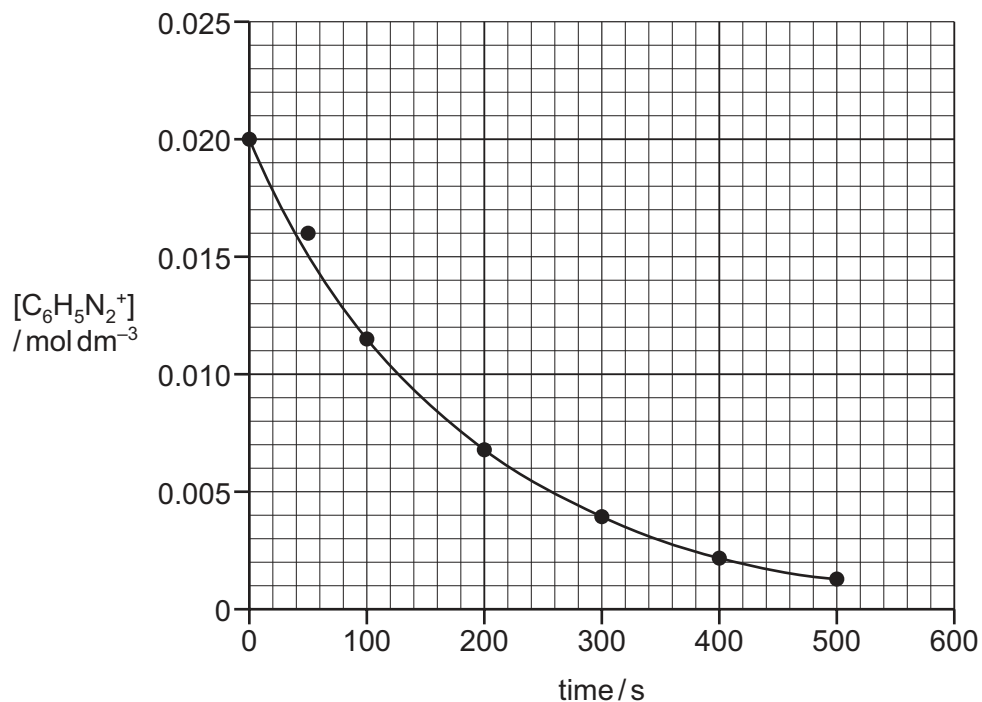
$k$  = ..... units ..... [2]

**Question 7 continues on the next page.**

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- (b) The decomposition of benzenediazonium ions,  $\text{C}_6\text{H}_5\text{N}_2^+$ , 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]

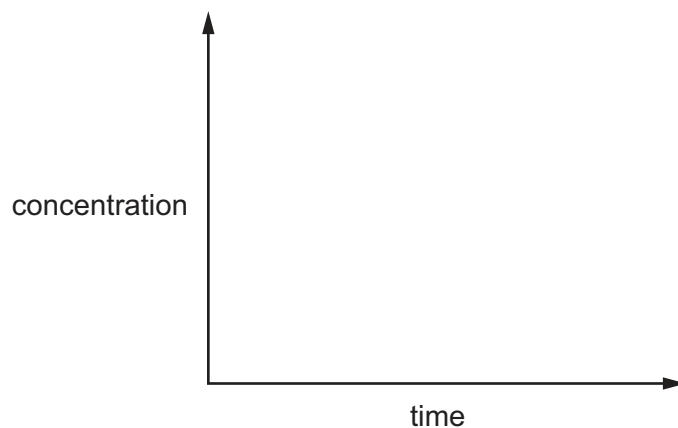
- (ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

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

19

(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<br>decrease | no change in<br>successive half-lives | successive half-lives<br>increase |
|-----------------------------------|---------------------------------------|-----------------------------------|
|                                   |                                       |                                   |

[1]

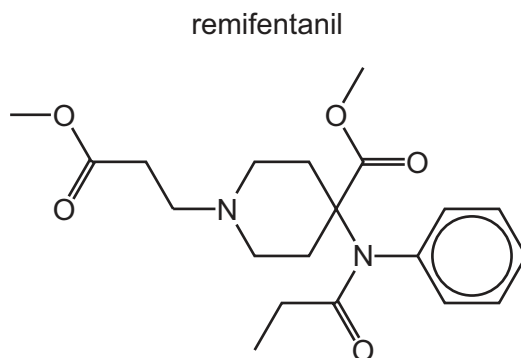
[Total: 9]

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

..... [3]

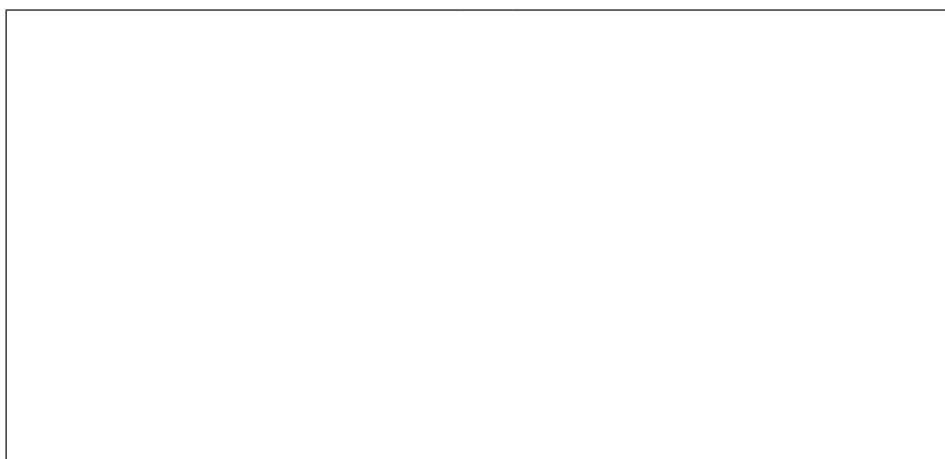
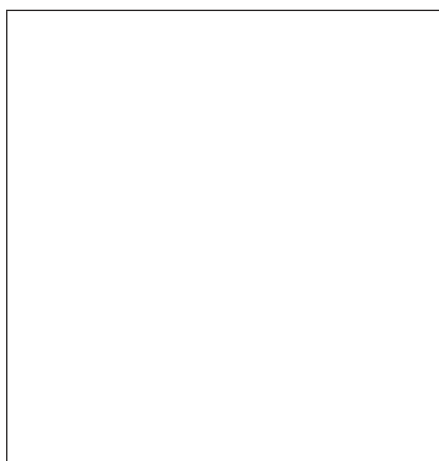
21

(b) The drug remifentanyl is shown.



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

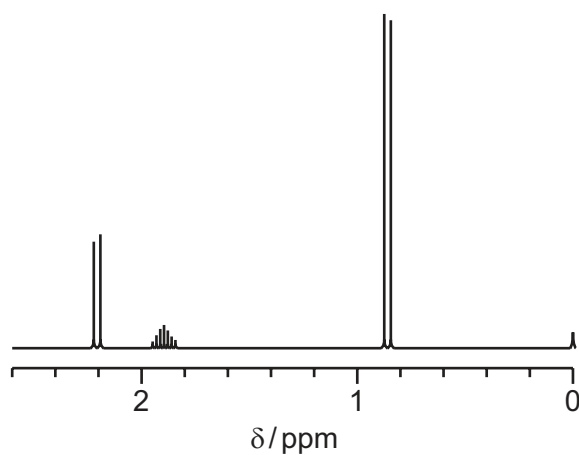
Draw the structures for these organic compounds in the boxes.



[3]

22

- (c) Compound **Y**,  $C_5H_{10}O_2$ , reacts with  $Na_2CO_3(aq)$  to evolve bubbles of gas. The proton ( $^1H$ ) 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 ( $^1H$ ) NMR spectrum and your answer to (c)(i) to complete the table.

| chemical shift ( $\delta$ ) | environment of proton | splitting pattern | number of $^1H$ atoms responsible for the peak |
|-----------------------------|-----------------------|-------------------|------------------------------------------------|
| 0.95                        |                       |                   |                                                |
| 1.90                        |                       |                   |                                                |
| 2.20                        |                       |                   |                                                |

[3]

[Total: 10]



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