Please check the examination details below before entering your candidate information

| Candidate surname | Other names |
|---|---|

Centre Number | Candidate Number

# Pearson Edexcel International Advanced Level

## Friday 2 June 2023

Morning (Time: 1 hour 45 minutes)

Paper reference **WCH14/01**

# Chemistry

## International Advanced Level
## UNIT 4: Rates, Equilibria and Further Organic Chemistry

**You must have:**
Scientific calculator, Data Booklet, ruler

Total Marks

### Instructions

- Use **black** ink or ball-point pen.
- If pencil is used for diagrams/sketches/graphs it must be dark (HB or B).
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
  – *there may be more space than you need.*

### Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- In the question marked with an **asterisk (*)**, marks will be awarded for your ability to structure your answer logically, showing how the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

### Advice

- Read each question carefully before you start to answer it.
- Show all your working in calculations and include units where appropriate.
- Try to answer every question.
- Check your answers if you have time at the end.

*Turn over* ▶

P71942A



N:1/1/1/1/

P 7 1 9 4 2 A 0 1 3 2

Pearson

## SECTION A

**Answer ALL the questions in this section.**

**You should aim to spend no more than 20 minutes on this section.**

**For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.**

**1** A homogeneous equilibrium is shown.

$$W + X \rightleftharpoons 2Y + Z$$

What is the $K_c$ expression for this equilibrium?

☒ **A** $K_c = \dfrac{2[Y][Z]}{[W][X]}$

☒ **B** $K_c = \dfrac{[Y]^2[Z]}{[W][X]}$

☒ **C** $K_c = \dfrac{[W][X]}{2[Y][Z]}$

☒ **D** $K_c = \dfrac{[W][X]}{[Y]^2[Z]}$

**(Total for Question 1 = 1 mark)**

**2** The reaction shown occurs at 360 °C and 1 atm.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H = -41.2\,kJ\,mol^{-1}$$

What is the type of equilibrium and how is $K_c$ affected by an **increase** in temperature?

| | Type of equilibrium | Effect of increasing temperature on $K_c$ |
|---|---|---|
| ☒ **A** | heterogeneous | decreases |
| ☒ **B** | homogeneous | decreases |
| ☒ **C** | heterogeneous | increases |
| ☒ **D** | homogeneous | increases |

**(Total for Question 2 = 1 mark)**

**3** What are the units of $K_p$ for the equilibrium shown?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

☒ **A** $atm^{-1}$

☒ **B** atm

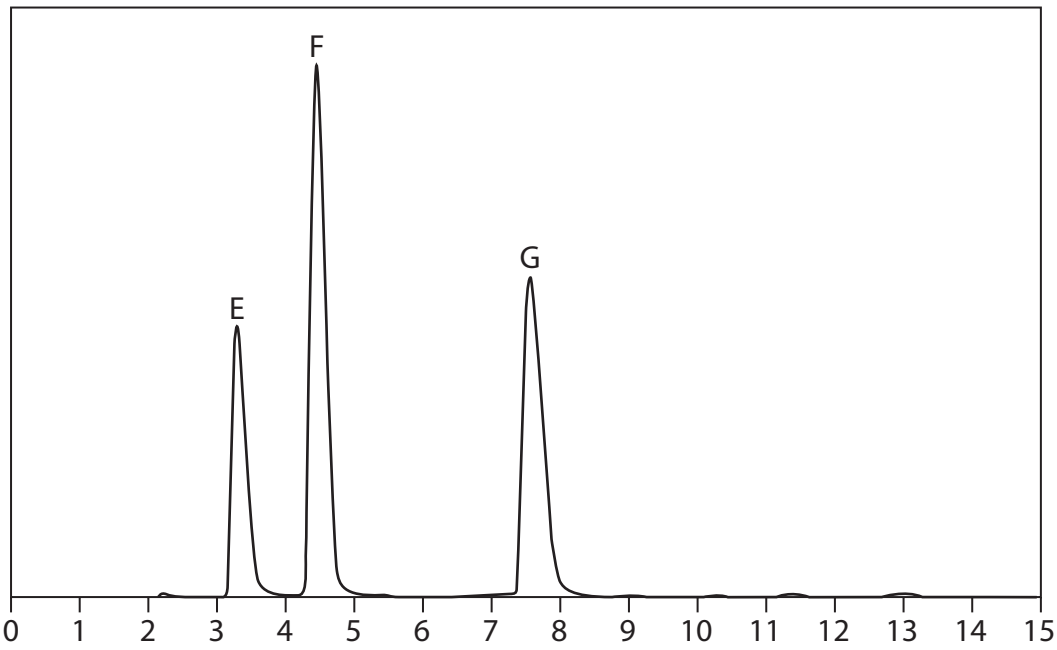
☒ **C** $atm^{-2}$

☒ **D** $atm^2$

**(Total for Question 3 = 1 mark)**

**4** High-performance liquid chromatography (HPLC) is used to separate a mixture into its three components.

The resulting chromatogram is shown.




(a) Which is correct for the labels on the axes?

**(1)**

| | | x-axis | y-axis |
|---|---|---|---|
| ☒ | **A** | absorption | time |
| ☒ | **B** | $R_f$ | absorption |
| ☒ | **C** | time | $R_f$ |
| ☒ | **D** | time | absorption |

(b) Which is correct for the components E, F and G ?

**(1)**

| | | Most attracted to stationary phase | Most abundant |
|---|---|---|---|
| ☒ | **A** | E | E |
| ☒ | **B** | G | E |
| ☒ | **C** | E | F |
| ☒ | **D** | G | F |

**(Total for Question 4 = 2 marks)**

**5** Which pair of compounds can form a racemic mixture when mixed?

☒ **A**


☒ **B**

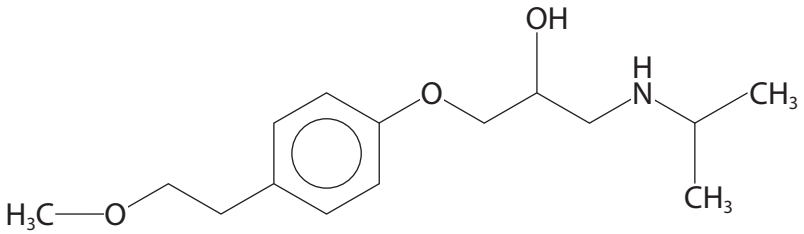

☒ **C**


☒ **D**


**(Total for Question 5 = 1 mark)**

**6** Metoprolol is a drug used to treat heart problems.

The structure of metoprolol is shown.




How many chiral centres are there in a molecule of metoprolol?

- ☒ **A** 0
- ☒ **B** 1
- ☒ **C** 2
- ☒ **D** 3

**(Total for Question 6 = 1 mark)**

**7** The decomposition of hydrogen peroxide is catalysed by iodide ions.

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

The mechanism for this reaction is shown.

Step 1: $H_2O_2(aq) + I^-(aq) \rightleftharpoons IO^-(aq) + H_2O(l)$ fast

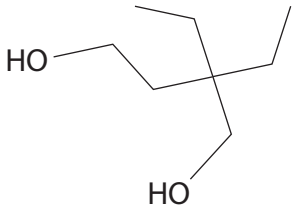
Step 2: $H_2O_2(aq) + IO^-(aq) \rightarrow I^-(aq) + H_2O(l) + O_2(g)$ slow

What is the rate equation for this reaction?

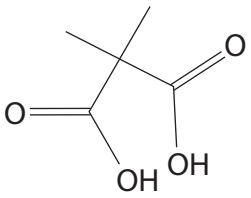
- ☒ **A** rate = $k[H_2O_2]^2[I^-]$
- ☒ **B** rate = $k[H_2O_2][I^-]$
- ☒ **C** rate = $k[H_2O_2]^2[I^-][IO^-]$
- ☒ **D** rate = $k[H_2O_2][IO^-]$

**(Total for Question 7 = 1 mark)**

**8** The two monomers shown react to form a polymer.



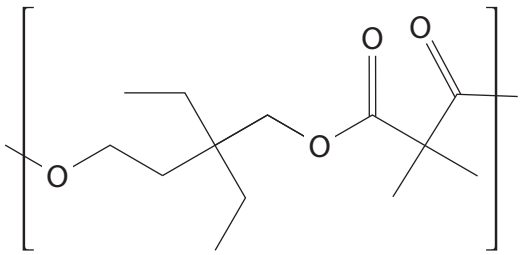

monomer 1



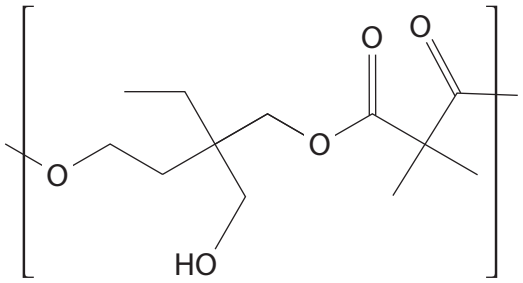

monomer 2

Which is a repeat unit of the resulting polymer?

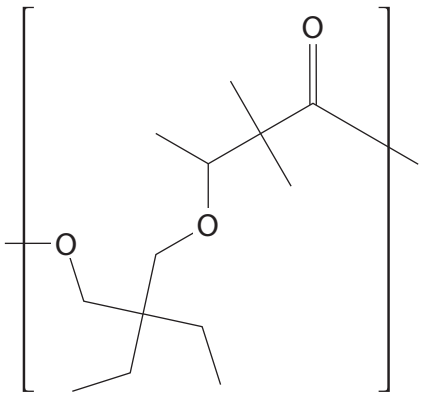
☒ **A**



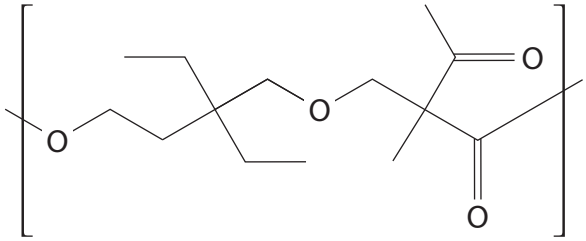

☒ **B**




☒ **C**

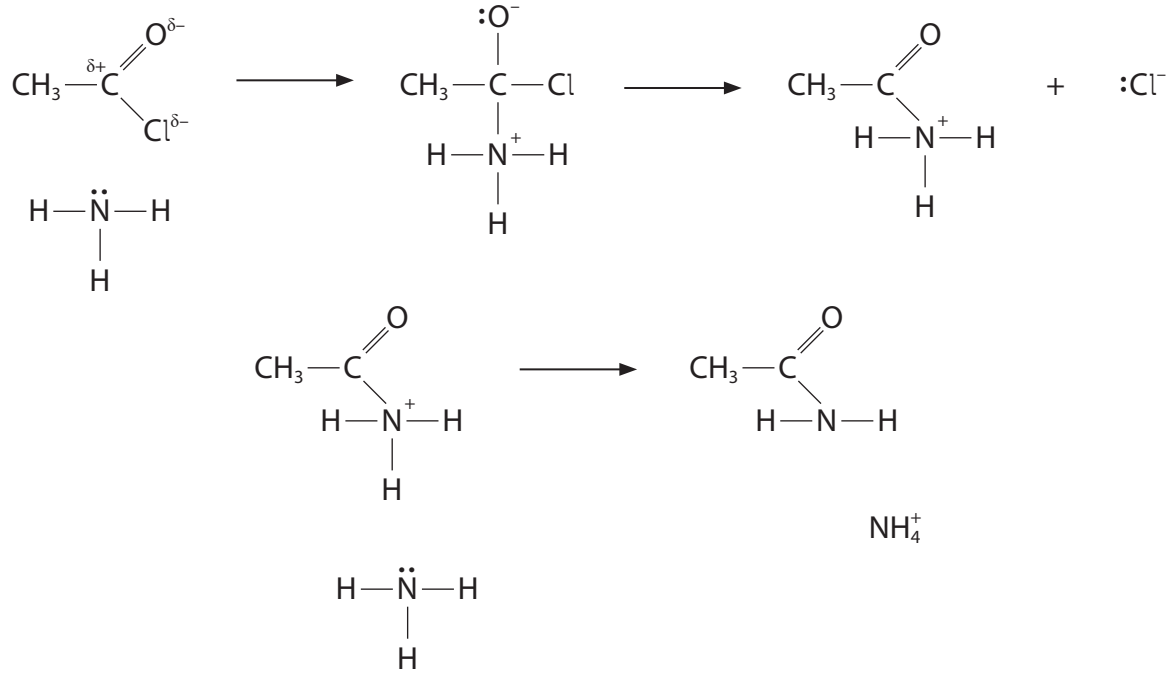



☒ **D**




**(Total for Question 8 = 1 mark)**

**9** A partial mechanism of the reaction between ethanoyl chloride and concentrated aqueous ammonia is shown.




(a) How many curly arrows are needed to complete the mechanism?

**(1)**

- ☒ **A** 4
- ☒ **B** 5
- ☒ **C** 6
- ☒ **D** 8

(b) What is the IUPAC name for the organic product?

**(1)**

- ☒ **A** amino ethanone
- ☒ **B** ethanamide
- ☒ **C** ethanoyl amine
- ☒ **D** methanamide

**(Total for Question 9 = 2 marks)**

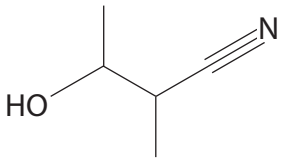
**Use this space for any rough working. Anything you write in this space will gain no credit.**

**10** How do the boiling temperature and the solubility in water of butanoic acid compare with the values for hexane?

| | Boiling temperature | Solubility in water |
|---|---|---|
| ☒ **A** | lower | lower |
| ☒ **B** | lower | higher |
| ☒ **C** | higher | lower |
| ☒ **D** | higher | higher |

**(Total for Question 10 = 1 mark)**

**11** Which acid would be produced by the hydrolysis of the molecule shown?




☒ **A** 2-hydroxy-3-methylbutanoic acid

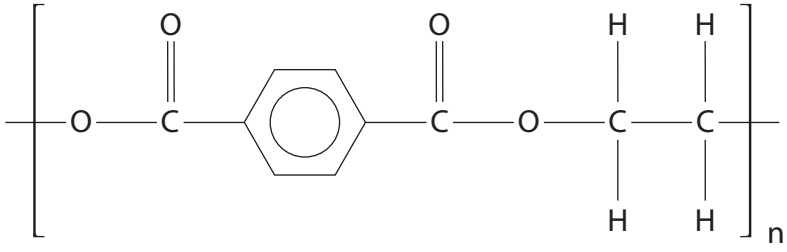
☒ **B** 3-hydroxy-2-methylbutanoic acid

☒ **C** 3-hydroxy-2,3-dimethylpropanoic acid

☒ **D** 4-hydroxypentanoic acid

**(Total for Question 11 = 1 mark)**

**12** Which is produced after the polyester shown is hydrolysed with excess sodium hydroxide?




☒ **A** benzene-1,4-dicarboxylic acid

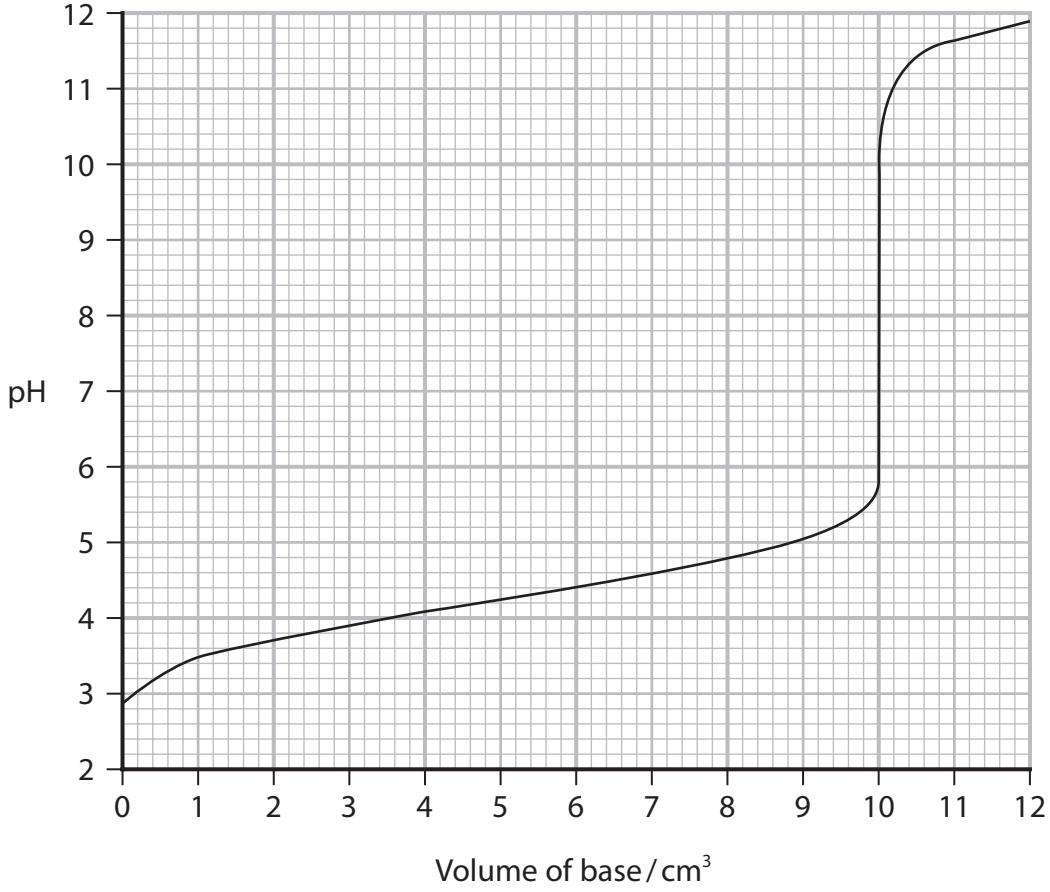
☒ **B** ethane-1,2-diol

☒ **C** sodium ethanedioate

☒ **D** water

**(Total for Question 12 = 1 mark)**

**13** The titration curve shown is produced when a base is added to an acid.




(a) Which indicators could be used for this titration? Use your Data Booklet.

**(1)**

- ☒ **A** bromocresol green, methyl red and phenolphthalein
- ☒ **B** bromothymol blue, phenol red and phenolphthalein
- ☒ **C** methyl red, bromothymol blue and phenol red
- ☒ **D** thymol blue, screened methyl orange and bromophenol blue

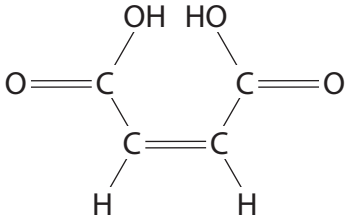
(b) Which acid and base could produce this curve?

**(1)**

- ☒ **A** $CH_3COOH$ and NaOH
- ☒ **B** $CH_3COOH$ and $NH_3$
- ☒ **C** HCl and NaOH
- ☒ **D** HCl and $NH_3$

**(Total for Question 13 = 2 marks)**

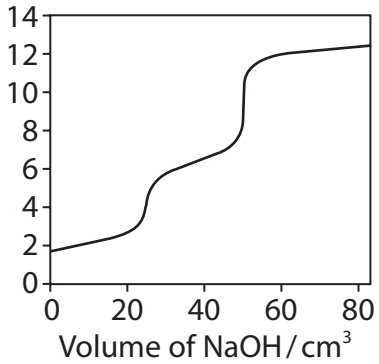
**14** The structure of maleic acid is shown.



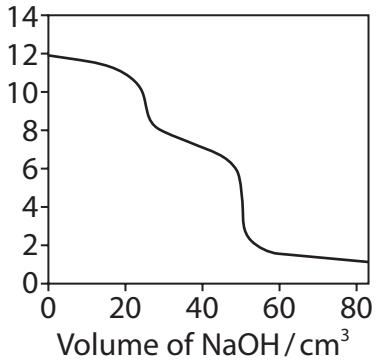

(a) Which could be the titration curve when sodium hydroxide is added to maleic acid?

**(1)**

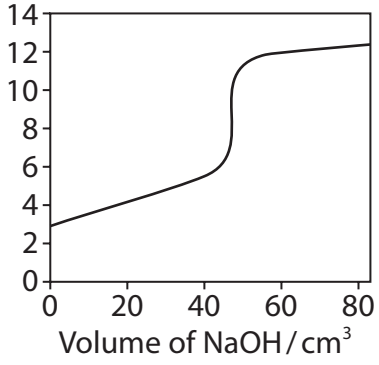
☒ **A**



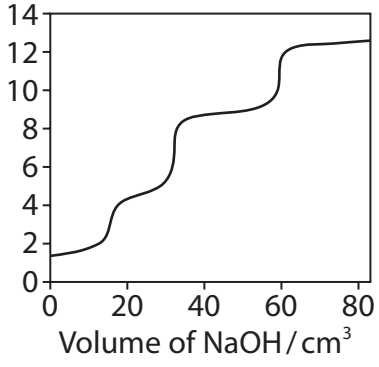

☒ **B**




☒ **C**

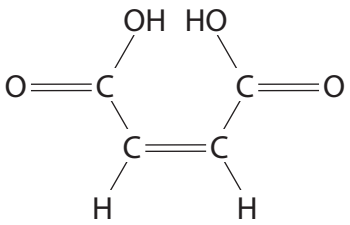



☒ **D**



(b) What is the IUPAC name for maleic acid?

**(1)**



maleic acid

- ☒ **A** (*E*)-but-2-enedioic acid
- ☒ **B** (*Z*)-but-2-enedioic acid
- ☒ **C** (*E*)-1,2-ethenedioic acid
- ☒ **D** (*Z*)-1,2-ethenedioic acid

**(Total for Question 14 = 2 marks)**

**15** Which is **not** a conjugate acid-base pair?

- ☒ **A** $NH_3$, $NH_2^-$
- ☒ **B** $NH_4^+$, $NH_3$
- ☒ **C** $H_2CO_3$, $CO_3^{2-}$
- ☒ **D** $H_2CO_3$, $HCO_3^-$

**(Total for Question 15 = 1 mark)**

**16** What is the pH of the solution when 2.15 g of barium hydroxide is dissolved in 200 $cm^3$ of deionised water?

[molar mass of barium hydroxide = 171.3 g $mol^{-1}$ $K_w = 1.00 \times 10^{-14}$ $mol^2$ $dm^{-6}$]

- ☒ **A** 10.1
- ☒ **B** 12.1
- ☒ **C** 12.8
- ☒ **D** 13.1

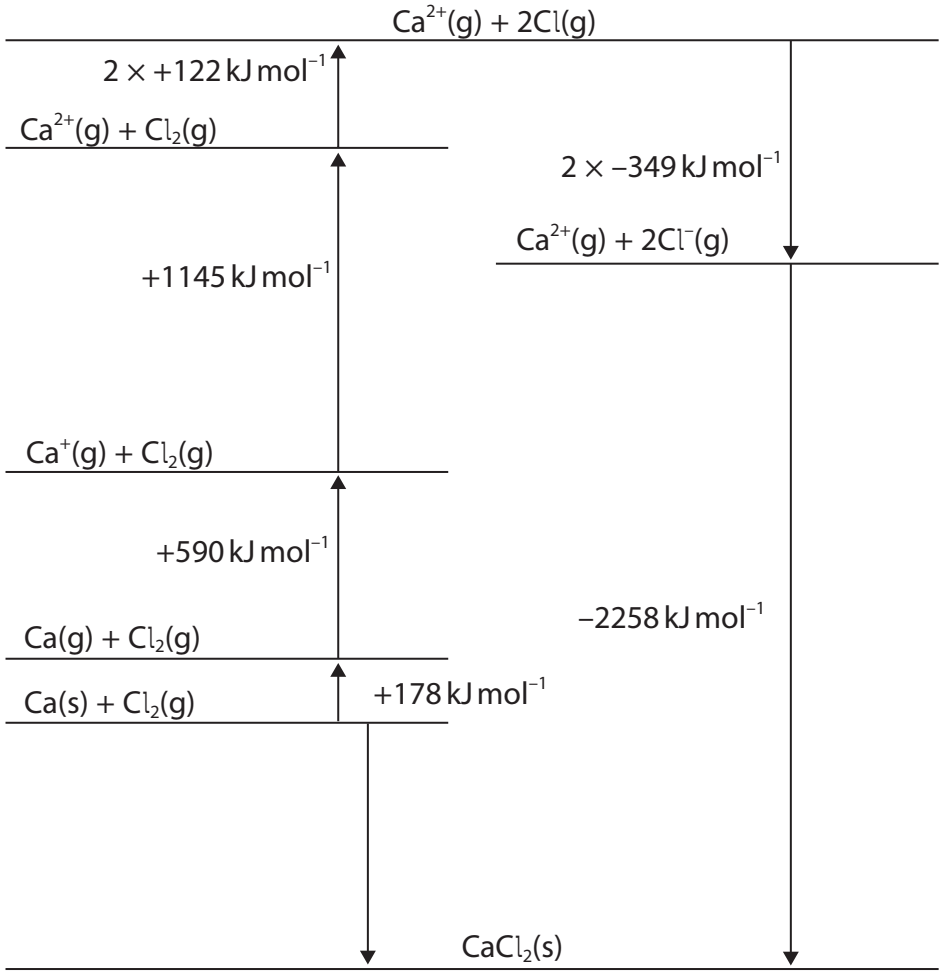
**(Total for Question 16 = 1 mark)**

**TOTAL FOR SECTION A = 20 MARKS**

## SECTION B

**Answer ALL the questions. Write your answers in the spaces provided.**

**17** A Born–Haber cycle for calcium chloride is shown.




(a) State the value of the $\Delta_{at}H$ for calcium.

**(1)**

(b) Calculate the enthalpy change of formation for calcium chloride.

**(2)**

(c) Some energy data are shown.

| Compound | Theoretical lattice energy / kJ mol$^{-1}$ | Experimental lattice energy / kJ mol$^{-1}$ |
|---|---|---|
| $CaCl_2$ | –2223 | –2258 |
| $CaI_2$ | –1905 | –2074 |

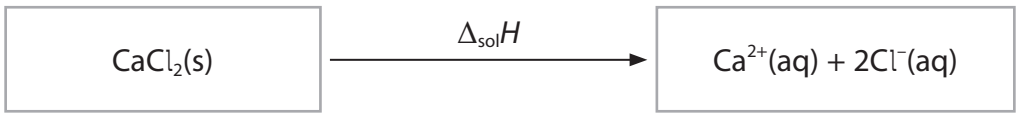
Explain why the difference between the theoretical and the experimental values for lattice energy is very much greater for calcium iodide than for calcium chloride.

**(4)**

(d) Calcium chloride is soluble in water.

(i) Complete the energy cycle including labelled arrows.

**(2)**




(ii) Calculate the enthalpy change of solution, $\Delta_{sol}H$, for calcium chloride using the data given and the completed energy cycle in (d)(i).

**(2)**

| Data | Energy change / kJ mol$^{-1}$ |
|---|---|
| LE ($CaCl_2(s)$) | –2258 |
| $\Delta_{hyd}H$ ($Ca^{2+}(g)$) | –1579 |
| $\Delta_{hyd}H$ ($Cl^-(g)$) | –378 |

**(Total for Question 17 = 11 marks)**

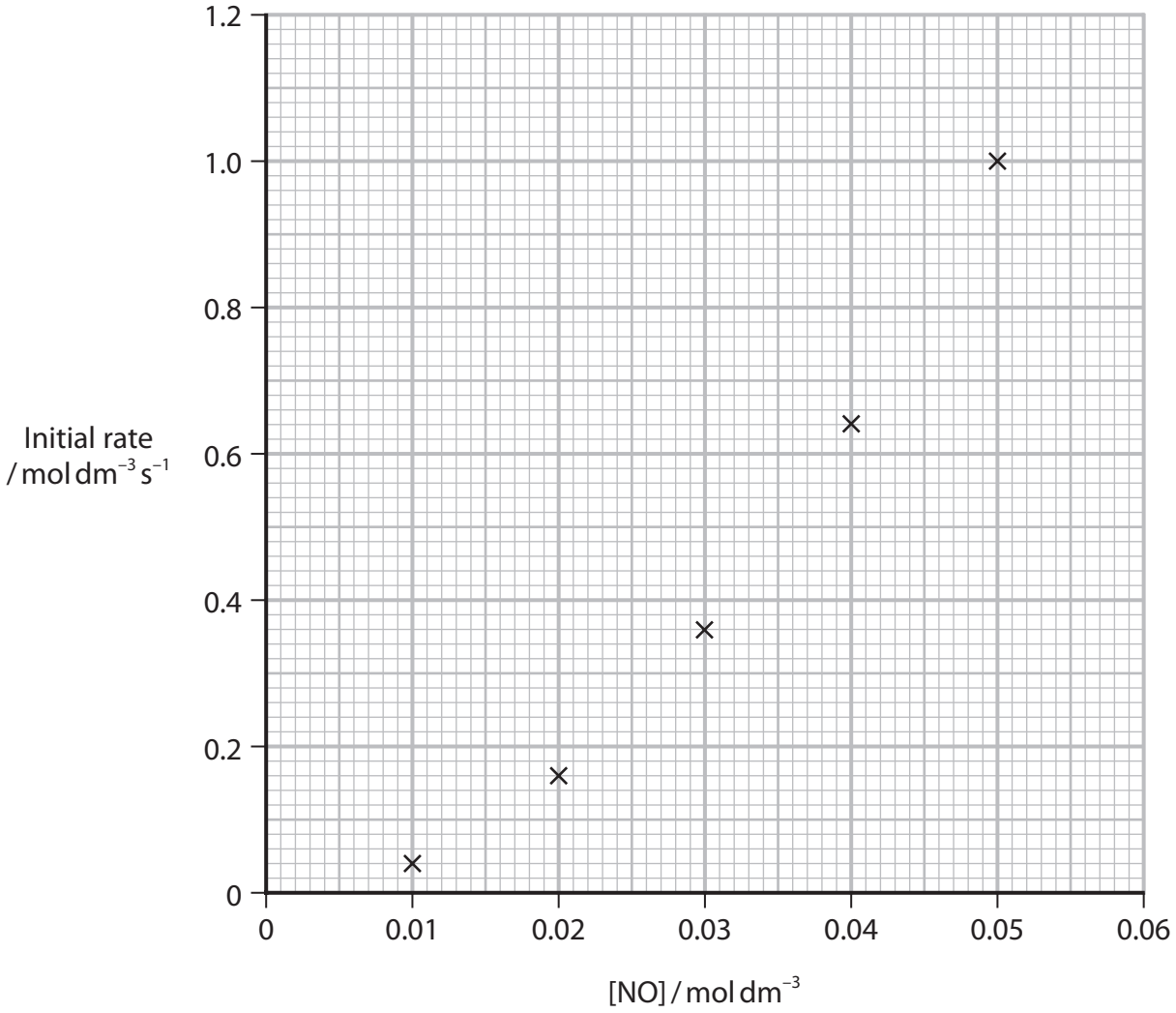
**18** This question is about the reaction between nitrogen monoxide and oxygen.

$$NO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$$

(a) The results of a series of kinetics experiments are shown.

| Experiment | Initial [NO] / mol dm$^{-3}$ | Initial [$O_2$] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | 0.010 | 0.050 | 0.040 |
| 2 | 0.020 | 0.050 | 0.160 |
| 3 | 0.030 | 0.050 | 0.360 |
| 4 | 0.040 | 0.050 | 0.641 |
| 5 | 0.050 | 0.050 | 1.001 |
| 6 | 0.020 | 0.025 | 0.080 |

The data for experiments 1–5 were plotted on a graph.




(i) Draw a best-fit line on the graph.

**(1)**

(ii) State how the graph shows that the reaction is **not** first order with respect to nitrogen monoxide.

**(1)**

.....

.....

(iii) Deduce the orders of reaction with respect to NO and $O_2$, using the data from experiments 1–6.

**(2)**

Order with respect to NO = .....

Order with respect to $O_2$ = .....

(iv) Write the rate equation for the reaction, using your answer to (a)(iii).

**(1)**

(v) Calculate the rate constant for this reaction using the data from experiment 1 and your rate equation. Include units in your answer.

**(2)**

(b) The equilibrium constant, $K_p$, for the reaction at 298 K is $1.55 \times 10^6$ $atm^{-½}$.

State what this value of the equilibrium constant indicates about the position of the equilibrium. Justify your answer.

**(2)**

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**(Total for Question 18 = 9 marks)**

**19** This question is about some bromoalkanes.

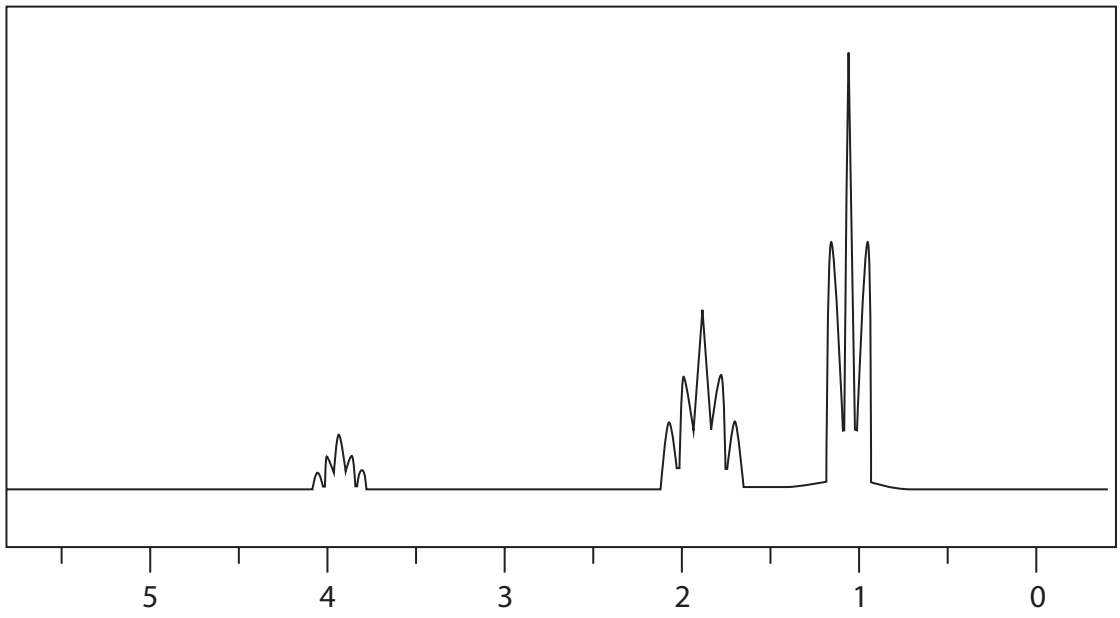
(a) There are three straight-chain structural isomers with the molecular formula $C_5H_{11}Br$.

(i) Complete the table for these three isomers.

**(3)**

| Isomer | Skeletal formula | Number of peaks in $^{13}C$ NMR spectrum |
|---|---|---|
| 1 | | ..... |
| 2 | | ..... |
| 3 | | ..... |

*(ii) The high resolution proton NMR spectrum of one of these isomers is shown.




Deduce which isomer is present in the sample, explaining the splitting patterns and chemical shifts seen in the spectrum.

Include the name of the isomer and the relative peak areas.

Use your Data Booklet.

**(6)**

(b) Draw the $S_N2$ mechanism for the reaction of 1-bromopropane with hydroxide ions in aqueous solution.

Include curly arrows, and relevant dipoles and lone pairs.

**(4)**

**(Total for Question 19 = 13 marks)**

**20** Nitrous oxide, $N_2O$, decomposes at high temperature to form nitrogen and oxygen.

$$N_2O(g) \rightleftharpoons N_2(g) + \tfrac{1}{2}O_2(g)$$

(a) (i) Some standard molecular entropy data are shown.

| Substance | Standard molecular entropy $S^{\ominus}$ / $JK^{-1}mol^{-1}$ |
|---|---|
| nitrogen, $N_2$ | 192 |
| oxygen, $O_2$ | 205 |
| nitrous oxide, $N_2O$ | 220 |

Calculate the standard entropy change of the system for the decomposition shown.
Include a sign and units in your answer.

**(2)**

(ii) The standard enthalpy change of the forward reaction is $-82\,kJ\,mol^{-1}$.

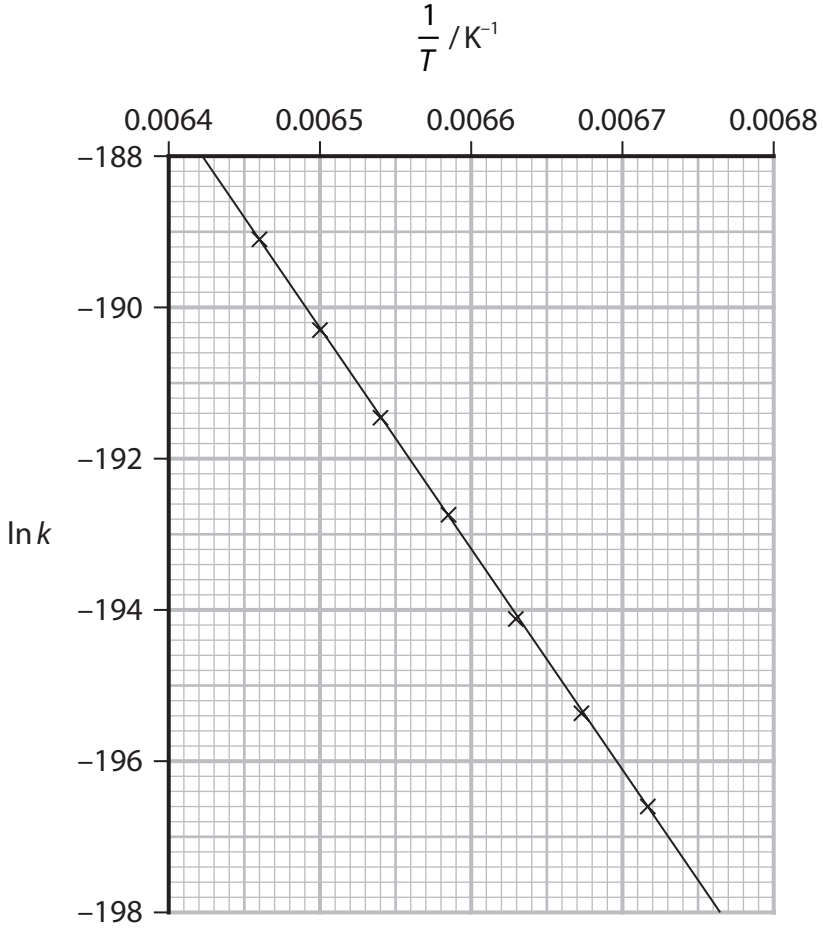
Calculate the entropy change of the surroundings at 2048 K.
Include a sign and units in your answer.

**(2)**

(iii) Calculate the total entropy change of the reaction at 2048 K.
Include a sign and units in your answer.

**(1)**

(b) Rate experiments on the decomposition of nitrous oxide produced the following graph.




Calculate the activation energy for the reaction in kJ mol$^{-1}$.
Include the value of the gradient.

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \text{constant}$$

$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$

**(2)**

(c) Explain whether or not this reaction occurs at 2048 K by considering the values calculated in (a) and (b).

**(2)**

.....

.....

.....

.....

**(Total for Question 20 = 9 marks)**

**21** Hexane-2,5-dione, $CH_3COCH_2CH_2COCH_3$, is a toxic compound formed in the human body if hexane is consumed.

(a) Complete the table for hexane-2,5-dione.

**Name** the organic product formed if a reaction takes place.

**(2)**

| Reagent and conditions | Reaction (✓ / ✗) | Name of organic product (if formed) |
|---|---|---|
| refluxed with excess acidified potassium dichromate(VI) | | |
| excess lithium tetrahydridoaluminate(III) in dry ether | | |

(b) State the observation when hexane-2,5-dione reacts with iodine in the presence of alkali.

**(1)**

.....

.....

(c) Hexane-2,5-dione reacts with **excess** hydrogen cyanide, HCN, in the presence of potassium cyanide, KCN.

(i) Name the type and mechanism of this reaction.

**(1)**

.....

(ii) Draw the structure of the product.

**(1)**

(d) (i) Give the observation when 2,4-dinitrophenylhydrazine (Brady's reagent) reacts with hexane-2,5-dione.

**(1)**

.....

(ii) Describe, in outline, how the product of this reaction may be used to confirm the identity of hexane-2,5-dione. Experimental details are not required.

**(2)**

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.....

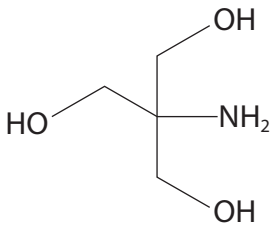
**(Total for Question 21 = 8 marks)**

**TOTAL FOR SECTION B = 50 MARKS**

## SECTION C

**Answer ALL the questions. Write your answers in the spaces provided.**

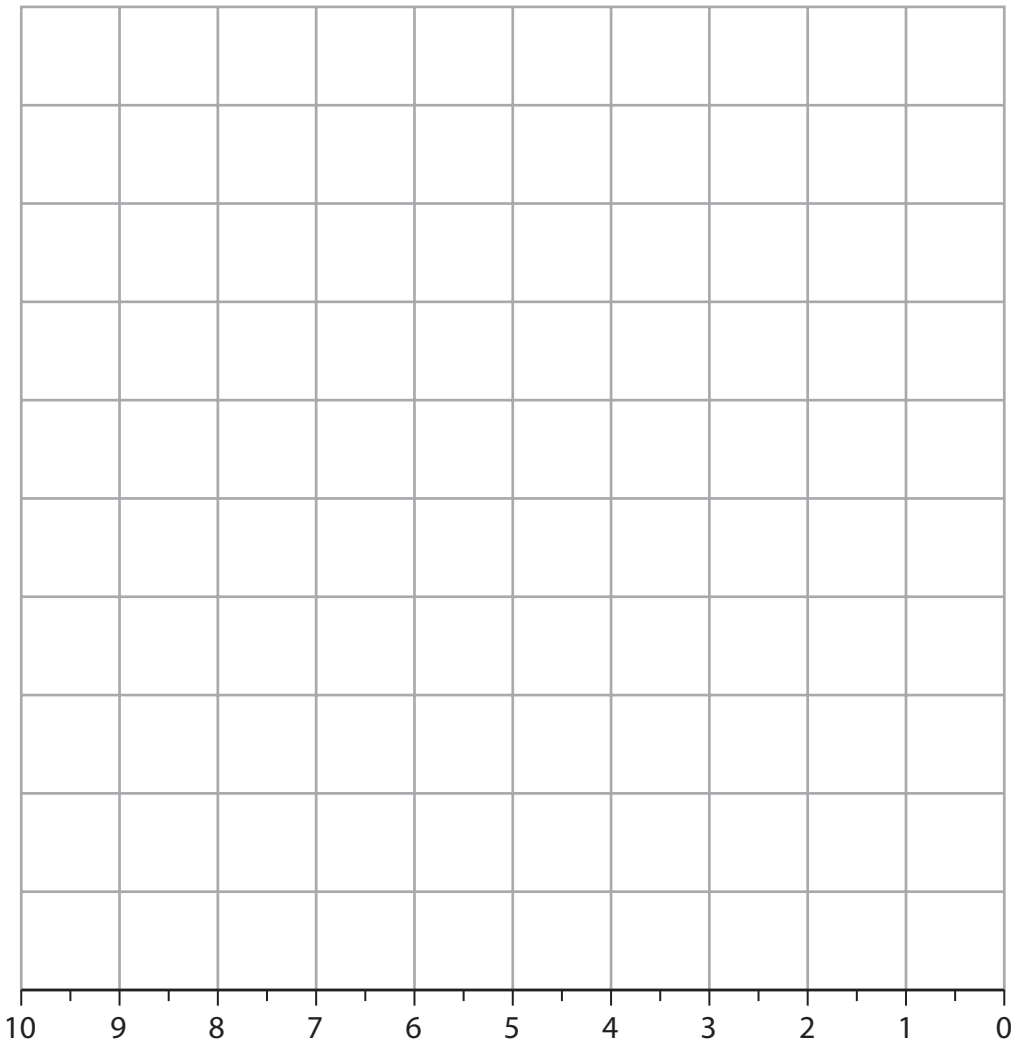
**22** The alkaline compound tris(hydroxymethyl)aminomethane, known as Tris, is used to make a buffer for biological research.



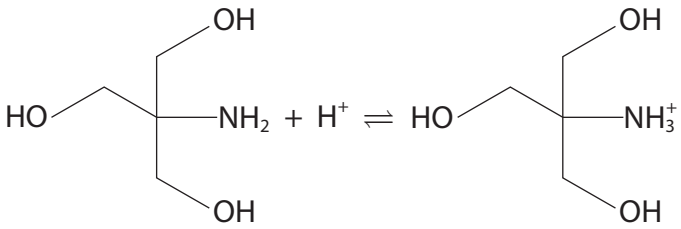

Tris

(a) Sketch the **low** resolution proton NMR spectrum of Tris ($C_4H_{11}NO_3$).
Use your Data Booklet.

**(3)**



(b) Tris is a Brønsted–Lowry base and its conjugate acid is formed as shown.




(i) Explain how a mixture of Tris and its conjugate acid acts as a buffer solution when a small amount of acid is added.

**(3)**

(ii) Write the expression for the $K_a$ of the conjugate acid of Tris ($C_4H_{12}NO_3^+$).

**(1)**

(iii) When hydrochloric acid is added to Tris, the acid salt is formed.
The acid salt is a solid, which has the formula $C_4H_{12}NO_3^+Cl^-$, and contains the conjugate acid of Tris.
When 100 g of the acid salt is mixed with 500 $cm^3$ of 0.200 mol $dm^{-3}$ Tris, an alkaline buffer is formed.

Calculate the pH of this buffer, assuming that there is no change in volume when the solid is added.

$K_a$ for the conjugate acid of Tris is $8.413 \times 10^{-9}$ mol $dm^{-3}$.

**(5)**

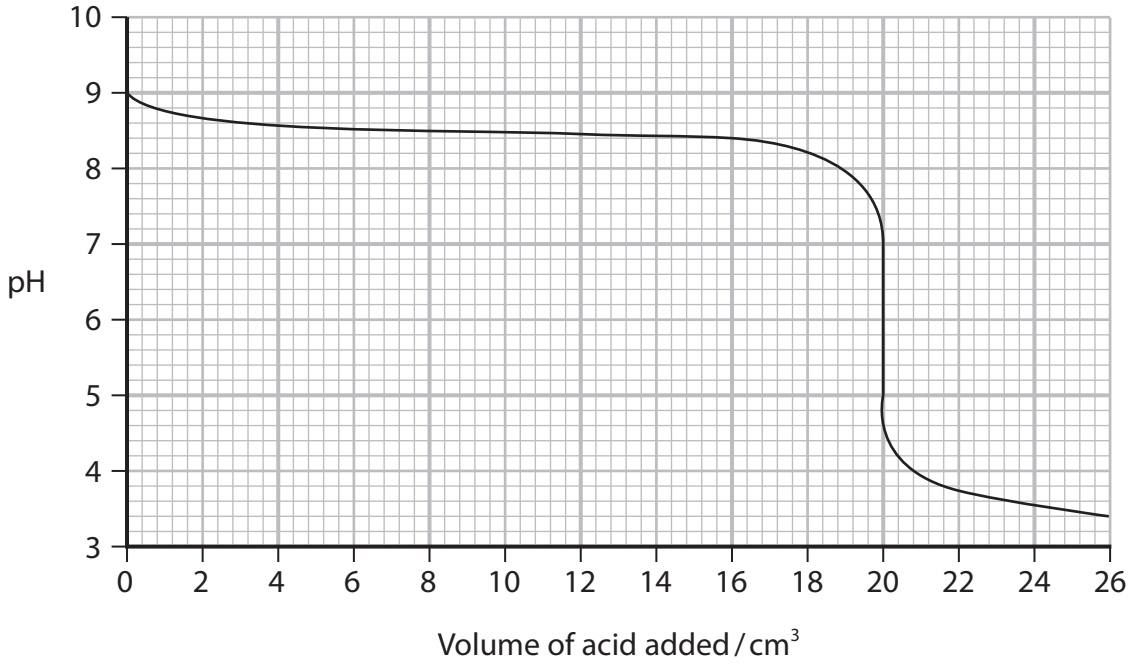
(c) A solution of chloroethanoic acid is prepared for titration with Tris.

0.0150 g of chloroethanoic acid ($M_r$ = 94.5) is dissolved in 1500 $cm^3$ of distilled water. The resulting solution has a pH of 3.42.

Calculate the $K_a$ of chloroethanoic acid.

**(4)**

(d) A titration curve of Tris with chloroethanoic acid is shown.



(i) Explain how this graph shows Tris and its conjugate acid act as a buffer.

**(2)**

(ii) Use the graph to estimate the pH of the salt formed when Tris is neutralised with chloroethanoic acid.

**(1)**

(iii) Suggest a reason why buffers are so important in biological systems.

**(1)**

**(Total for Question 22 = 20 marks)**

**TOTAL FOR SECTION C = 20 MARKS**
**TOTAL FOR PAPER = 90 MARKS**

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# The Periodic Table of Elements

| 1 | 2 | | | | | | | | | | | 3 | 4 | 5 | 6 | 7 | 0 (8) (18) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 1.0 H hydrogen 1 | | | | | | | | | | 4.0 He helium 2 |
| (1) | (2) | | | | | | | | | | | (13) | (14) | (15) | (16) | (17) | |
| 6.9 Li lithium 3 | 9.0 Be beryllium 4 | | | | | | | | | | | 10.8 B boron 5 | 12.0 C carbon 6 | 14.0 N nitrogen 7 | 16.0 O oxygen 8 | 19.0 F fluorine 9 | 20.2 Ne neon 10 |
| 23.0 Na sodium 11 | 24.3 Mg magnesium 12 | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) | (11) | (12) | 27.0 Al aluminium 13 | 28.1 Si silicon 14 | 31.0 P phosphorus 15 | 32.1 S sulfur 16 | 35.5 Cl chlorine 17 | 39.9 Ar argon 18 |
| 39.1 K potassium 19 | 40.1 Ca calcium 20 | 45.0 Sc scandium 21 | 47.9 Ti titanium 22 | 50.9 V vanadium 23 | 52.0 Cr chromium 24 | 54.9 Mn manganese 25 | 55.8 Fe iron 26 | 58.9 Co cobalt 27 | 58.7 Ni nickel 28 | 63.5 Cu copper 29 | 65.4 Zn zinc 30 | 69.7 Ga gallium 31 | 72.6 Ge germanium 32 | 74.9 As arsenic 33 | 79.0 Se selenium 34 | 79.9 Br bromine 35 | 83.8 Kr krypton 36 |
| 85.5 Rb rubidium 37 | 87.6 Sr strontium 38 | 88.9 Y yttrium 39 | 91.2 Zr zirconium 40 | 92.9 Nb niobium 41 | 95.9 Mo molybdenum 42 | [98] Tc technetium 43 | 101.1 Ru ruthenium 44 | 102.9 Rh rhodium 45 | 106.4 Pd palladium 46 | 107.9 Ag silver 47 | 112.4 Cd cadmium 48 | 114.8 In indium 49 | 118.7 Sn tin 50 | 121.8 Sb antimony 51 | 127.6 Te tellurium 52 | 126.9 I iodine 53 | 131.3 Xe xenon 54 |
| 132.9 Cs caesium 55 | 137.3 Ba barium 56 | 138.9 La* lanthanum 57 | 178.5 Hf hafnium 72 | 180.9 Ta tantalum 73 | 183.8 W tungsten 74 | 186.2 Re rhenium 75 | 190.2 Os osmium 76 | 192.2 Ir iridium 77 | 195.1 Pt platinum 78 | 197.0 Au gold 79 | 200.6 Hg mercury 80 | 204.4 Tl thallium 81 | 207.2 Pb lead 82 | 209.0 Bi bismuth 83 | [209] Po polonium 84 | [210] At astatine 85 | [222] Rn radon 86 |
| [223] Fr francium 87 | [226] Ra radium 88 | [227] Ac* actinium 89 | [261] Rf rutherfordium 104 | [262] Db dubnium 105 | [266] Sg seaborgium 106 | [264] Bh bohrium 107 | [277] Hs hassium 108 | [268] Mt meitnerium 109 | [271] Ds darmstadtium 110 | [272] Rg roentgenium 111 | | | | | | | |

Key: relative atomic mass / **atomic symbol** / name / atomic (proton) number

Elements with atomic numbers 112-116 have been reported but not fully authenticated

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| * Lanthanide series | 140 Ce cerium 58 | 141 Pr praseodymium 59 | 144 Nd neodymium 60 | [147] Pm promethium 61 | 150 Sm samarium 62 | 152 Eu europium 63 | 157 Gd gadolinium 64 | 159 Tb terbium 65 | 163 Dy dysprosium 66 | 165 Ho holmium 67 | 167 Er erbium 68 | 169 Tm thulium 69 | 173 Yb ytterbium 70 | 175 Lu lutetium 71 |
| * Actinide series | 232 Th thorium 90 | [231] Pa protactinium 91 | 238 U uranium 92 | [237] Np neptunium 93 | [242] Pu plutonium 94 | [243] Am americium 95 | [247] Cm curium 96 | [245] Bk berkelium 97 | [251] Cf californium 98 | [254] Es einsteinium 99 | [253] Fm fermium 100 | [256] Md mendelevium 101 | [254] No nobelium 102 | [257] Lr lawrencium 103 |