

# Cambridge International AS & A Level

| CANDIDATE<br>NAME |  |  |                     |  |  |
|-------------------|--|--|---------------------|--|--|
| CENTRE<br>NUMBER  |  |  | CANDIDATE<br>NUMBER |  |  |

974299879

CHEMISTRY 9701/42

Paper 4 A Level Structured Questions

October/November 2023

2 hours

You must answer on the question paper.

No additional materials are needed.

### 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 guestion 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 and use appropriate units.

#### INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets.
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has 28 pages. Any blank pages are indicated.

1 Propanone,  $CH_3COCH_3$ , reacts with iodine,  $I_2$ , in the presence of an acid catalyst.

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

The rate equation for this reaction is shown.

rate = 
$$k[CH_3COCH_3][H^+]$$

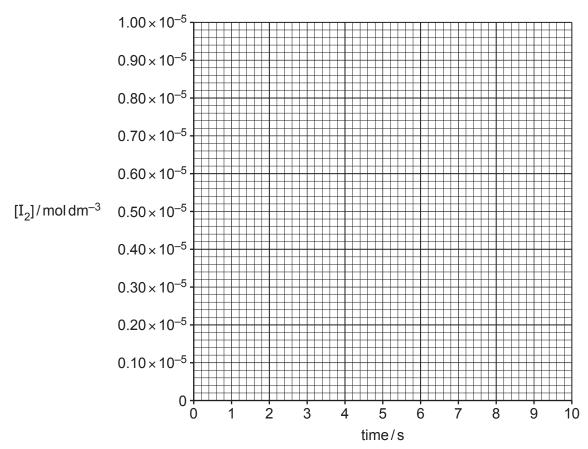
(a) Complete Table 1.1 to describe the order of the reaction.

Table 1.1

| order of the reaction with respect to [CH <sub>3</sub> COCH <sub>3</sub> ] |  |  |
|--|--|--|
| order of the reaction with respect to $[{\rm I_2}]$                        |  |  |
| order of the reaction with respect to [H <sup>+</sup> ]                    |  |  |
| overall order of the reaction  |  |  |

[2]

- (b) An experiment is performed using a large excess of CH $_3$ COCH $_3$  and a large excess of H $^+$ (aq). The initial concentration of I $_2$  is 1.00 × 10 $^{-5}$  mol dm $^{-3}$ . The initial rate of decrease in the I $_2$  concentration is 2.27 × 10 $^{-7}$  mol dm $^{-3}$  s $^{-1}$ .
  - (i) Use the axes to draw a graph of  $[I_2]$  against time for the first 10 seconds of the reaction.





| (ii) | State whether it is possible to calculate the numerical value of the rate constant, $k$ , for |
|------|---|
|      | this reaction from your graph. Explain your answer.   |

(c) The experiment is repeated at a different temperature. The initial concentrations of  $H^+$  ions,  $I_2$  and  $CH_3COCH_3$  are all  $0.200\,\mathrm{mol\,dm^{-3}}$ .

The value of k at this temperature is  $2.31 \times 10^{-5} \,\mathrm{mol}^{-1} \,\mathrm{dm}^3 \,\mathrm{s}^{-1}$ .

Calculate the initial rate of this reaction.

rate = ..... 
$$moldm^{-3}s^{-1}$$
 [1]

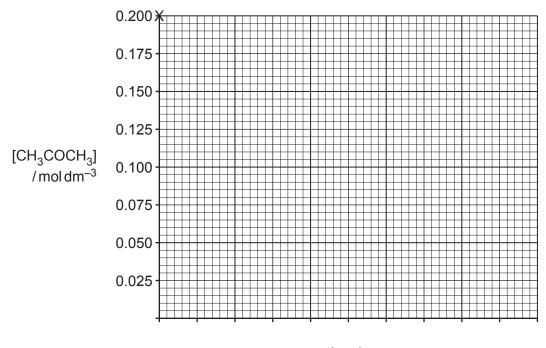
(d) The experiment is repeated using an excess of H<sup>+</sup>(aq). The new rate equation is shown.

rate = 
$$k_1$$
[CH<sub>3</sub>COCH<sub>3</sub>]

(i) The value of  $k_1$  is  $1.1 \times 10^{-3}$  s<sup>-1</sup>. Calculate the value of the half-life,  $t_{\frac{1}{2}}$ .

$$t_{\frac{1}{2}} = \dots s [1]$$

(ii) Use your answer to (i) to draw a graph of [CH<sub>3</sub>COCH<sub>3</sub>] against time for this reaction. The initial value of [CH<sub>3</sub>COCH<sub>3</sub>] on your graph should be 0.200 mol dm<sup>-3</sup>. The final value of [CH<sub>3</sub>COCH<sub>3</sub>] on your graph should be 0.0250 mol dm<sup>-3</sup>.







| ( | (e) | A four-ste   | p mechanism | is suggested | for the  | overall | reaction. |
|---|-----|--------------|-------------|--------------|----------|---------|-----------|
| ۱ |     | , Alloui Sic | p moonamom  | is suggested | וטו נווכ | Ovcian  | reaction  |

$$\mathsf{CH_3COCH_3} + \mathsf{I_2} \to \mathsf{CH_3COCH_2I} + \mathsf{H^+} + \mathsf{I^-} \qquad \qquad \mathsf{rate} = k[\mathsf{CH_3COCH_3}][\mathsf{H^+}]$$

Part of this mechanism is shown.

step 1: 
$$CH_3COCH_3 + H^+ \rightarrow CH_3C^+(OH)CH_3$$

$$\mathsf{step}\ 2 \colon \quad \mathsf{CH}_3\mathsf{C}^+(\mathsf{OH})\mathsf{CH}_3 \to \mathsf{CH}_3\mathsf{C}(\mathsf{OH}) = \mathsf{CH}_2 + \mathsf{H}^+$$

step 4: 
$$CH_3C^+(OH)CH_2I \rightarrow CH_3COCH_2I + H^+$$

| [1] |
|-----|
|-----|

(ii) Suggest the slowest step of the mechanism. Explain your answer.

| <br> | <br> |
|------|------|
|      | [1]  |

(iii) Identify one conjugate acid-conjugate base pair in the mechanism.

[Total: 10]



## **BLANK PAGE**



| _ |               | 0 11 00 011 :       |                | El 16 61       | 0.04               | 40.5  | ,  |
|---|---------------|---------------------|----------------|----------------|--------------------|---|----|
| 2 | Benzoic acid, | $C_6H_5COOH$ , is a | a weak acid. I | he Ka of benzo | oic acid is 6.31 : | < 10 <sup>–5</sup> moldm <sup>–3</sup> at 298 K | ١. |

A 1.00 dm $^3$  buffer solution is made at 298 K containing 1.00 g of  $C_6H_5COOH$  and a slightly greater mass of sodium benzoate,  $C_6H_5COO^-Na^+$ .

This buffer solution has a pH of 4.15.

| (a) | Defi | ne buffer solution.   |     |
|-----|------|---|-----|
|     |      |   |     |
| (b) |      | e equations to show how this solution acts as a buffer solution when the nan<br>tances are added to it: | ned |
|     | (i)  | dilute aqueous sodium hydroxide   |     |
|     | (ii) | dilute aqueous nitric acid.   | [1  |
|     |      |   | F 4 |

(c) Calculate the H $^+$  concentration and the C $_6$ H $_5$ COOH concentration in the buffer solution described. Use the expression for the  $K_a$  of C $_6$ H $_5$ COOH to calculate the concentration of C $_6$ H $_5$ COO $^-$ Na $^+$  in the buffer solution.

Show your working and give each answer to a minimum of **three** significant figures.

$$[H^{+}] = ...... moldm^{-3}$$
 
$$[C_{6}H_{5}COO^{-}Na^{+}] = ...... moldm^{-3}$$
 
$$[C_{6}H_{5}COO^{-}Na^{+}] = ....... moldm^{-3}$$
 [3]



(d) A 10.0 cm<sup>3</sup> sample of the buffer solution is mixed with 10.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> KOH. Both solutions are at 298 K. A reaction is allowed to occur without stirring.

Two observations are recorded:

- the temperature, after the reaction is complete, is fractionally above 298 K
- the pH, after the reaction, is greater than 13.

|     | Exp  | plain these two observations.  |
|-----|------|--|
|     |      |  |
|     |      |  |
|     |      | [2]  |
| (e) |      | gnesium benzoate, ${\rm Mg(C_6H_5COO)_2}$ , has a solubility in water of less than 1.00 g dm $^{-3}$ 98 K.   |
|     |      | $K_{\rm sp} = [{\rm Mg^{2+}}][{\rm C_6H_5COO^-}]^2 = 1.76 \times 10^{-7} \text{ at } 298 {\rm K}$  |
|     | (i)  | Calculate the solubility of ${\rm Mg(C_6H_5COO)_2}$ in water at 298 K. Give your answer in g dm <sup>-3</sup> .  |
|     |      | Show your working.   |
|     |      | $[M_{\rm r}: {\rm Mg(C_6H_5COO)_2}, 266.3]$  |
|     |      |  |
|     |      | solubility = $g dm^{-3}$ [2]   |
|     | (ii) | An excess of $\mathrm{Mg(C_6H_5COO)_2}$ is added to a sample of 0.50 mol dm $^{-3}$ MgSO $_4$ at 298 K.  |
|     |      | State whether the equilibrium concentration of ${\rm Mg(C_6H_5COO)_2}$ is higher than, the same as, or lower than your answer to <b>(i)</b> . Explain your answer. |
|     |      | The concentration is the concentration in (i).   |
|     |      | explanation  |
|     |      | [1]  |

[Total: 11]



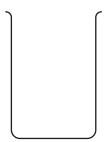
3 Some electrode potentials are shown in Table 3.1.

Table 3.1

| electrode reaction   | E <sup>e</sup> /V |
|--|-------------------|
| V <sup>2+</sup> + 2e <sup>−</sup> <del>←</del> V   | -1.20             |
| V <sup>3+</sup> + e <sup>−</sup> <del>←</del> V <sup>2+</sup>  | -0.26             |
| $VO^{2+} + 2H^{+} + e^{-} \rightleftharpoons V^{3+} + H_{2}O$  | +0.34             |
| VO <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup> + e <sup>−</sup> ₩ VO <sup>2+</sup> + H <sub>2</sub> O                  | +1.00             |
| Fe <sup>2+</sup> + 2e <sup>−</sup> <del>←</del> Fe   | -0.44             |
| Fe <sup>3+</sup> + 3e <sup>−</sup> <del>←</del> Fe   | -0.04             |
| $Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$   | +0.77             |
| 2H <sup>+</sup> + 2e <sup>-</sup> ₩ H <sub>2</sub>   | 0.00              |
| C <i>l</i> O <sup>-</sup> + H <sub>2</sub> O + 2e <sup>-</sup> <del>←</del> C <i>l</i> <sup>-</sup> + 2OH <sup>-</sup> | +0.89             |

(a) (i) Complete the diagram to show a standard hydrogen electrode.

Label your diagram. Identify all substances. You do **not** need to state standard conditions.



[1]

(ii) An electrochemical cell is set up using an Fe<sup>3+</sup>/Fe<sup>2+</sup> electrode and a standard hydrogen electrode.

Identify the positive electrode in the electrochemical cell and the direction of electron flow in the external circuit.

positive electrode .....

Electrons flow from the ...... electrode to the .....



| (b) |                         | he vanadium-containing species in the electrode reactions given in Table 3.1 are V, $V^{2+}$ $^{3+}$ , $VO^{2+}$ and $VO_2^{-+}$ .                       |  |  |  |  |  |  |
|-----|-------------------------|--|--|--|--|--|--|--|
|     | (i)                     | Identify ${\bf one}$ vanadium-containing species that does ${\bf not}$ react with ${\rm Fe^{2^+}}$ ions under standard conditions.                       |  |  |  |  |  |  |
|     |                         | Use data from Table 3.1 to explain your answer.  |  |  |  |  |  |  |
|     |                         |  |  |  |  |  |  |  |
|     |                         | [1]  |  |  |  |  |  |  |
|     | (ii)                    | Identify <b>all</b> the vanadium-containing species that will react with ${\rm Fe^{2^+}}$ ions under standard conditions.                                |  |  |  |  |  |  |
|     |                         | [1]  |  |  |  |  |  |  |
|     | (iii)                   | Write an equation for <b>one</b> of the possible reactions identified in (ii).   |  |  |  |  |  |  |
|     |                         | [1]  |  |  |  |  |  |  |
| (c) |                         | ther electrochemical cell is set up using an Fe $^{3+}$ /Fe $^{2+}$ electrode and an alkaline C $l$ O $^-$ /C $l^-$ trode.                               |  |  |  |  |  |  |
|     | The<br>Fe <sup>3+</sup> | concentration of $Fe^{3+}$ is 1000 times greater than the concentration of $Fe^{2+}$ in the $^{2}/Fe^{2+}$ electrode. All other conditions are standard. |  |  |  |  |  |  |
|     | (i)                     | Use the Nernst equation to calculate the $E$ value of the $\mathrm{Fe^{3+}/Fe^{2+}}$ electrode.  |  |  |  |  |  |  |
|     |                         | Show your working.   |  |  |  |  |  |  |
|     |                         |  |  |  |  |  |  |  |
|     |                         |  |  |  |  |  |  |  |
|     |                         | <i>E</i> = V [2]   |  |  |  |  |  |  |
|     | (ii)                    | Write an equation for the reaction that occurs in the cell, under these conditions.  |  |  |  |  |  |  |
|     |                         | [1]  |  |  |  |  |  |  |
| (d) |                         | ther electrochemical cell is set up using an Fe $^{2+}$ /Fe electrode and an alkaline C $l$ O $^-$ /C $l^-$ trode under standard conditions.             |  |  |  |  |  |  |
|     | Calc                    | culate the value of $\Delta G^{e}$ for the cell.   |  |  |  |  |  |  |

 $AG^{\Theta} = \dots \qquad kJmol \qquad [3]$ 

(e) A solution of iron(II) sulfate,  $FeSO_4(aq)$  is electrolysed with iron electrodes. Under the conditions used, no gas is evolved at the cathode.

A current of 0.640 A is passed for 17.0 minutes. The mass of the cathode increases by 0.185 g.

Use these results to calculate an experimental value for the Avogadro constant, L.

Show your working.

$$L = \dots \mod^{-1} [3]$$

(f) Iron(II) chloride,  $FeCl_2$ , is oxidised by chlorine to form iron(III) chloride,  $FeCl_3$ , under standard conditions.

$$2 \text{FeC} l_2(\text{s}) + \text{C} l_2(\text{g}) \rightarrow 2 \text{FeC} l_3(\text{s}) \qquad \qquad \Delta H^{\Theta} = -128 \, \text{kJ} \, \text{mol}^{-1}$$

Table 3.2

| species               | S <sup>e</sup> /JK <sup>-1</sup> mol <sup>-1</sup> |
|-----------------------|--|
| Cl <sub>2</sub> (g)   | 223  |
| FeCl <sub>2</sub> (s) | 120  |
| FeCl <sub>3</sub> (s) | 142  |

(i) Use Table 3.2 and other data to calculate the Gibbs free energy change,  $\Delta G^{\theta}$ , for this reaction.

Show your working.



| II) | Predict whether this reaction becomes more or less feasible at a higher temperature | e.  |
|-----|---|-----|
|     | Explain your answer.  |     |
|     | The reaction becomes feasible.  |     |
|     | explanation   |     |
|     |   |     |
|     |   | [1] |

[Total: 18]



4 The structure of the polydentate ligand, EDTA<sup>4-</sup>, is shown in Fig. 4.1.

Fig. 4.1

The stability constants, at 298 K, of five octahedral complexes are given in Table 4.1.

Table 4.1

| complex                  | K <sub>stab</sub>       |
|--------------------------|-------------------------|
| [Cu(EDTA)] <sup>2-</sup> | 6.31 × 10 <sup>19</sup> |
| [Cr(EDTA)] <sup>2-</sup> | 1.00 × 10 <sup>13</sup> |
| [Cr(EDTA)]-              | 1.00 × 10 <sup>24</sup> |
| [Fe(EDTA)] <sup>2-</sup> | 2.00 × 10 <sup>14</sup> |
| [Fe(EDTA)] <sup>-</sup>  | 1.26 × 10 <sup>25</sup> |

| (a) | Define stability constant.  |                  |
|-----|---|------------------|
|     |   |                  |
|     |   | [1]              |
| (b) | Calculate the oxidation states of Cu in [Cu(EDTA)] <sup>2-</sup> and Cr in [Cr(EDTA)] <sup>-</sup> .        |                  |
|     | Cu  |                  |
|     | Cr  | [1]              |
|     |   | ניו              |
| (c) | Deduce the number of lone pairs donated by each EDTA <sup>4-</sup> ligand in a single [Fe(EDTA complex ion. | )] <sup>2–</sup> |
|     |   | [1]              |
| (d) | Identify the most stable complex in Table 4.1. Explain your choice.   |                  |
|     |   |                  |
|     |   | [1]              |



| (e) | In a solution at equilibrium at 298 K, [[Cu(H $_2$ O) $_6$ ] $^{2+}$ ] = 3.00 × 10 $^{-10}$ mol dm $^{-3}$ and [EDTA $^{4-}$ ] = 5.00 × 10 $^{-12}$ mol dm $^{-3}$ . |
|-----|--|
|     | Use the expression for $K_{\rm stab}$ to calculate the concentration of [Cu(EDTA)] $^{2-}$ in this solution.   |
|     | Show your working.   |
|     |  |
|     |  |
|     |  |
|     | $[[Cu(EDTA)]^{2-}] = \dots moldm^{-3}$ [2]   |
|     |  |
| (f) | A solution of $[Cu(EDTA)]^{2-}$ ions is pale blue while a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions is deep blue.   |
|     | Explain this difference in colour.   |
|     |  |
|     |  |
|     | [2]  |
|     | [Total: 8]   |



5 Some of the ionic compounds of Group 2 elements undergo thermal decomposition.

Thermal decomposition of solid anhydrous magnesium ethanedioate,  $MgC_2O_4$ , occurs above 650 °C. The products are magnesium oxide and a mixture of two different gases, one of which gives a white precipitate with saturated calcium hydroxide solution.

(a) Complete the equation for the thermal decomposition of MgC<sub>2</sub>O<sub>4</sub>.

$$MgC_2O_4 \rightarrow$$
 [1]

- (b) Suggest which of MgC<sub>2</sub>O<sub>4</sub> or CaC<sub>2</sub>O<sub>4</sub> undergoes thermal decomposition at a **lower** temperature. Explain your answer.
- (c) The ethanedioate ion is oxidised by acidified KMnO<sub>4</sub>.

$$5C_2O_4^{2-} + 2MnO_4^{-} + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O_4^{-}$$

An experiment is performed to find the solubility of MgC<sub>2</sub>O<sub>4</sub> in water.

A 40.0 cm³ sample of saturated aqueous  $\rm MgC_2O_4$  requires 27.05 cm³ of 0.00200 mol dm³ acidified KMnO4 to oxidise all the  $\rm C_2O_4^{2-}$  ions.

Calculate the solubility, in  $\rm mol\,dm^{-3}$ , of  $\rm MgC_2O_4$  in water. Show your working.

solubility = .....  $mol dm^{-3}$  [3]

[Total: 6]



| 6 | (a) |       | sphine, : $\mathrm{PH}_3$ , and carbon monoxide, : $\mathrm{CO}$ , are monodentate ligands found in some sition element complexes.                             |
|---|-----|-------|--|
|   |     | (i)   | Define monodentate ligand.   |
|   |     |       | [1]  |
|   |     | (ii)  | Define transition element complex.   |
|   |     |       | [1]  |
|   | (   | (iii) | Explain why transition elements form complexes.  |
|   |     |       | [1]  |
|   | (b) | The   | formulae of six complexes are given in Table 6.1.  |
|   |     | The   | abbreviation en is used for 1,2-diaminoethane.   |
|   |     | The   | abbreviation <i>dien</i> is used for the tridentate ligand H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> . |
|   |     | The   | dien ligand forms three bonds to the gold ion in $[Au(dien)(H_2O)_2Cl]^{2+}$ and $Au(dien)Cl_3$ .  |
|   |     | The   | se three bonds all lie in the same plane.  |

Table 6.1

The CO ligand coordinates through the carbon atom in  $[Rh(CO)_2Cl_2]^+$ .

| formula  | isomerism shown | geometry   |
|--|-----------------|------------|
| $[Rh(\mathit{en})_2^{}Cl_2^{}]^+$  | yes             |            |
| $[\mathrm{Rh}(\mathrm{CO})_2\mathrm{C}l_2]^+$                                      | yes             |            |
| [Au(dien)(H <sub>2</sub> O) <sub>2</sub> Cl] <sup>2+</sup>                         |                 |            |
| Au(dien)Cl <sub>3</sub>  | no              | octahedral |
| $\mathrm{Ni(PH_3)_2C}l_2$  | no              |            |
| [Ni(H <sub>2</sub> O) <sub>2</sub> (NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> | yes             |            |

(i) Complete Table 6.1 to state the geometry of the first three complexes. Each complex is either square planar, tetrahedral or octahedral. [1]

| (ii) | Use complexes [Au(dien)(H <sub>2</sub> O) <sub>2</sub> Cl] <sup>2</sup> ligand exchange. | ?+ and | $\mathrm{Au}(\mathit{dien})\mathrm{C} l_3$ | to | write | an | equation | show | ing |
|------|--|--------|--|----|-------|----|----------|------|-----|
|      | ligand exchange.   |        |  |    |       |    |          |      | C   |
|      |  |        |  |    |       |    |          | A    | [1] |

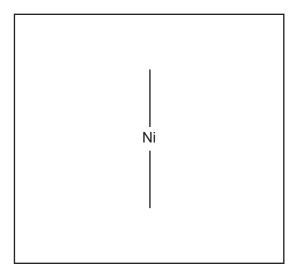
|       |                                      | 16   |                              |
|-------|--------------------------------------|--|------------------------------|
| (iii) | Draw the three-dimensio drawn as N N | nal structure of Au( $\mathit{dien}$ )C $\mathit{l}_3$ in the box. T | he <i>dien</i> ligand can be |
|       |                                      | Au<br> <br>  |                              |
| (iv)  | Draw the three-dimension             | nal structure of Ni(PH $_3$ ) $_2$ C $l_2$ in the box.               | [1]                          |
|       |                                      | Ni   |                              |

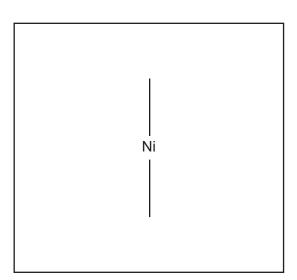
[1]

(v) One of the complexes,  $[Rh(en)_2Cl_2]^+$  or  $[Rh(CO)_2Cl_2]^+$ , can exist in three isomeric forms. Identify this complex and the types of isomerism shown.



(vi) Draw the three-dimensional structures of the two isomers of  $[Ni(H_2O)_2(NH_3)_4]^{2+}$  in the boxes and identify the type of isomerism shown.





type of isomerism shown .....

[2]

[Total: 10]



7 Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

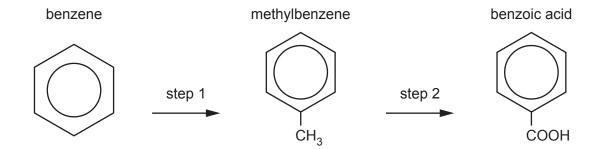


Fig. 7.1

| (2) | Civo tho    | reagents and | conditions | for cton | 1 and aton 2  |
|-----|-------------|--------------|------------|----------|---------------|
| (a) | , Give lile | reagents and | COHUILIONS | ioi sieb | i aliu siep z |

| step 1 | <br> | <br> | <br> |
|--------|------|------|------|
| step 2 | <br> | <br> | <br> |

**(b)** Methylbenzene and benzoic acid each have five different peaks in the carbon (<sup>13</sup>C) NMR spectrum.

Table 7.1

| hybridisation of the carbon atom | environment of carbon atom | example  | chemical<br>shift range<br>/ppm |
|----------------------------------|----------------------------|--|---------------------------------|
| sp <sup>3</sup>                  | alkyl                      | CH <sub>3</sub> -, -CH <sub>2</sub> -, -CH<, >C< | 0–50                            |
| sp <sup>3</sup>                  | next to alkene/arene       | <b>-C</b> −C=C, <b>-C</b> −Ar                    | 25–50                           |
| sp <sup>3</sup>                  | next to carbonyl/carboxyl  | <b>C</b> -COR, <b>C</b> -O <sub>2</sub> R        | 30–65                           |
| sp <sup>3</sup>                  | next to halogen            | C-X  | 30–60                           |
| sp <sup>3</sup>                  | next to oxygen             | <b>C</b> -O                                      | 50–70                           |
| sp <sup>2</sup>                  | alkene or arene            | >C=C<, c c c c                                   | 110–160                         |
| sp <sup>2</sup>                  | carboxyl                   | R-COOH, R-COOR                                   | 160–185                         |
| sp <sup>2</sup>                  | carbonyl                   | R-CHO, R-CO-R                                    | 190–220                         |
| sp                               | nitrile                    | R-C≡N  | 100–125                         |

Use Table 7.1 to complete the two sentences to suggest descriptions of these two spectra.

The carbon (<sup>13</sup>C) NMR spectrum of methylbenzene:

- has ...... peak(s) in the chemical shift range of ...... and
- has ...... peak(s) in the chemical shift range of ......



The carbon (13C) NMR spectrum of benzoic acid:

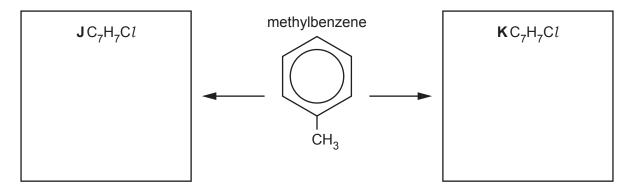
- has ...... peak(s) in the chemical shift range of ...... and
- has ...... peak(s) in the chemical shift range of ......

[2]

(c) (i) When treated with  $Cl_2$  under suitable conditions, methylbenzene forms compound **J**.

When treated with Cl<sub>2</sub> under **different** conditions with **different** reagents, methylbenzene forms compound **K**.

Suggest and draw structures of compounds J and K in the boxes. The molecular formula of each compound is given.



State the reagents and conditions required to form each product.

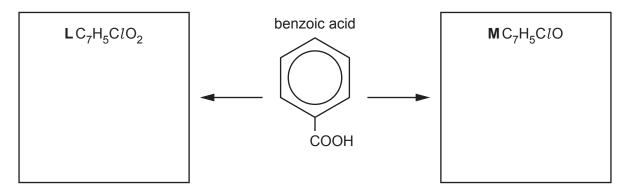
to form compound **J** 

to form compound K .....

(ii) When treated with a chlorine-containing reagent under suitable conditions, benzoic acid forms compound L.

When treated with a different chlorine-containing reagent under different conditions, benzoic acid forms compound M.

Suggest and draw structures of compounds L and M in the boxes. The molecular formula of each product is given.



State the reagents and conditions to form compound **M** from benzoic acid.



© UCLES 2023

- 8 Lactic acid, CH<sub>3</sub>CH(OH)COOH, is the only monomer needed to form the polymer polylactic acid, PLA.
  - (a) (i) Draw a short length of the PLA polymer chain, including a minimum of two monomer residues. The methyl groups may be written as -CH<sub>3</sub> but all other bonds should be shown fully displayed.

Label one repeat unit of polylactic acid on your diagram.

[1]

(ii) Give the name of the type of polymerisation involved in the formation of PLA and the name of the functional group that forms between the monomers.

| type of polymerisation |  |
|------------------------|--|
| functional group       |  |

(iii) Predict whether PLA is readily biodegradable. Explain your answer.

| <br> |
|------|
| [41  |

(b) The proton ( $^{1}$ H) NMR spectrum of CH $_{3}$ CH(OH)COOH in CDC $l_{3}$  is shown in Fig. 8.1. The proton NMR chemical shift ranges are shown in Table 8.1.

#### Lactic acid

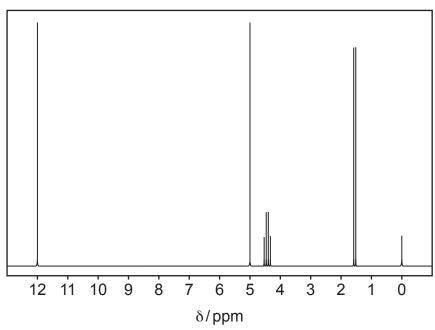


Fig. 8.1

STA WWW.STAN

Table 8.1

| environment of proton              | example   | chemical<br>shift range<br>δ/ppm |
|------------------------------------|---|----------------------------------|
| alkane                             | -CH <sub>3</sub> , -CH <sub>2</sub> -, >CH-                                   | 0.9–1.7                          |
| alkyl next to C=O                  | CH <sub>3</sub> -C=O, -CH <sub>2</sub> -C=O, >CH-C=O                          | 2.2–3.0                          |
| alkyl next to aromatic ring        | CH <sub>3</sub> -Ar, -CH <sub>2</sub> -Ar, >CH-Ar                             | 2.3–3.0                          |
| alkyl next to electronegative atom | $\mathrm{CH_3}	ext{-O}$ , $\mathrm{-CH_2}	ext{-O}$ , $\mathrm{-CH_2}	ext{-C}$ | 3.2–4.0                          |
| attached to alkene                 | =C <b>H</b> R   | 4.5–6.0                          |
| attached to aromatic ring          | H–Ar  | 6.0–9.0                          |
| aldehyde                           | HCOR  | 9.3–10.5                         |
| alcohol                            | ROH   | 0.5–6.0                          |
| phenol                             | Ar–O <b>H</b>   | 4.5–7.0                          |
| carboxylic acid                    | RCOO <b>H</b>   | 9.0–13.0                         |

(i) Use Fig. 8.1 and Table 8.1 to complete Table 8.2.

Table 8.2

| proton environment | chemical shift (δ) | name of splitting pattern |
|--------------------|--------------------|---------------------------|
| -COOH              |                    |                           |
| ⇒ch                |                    |                           |
| –OH                |                    |                           |
| -CH <sub>3</sub>   |                    |                           |

|       |   | [3] |
|-------|---|-----|
| (ii)  | Name the substance responsible for the peak at $\delta$ = 0.0.                                  |     |
|       |   | [1] |
| (iii) | Explain why $\mathrm{CDC}l_3$ is a better solvent than $\mathrm{CHC}l_3$ for use in proton NMR. |     |
|       |   |     |
|       |   | [1] |

AHEAD WWW.sty

longer retention time than the lactic acid.

(c) An impure sample of CH<sub>3</sub>CH(OH)COOH contains pentan-3-one as the only contaminant. The mixture is analysed using gas/liquid chromatography. The pentan-3-one is found to have a

| (i)   | Explain what is meant by retention time.   |
|-------|--|
|       |  |
|       | [1]  |
| (ii)  | Suggest suitable substances, or types of substances, that could be used as the mobile and stationary phases.   |
|       | mobile phase   |
|       | stationary phase   |
| (iii) | [1] Describe how the percentage composition of the mixture can be determined from the gas/liquid chromatogram. |
|       | [1]<br>[Total: 12]   |

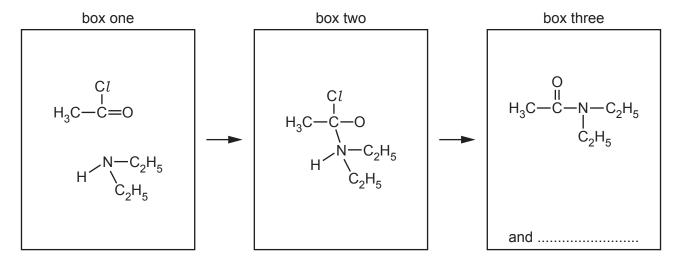


| 9 | (a) | State the reactants and conditions for two different types of reactions that both produce diethylamine, $\mathrm{CH_3CH_2NHCH_2CH_3}$ .   |
|---|-----|---|
|   |     | reaction one  |
|   |     |   |
|   |     | reaction two  |
|   |     | [4]   |
|   | (b) | Describe the relative basicities of diethylamine, phenylamine and ammonia in aqueous solution.  |
|   |     | Explain your answer in terms of structure.  |
|   |     | least basic most basic  |
|   |     | explanation   |
|   |     |   |
|   |     |   |
|   |     |   |
|   |     | [3]   |
|   | (c) | Phenylamine reacts with $HNO_2(aq)$ at $4^\circ C$ to form compound <b>P</b> . Compound <b>P</b> reacts with phenol under alkaline conditions at $4^\circ C$ . The product of this reaction is acidified, forming azo compound <b>Q</b> . |
|   |     | Draw the structure of compound <b>Q</b> .   |
|   |     | Circle the azo group on your structure.   |
|   |     | State one use of an azo compound such as <b>Q</b> .   |
|   |     |   |
|   |     | compound <b>Q</b> :   |
|   |     |   |
|   |     | An azo compound can be used[2]  |



(d)  $CH_3CH_2NHCH_2CH_3$  reacts with ethanoyl chloride,  $CH_3COC_l$ , to give the amide N,N-diethylethanamide,  $CH_3CON(C_2H_5)_2$ .

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.



reactants intermediate products

Fig. 9.1

- (i) Complete the mechanism in Fig. 9.1. You should include:
  - all relevant dipoles ( $\delta$ + and  $\delta$ –) and full electric charges (+ and –) on the species in box one and in box two
  - all relevant lone pairs on the species in box one and in box two
  - all relevant curly arrows to show the movement of electron pairs in box one and in box two
  - the formula of the second product in box three.

[4]

(ii) Name this mechanism.

.....[1]

[Total: 14]



## **BLANK PAGE**



## **BLANK PAGE**



27

## Important values, constants and standards

| molar gas constant              | $R = 8.31 \mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1}$   |
|---------------------------------|---|
| Faraday constant                | $F = 9.65 \times 10^4 \mathrm{C}\mathrm{mol}^{-1}$  |
| Avogadro constant               | $L = 6.022 \times 10^{23} \text{mol}^{-1}$  |
| electronic charge               | $e = -1.60 \times 10^{-19} \mathrm{C}$  |
| molar volume of gas             | $V_{\rm m} = 22.4 {\rm dm^3 mol^{-1}}$ at s.t.p. (101 kPa and 273 K)<br>$V_{\rm m} = 24.0 {\rm dm^3 mol^{-1}}$ at room conditions |
| ionic product of water          | $K_{\rm w}$ = 1.00 × 10 <sup>-14</sup> mol <sup>2</sup> dm <sup>-6</sup> (at 298 K (25 °C))                                       |
| specific heat capacity of water | $c = 4.18 \mathrm{kJ  kg^{-1}  K^{-1}}  (4.18 \mathrm{J  g^{-1}  K^{-1}})$  |



The Periodic Table of Elements

|       | 18 | <sup>2</sup> He | mail 0:         | 01            | <u>e</u>     | 30n<br>).2                   | 8  | <b>-</b> | argon<br>39.9      | 9,  | ۶  | pton<br>3.8       | <b>'</b> 4 | e        | non<br>1.3         | ي ا   | ,<br>L      | - nob             | 18     | g              | esson              |
|-------|----|-----------------|-----------------|---------------|--------------|------------------------------|----|----------|--------------------|-----|----|-------------------|------------|----------|--------------------|-------|-------------|-------------------|--------|----------------|--------------------|
|       |    |                 | <br>■ 4         | _             | _            | ₩<br>₩                       |    | _        | 36 ar              | (6) | _  | <u>Ā</u> 8        | 4)         | <u>×</u> | 13 ×e              | ω     | <u> </u>    | rac               | +      | _              | ogan               |
|       | 17 |                 |                 | 6             | ш            | fluorine<br>19.0             | 17 | Cl       | chlorine<br>35.5   | 35  | Ā  | bromine<br>79.9   | 53         | Н        | iodine<br>126.9    | 85    | At          | astatine<br>-     | 117    | <u>s</u>       | tennessine<br>-    |
|       | 16 |                 |                 | 80            | 0            | oxygen<br>16.0               | 16 | S        | sulfur<br>32.1     | 34  | Se | selenium<br>79.0  | 52         | <u>e</u> | tellurium<br>127.6 | 84    | Ро          | polonium<br>–     | 116    | _              | livermorium<br>-   |
|       | 15 |                 |                 | 7             | z            | nitrogen<br>14.0             | 15 | ۵        | phosphorus<br>31.0 | 33  | As | arsenic<br>74.9   | 51         | Sb       | antimony<br>121.8  | 83    | <u>.</u>    | bismuth<br>209.0  | 115    | Mc             | moscovium          |
|       | 14 |                 |                 | 9             | O            | carbon<br>12.0               | 14 | S        | silicon<br>28.1    | 32  | Ge | germanium<br>72.6 | 20         | Sn       | tin<br>118.7       | 82    | Pb          | lead<br>207.2     | 114    | ŁΙ             | flerovium          |
|       | 13 |                 |                 | 2             | В            | boron<br>10.8                | 13 | Ρl       | aluminium<br>27.0  | 31  | Ga | gallium<br>69.7   | 49         | In       | indium<br>114.8    | 18    | 11          | thallium<br>204.4 | 113    | Ę              | nihonium           |
|       |    |                 |                 |               |              |                              |    |          | 12                 | 30  | Zu | zinc<br>65.4      | 48         | g        | cadmium<br>112.4   | 80    | £           | mercury<br>200.6  | 112    | 5              | copernicium        |
|       |    |                 |                 |               |              |                              |    |          | 7                  | 29  | Cn | copper<br>63.5    | 47         | Ag       | silver<br>107.9    | 62    | Au          | gold<br>197.0     | 111    | Rg             | oentgenium<br>-    |
| dr    |    |                 |                 |               |              |                              |    |          |                    |     |    | nickel<br>58.7    |            |          |                    |       |             |                   |        |                | Ε                  |
| Group |    |                 |                 |               |              |                              |    |          | 6                  | 27  | රි | cobalt<br>58.9    | 45         | 몬        | rhodium<br>102.9   | 77    | ٦           | iridium<br>192.2  | 109    | ¥              | meitnerium<br>-    |
|       |    | - I             | hydrogen<br>1.0 |               |              |                              |    |          | 80                 | 26  | Ьe | iron<br>55.8      | 4          | Ru       | ruthenium<br>101.1 | 9/    | SO          | osmium<br>190.2   | 108    | H <sub>s</sub> | hassium            |
|       |    |                 |                 | J             |              |                              |    |          | 7                  | 25  | Mn | manganese<br>54.9 | 43         | ည        | technetium<br>-    | 75    | Re          | rhenium<br>186.2  | 107    | 뭠              | bohrium            |
|       |    |                 |                 |               | Ю            | s                            |    |          | 9                  | 24  | ပ် | chromium<br>52.0  | 42         | Mo       | molybdenum<br>95.9 | 74    | >           | tungsten<br>183.8 | 106    | Sg             | seaborgium<br>-    |
|       |    |                 | Key             | atomic number | atomic symbo | name<br>relative atomic mass |    |          | 2                  | 23  | >  | vanadium<br>50.9  | 14         | g        | niobium<br>92.9    | 73    | <u>a</u>    | tantalum<br>180.9 | 105    | 9              | dubnium<br>-       |
|       |    |                 |                 | atı           | aton         | relati                       |    |          | 4                  | 22  | F  | titanium<br>47.9  | 40         | Z        | zirconium<br>91.2  | 72    | Ξ̈́         | hafnium<br>178.5  | 104    | ¥              | rutherfordium<br>- |
|       |    |                 |                 |               |              |                              | T  |          | က                  | 21  | Sc | scandium<br>45.0  | 39         | >        | yttrium<br>88.9    | 57-71 | lanthanoids |                   | 89–103 | actinoids      |                    |
|       | 2  |                 |                 | 4             | Be           | beryllium<br>9.0             | 12 | Mg       | magnesium<br>24.3  | 20  | Ca | calcium<br>40.1   | 38         | Š        | strontium<br>87.6  | 56    | Ва          | barium<br>137.3   | 88     | Ra             | radium             |
|       | ~  |                 |                 | 3             | :=           | lithium<br>6.9               | =  | Na       | sodium<br>23.0     | 19  | ×  | potassium<br>39.1 | 37         | Rb       | rubidium<br>85.5   | 55    | S           | caesium<br>132.9  | 87     | ъ              | francium<br>—      |

| 71         | Lu              | 175.0 | 103 | ۲         | lawrencium   | ı     |
|------------|-----------------|-------|-----|-----------|--------------|-------|
| 02         |                 |       |     |           |              |       |
| 69 F       | <b>E</b>        | 168.9 | 101 | Md        | mendelevium  | -     |
| 89 [       | i ii            | 167.3 | 100 | Fm        | ferminm      | I     |
| 29         | D Indiminum     | 164.9 | 66  | Es        | einsteinium  | _     |
| 99         | dysprosium      | 162.5 | 86  | ರ         | californium  | _     |
| 65         | terbium         | 158.9 | 26  | 番         | berkelium    | -     |
| 2 <b>(</b> | o dadolinium    | 157.3 | 96  | CB        | curium       | 1     |
| 63         | europium        | 152.0 | 92  | Am        | americium    | ı     |
| 62         | Samarium        | 150.4 | 8   | Pn        | plutonium    | 1     |
| 9 م        | Eromethium      | ı     | 93  | ď         | neptrnium    | ı     |
| 09         | DQ<br>neodymium | 144.4 | 92  | $\supset$ | uranium      | 238.0 |
| 59         | D praseodymium  | 140.9 | 91  | Ра        | protactinium | 231.0 |
| 28         | e di            | 140.1 | 06  | Т         | thorium      | 232.0 |
| 57         | <b>La</b>       | 138.9 | 89  | Ac        | actinium     | ı     |

lanthanoids actinoids

To avoid the issue of disclosure of answer-related information to candidates, all copyright acknowledgements are reproduced online in the Cambridge Assessment International Education Copyright Acknowledgements Booklet. This is produced for each series of examinations and is freely available to download at www.cambridgeinternational.org after the live examination series.