Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number | | | | | |

Candidate Number | | | | |

Pearson Edexcel International Advanced Level

Wednesday 8 January 2025

Afternoon (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

Pearson

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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 Which reducing reagent is used to convert carboxylic acids to alcohols?

☐ **A** acidified potassium dichromate(VI)

☐ **B** concentrated sulfuric acid

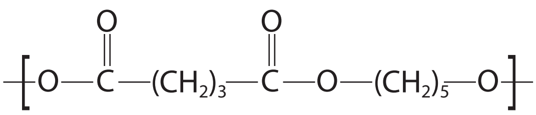
☐ **C** hydrogen gas with a nickel catalyst

☐ **D** lithium tetrahydridoaluminate(III) in dry ether

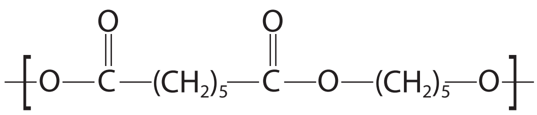
(Total for Question 1 = 1 mark)

2 A polyester is made from pentane-1,5-diol and pentanedioic acid.
Which is the repeat unit of this polyester?

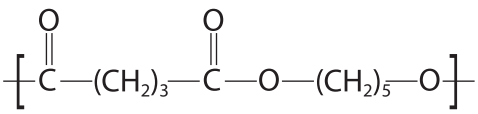
☐ **A**



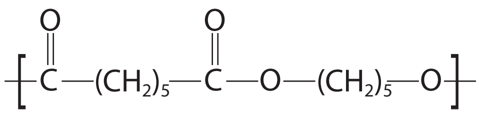
☐ **B**



☐ **C**



☐ **D**



(Total for Question 2 = 1 mark)

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

3 When ammonia dissolves in water, an equilibrium results.
The equation for this equilibrium is shown.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Which of these species act as a Brønsted–Lowry acid in this equilibrium?

☒ **A** H_2O only

☒ **B** NH_3 and OH^-

☒ **C** NH_4^+ only

☒ **D** NH_4^+ and H_2O

(Total for Question 3 = 1 mark)

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4 A strong monoprotic acid, of concentration 0.0100 mol dm^{-3}, has a pH = 2.0.

What is the **decrease in pH** if the concentration is increased to 0.0110 mol dm^{-3}?

☒ **A** 0.001

☒ **B** 0.04

☒ **C** 1.04

☒ **D** 1.96

(Total for Question 4 = 1 mark)

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

5 One of the stages in the manufacture of sulfuric acid involves the oxidation of sulfur dioxide to sulfur trioxide.
The equation for this reaction can be written in either of the two ways shown.

Equation **1** $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Equation **2** $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

The value of K_p at 25°C using Equation **1** is 4.0×10^{24} atm^{-1}.

(a) What is the numerical value of K_p at 25°C using Equation **2**?

(1)

☒ **A** 2.0×10^{12}

☒ **B** 2.0×10^{22}

☒ **C** 2.0×10^{24}

☒ **D** 4.0×10^{24}

(b) The relationship between K_p and K_c is shown.

$$K_c = \frac{K_p}{(R \times T)^{\Delta n}}$$

where T is the temperature in kelvin,
R is the gas constant 0.082 dm^3 atm mol^{-1} K^{-1} and
Δn = moles of product – moles of reactants.

What is the value of K_c at 25°C for the equilibrium using Equation **1**?

(1)

☒ **A** 1.64×10^{23}

☒ **B** 1.95×10^{24}

☒ **C** 8.20×10^{24}

☒ **D** 9.77×10^{25}

(Total for Question 5 = 2 marks)

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

6 Which equation represents the standard enthalpy change of atomisation of iodine?

- ☒ **A** $\frac{1}{2}I_2(s) \rightarrow I(g)$
- ☒ **B** $\frac{1}{2}I_2(g) \rightarrow I(g)$
- ☒ **C** $I_2(s) \rightarrow 2I(g)$
- ☒ **D** $I_2(g) \rightarrow 2I(g)$

(Total for Question 6 = 1 mark)

7 Which equation represents the second electron affinity of oxygen?

- ☒ **A** $O^-(g) + e^- \rightarrow O^{2-}(g)$
- ☒ **B** $O(g) + 2e^- \rightarrow O^{2-}(g)$
- ☒ **C** $O^+(g) \rightarrow O^{2+}(g) + e^-$
- ☒ **D** $O(g) \rightarrow O^{2+}(g) + 2e^-$

(Total for Question 7 = 1 mark)

8 Which compound has the greatest covalent character?

- ☒ **A** $CaBr_2$
- ☒ **B** CaI_2
- ☒ **C** $MgBr_2$
- ☒ **D** MgI_2

(Total for Question 8 = 1 mark)

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

9 Which pair of values will **always** give a thermodynamically feasible reaction?

		Entropy change of the system	Enthalpy change of reaction
☒	**A**	negative	positive
☒	**B**	negative	negative
☒	**C**	positive	negative
☒	**D**	positive	positive

(Total for Question 9 = 1 mark)

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

10 This question is about the effect of changes on a system at equilibrium.

(a) The equation for the reaction between hydrogen and iodine is shown.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

What is the effect, if any, of an **increase** in pressure on the appearance of the equilibrium mixture?

(1)

- ☒ **A** no change
- ☒ **B** the mixture becomes more purple
- ☒ **C** the mixture becomes more brown
- ☒ **D** the mixture becomes less brown

(b) The equation for the manufacture of ammonia by the Haber process is shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92.2\,kJ\,mol^{-1}$$

(1)

$K_p = 6.76 \times 10^5\,atm^{-2}$ at 298 K

Which change(s), if any, will result in an **increase** in the value of K_p?

- ☒ **A** an increase in pressure only
- ☒ **B** a decrease in temperature only
- ☒ **C** an increase in pressure and an increase in temperature
- ☒ **D** no changes in pressure or temperature will affect the value of K_p

(c) The equation for the equilibrium between nitrogen dioxide and dinitrogen tetroxide is shown.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

A change in conditions results in K_p increasing from 0.115 atm to 3.89 atm.

What can be deduced about the change in position of the equilibrium?

(1)

- ☒ **A** the equilibrium position has shifted towards the products
- ☒ **B** the equilibrium position has shifted towards the reactants
- ☒ **C** the equilibrium position is unchanged
- ☒ **D** there is almost complete conversion of reactants into products

(Total for Question 10 = 3 marks)

11 What is the pH of a 0.100 mol dm^{-3} solution of sodium hydroxide at 283 K?

[pK_w = 14.53 at 283 K]

☒ **A** 13.00

☒ **B** 13.53

☒ **C** 14.43

☒ **D** 14.53

(Total for Question 11 = 1 mark)

12 The pH of a dilute solution of a weak carboxylic acid can be calculated from its K_a value.

Which is **not** a relevant assumption in the calculation of pH?

☒ **A** the ionisation of water is insignificant

☒ **B** the initial and equilibrium concentrations of the acid are the same

☒ **C** the concentrations of the protons and carboxylate ions are the same

☒ **D** the dissociation of the carboxylic acid is almost complete

(Total for Question 12 = 1 mark)

13 This is a question about buffers.

(a) The Henderson–Hasselbalch equation can be used to determine the pH of a buffer solution. This equation is shown.

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

What is the pH of a buffer solution containing 0.100 mol dm^{-3} ethanoic acid and 0.200 mol dm^{-3} sodium ethanoate?
[K_a(ethanoic acid) = 1.7×10^{-5} mol dm^{-3} at 298 K]

(1)

☒ **A** 4.47

☒ **B** 4.77

☒ **C** 5.07

☒ **D** 5.46

(b) What is the **best** reason for the use of buffers in foods?

(1)

- **A** to improve taste
- **B** to help digestion of the food
- **C** to prevent deterioration by fungal activity
- **D** to enhance the colour and appearance of the food

(c) The carbonic acid/hydrogencarbonate ion buffer system in the blood involves the equilibria shown.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

How is the pH of blood affected by increased exercise?

(1)

- **A** there is no effect because the equilibria are not affected by activity
- **B** the pH will decrease due to the equilibria shifting to the left
- **C** the pH will decrease due to the equilibria shifting to the right
- **D** the pH is constant because it is a buffer system

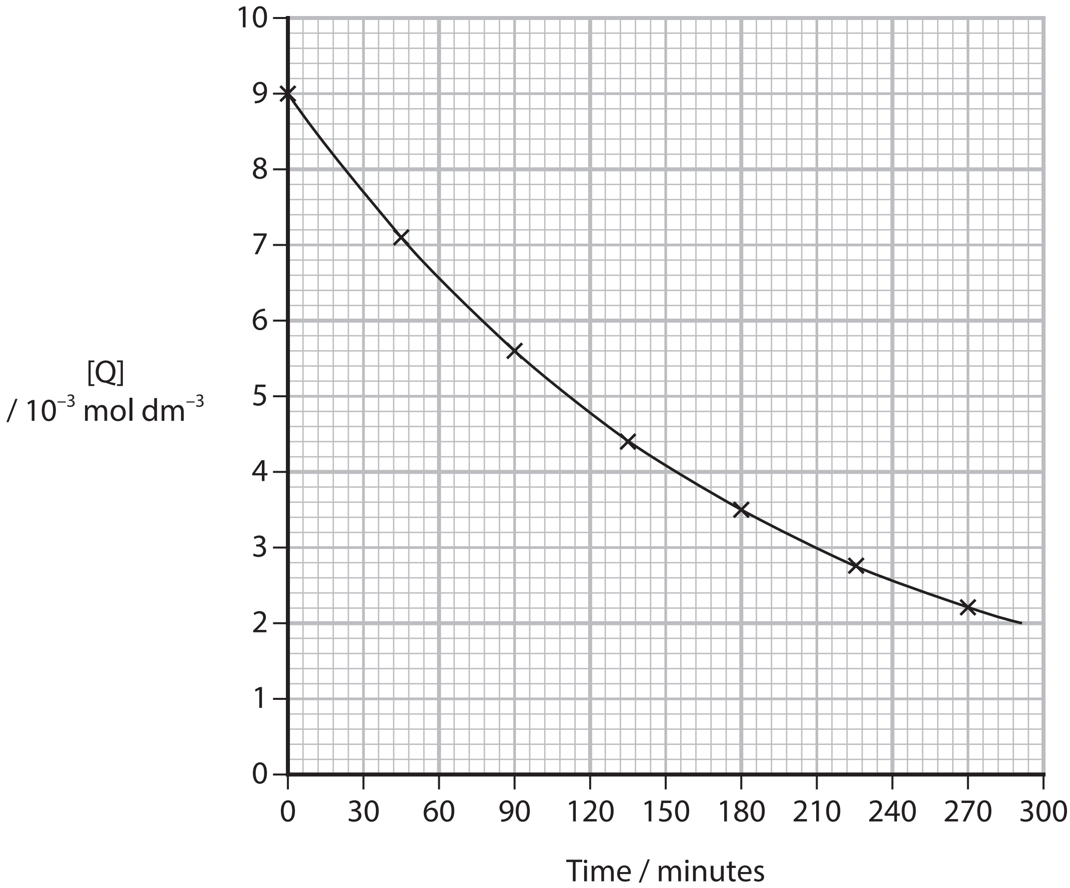
(Total for Question 13 = 3 marks)

14 Which has the greatest molar entropy?

- **A** $Hg(l)$
- **B** $H_2O(l)$
- **C** $NO(g)$
- **D** $NO_2(g)$

(Total for Question 14 = 1 mark)

15 A graph of the concentration of Q during decomposition is shown.



What is the half-life for this decomposition?

☒ **A** 93 minutes

☒ **B** 132 minutes

☒ **C** 146 minutes

☒ **D** 291 minutes

(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

16 This question is about pentan-2-one, $CH_3COCH_2CH_2CH_3$.

(a) Explain why pentan-2-one has a lower boiling temperature than pentan-2-ol.

(2)

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(b) Give a chemical test which distinguishes between pentan-2-one and pentan-3-one, $CH_3CH_2COCH_2CH_3$.
Include the results for both substances.

(2)

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(c) Give a different chemical test which distinguishes between pentan-2-one and pentanal, $CH_3CH_2CH_2CH_2CHO$.
Include the results for both substances.

(2)

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(d) Pentan-2-one, pentan-3-one and pentanal react in a similar way with one test reagent to form solid products.
Identify the reagent and describe how these solid products may be used to distinguish the original compounds.

(3)

(e) Pentan-2-one and pentan-3-one both react with hydrogen cyanide in the presence of KCN. With pentan-2-one a racemic mixture is formed but with pentan-3-one there is only one product.

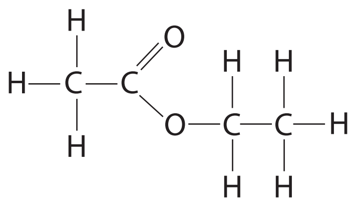
Explain this difference by referring **both** to the reaction mechanism and to the structures of the two molecules.

(4)

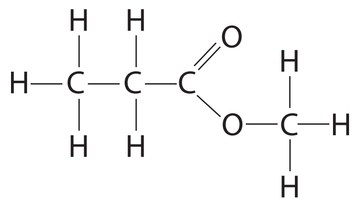
(Total for Question 16 = 13 marks)

17 Esters are difficult to distinguish from each other using chemical tests, so NMR spectroscopy is often used.

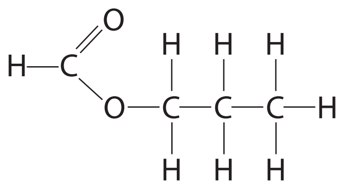
(a) There are four ester isomers with the molecular formula $C_4H_8O_2$. Their displayed formulae are shown.



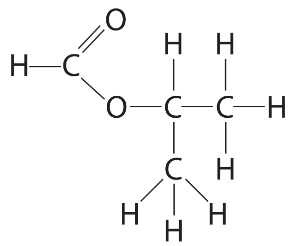
Ester **P**



Ester **Q**



Ester **R**



Ester **S**

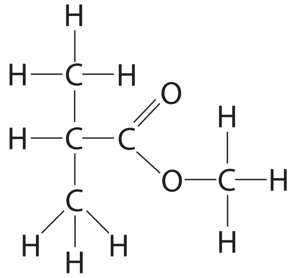
Explain which of the four esters can be distinguished from the other three by the numbers of peaks in the carbon-13 (^{13}C) NMR spectra.

Justify your answer by labelling any equivalent carbon atoms.

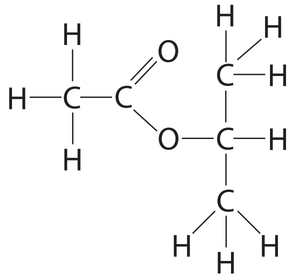
(3)

(b) There are nine ester isomers with the molecular formula $C_5H_{10}O_2$.

(i) The displayed formulae of two of these esters are shown.



Ester **W**



Ester **X**

Esters **W** and **X** both have one peak with a relative area of 3 in their **low**-resolution proton NMR spectra.

Explain how these peaks can be used to distinguish these two esters.

(2)

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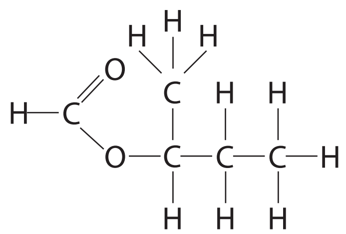
(ii) The displayed formulae of two different esters are shown in the boxes.

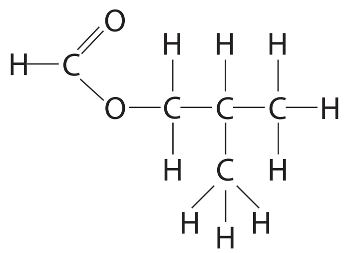
Label the displayed formulae of the two esters **Y** and **Z** to show the proton environments and the splitting patterns of the peaks in the **high**-resolution proton NMR spectra.
Clearly indicate any equivalent proton environments.

For any multiplet, you may refer to the number of separate peaks in the multiplet rather than giving a name.

(4)



Ester **Y**



Ester **Z**

(iii) Draw the displayed formula of the $C_5H_{10}O_2$ ester which has **only** 2 peaks in its low-resolution proton NMR structure.

(1)

(Total for Question 17 = 10 marks)

18 This question is about reaction kinetics.

*(a) Halogenoalkanes are hydrolysed by aqueous alkali to form alcohols.

$$RX + OH^- \rightarrow ROH + X^-$$

The rate equations for these reactions with two halogenoalkanes are shown.

1-bromobutane	rate = $k[CH_3CH_2CH_2CH_2Br][OH^-]$
2-bromo-2-methylpropane	rate = $k[(CH_3)_3CBr]$

Explain how these rate equations can be used to deduce the different reaction mechanisms of the reaction of hydroxide ions with these halogenoalkanes.

(6)

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(b) An initial-rates method may be used to investigate the kinetics of the reaction between hydrogen peroxide and iodide ions in acid solution.
The equation for this reaction is shown.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The reaction mixture contains a small amount of thiosulfate ions which reduce the iodine back to iodide ions.
The equation for this reduction is shown.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

As soon as the thiosulfate is used up, the iodine that is further produced reacts with the starch present and results in a colour change. The time taken for this colour change is noted and the reciprocal of this time is used as a measure of reaction rate.

The results from a series of experiments where the volume of the hydrogen peroxide was changed are given in the table.

Reaction rate / s^{-1}	0.9×10^{-2}	1.8×10^{-2}	2.5×10^{-2}	3.7×10^{-2}	4.6×10^{-2}
Volume of H_2O_2 / cm^3	10	20	30	40	50

(i) Give the colour **change** after all the thiosulfate is used up.

(2)

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(ii) Plot a graph of reaction rate against volume of hydrogen peroxide.

(3)

(iii) State and justify the reaction order with respect to hydrogen peroxide by using your graph.

(1)

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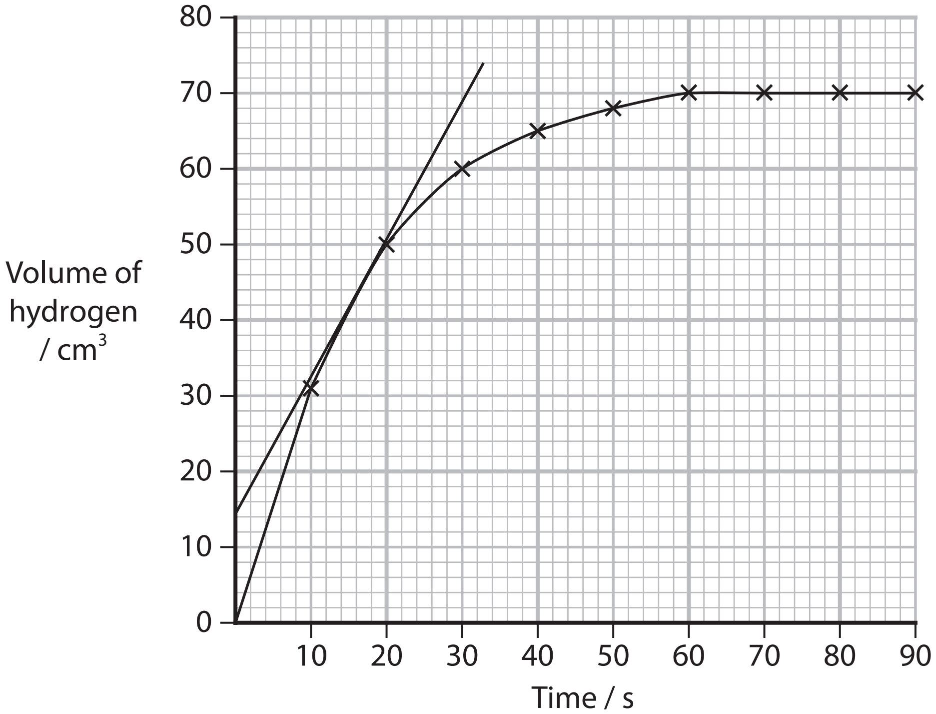
(c) The continuous monitoring method was used to investigate the kinetics of the reaction between magnesium and sulfuric acid at different temperatures. The equation for the reaction is shown.

$$Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$$

(i) The graph shows the results of an experiment at 80°C.



Calculate the reaction rate at 15 seconds using the tangent shown.

Give your answer to two significant figures and include units, if any.

(2)

(ii) The temperature of the reaction was changed to 75°C.
Draw a line on the graph to show the possible results if this was the only change. Justify any similarities and differences in the lines.

(2)

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(Total for Question 18 = 16 marks)

19 Many effervescent products such as vitamin tablets are solids which contain citric acid, $C_6H_8O_7$, and sodium hydrogencarbonate. Only when these tablets are added to water is fizzing observed. The equation for the reaction is shown.

$$C_6H_8O_7 + 3NaHCO_3 \rightarrow 3H_2O + 3CO_2 + Na_3C_6H_5O_7$$

(a) Give **two** reasons why this reaction is thermodynamically feasible when considering the entropy of the system.

(2)

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(b) Describe, in terms of the particles involved, why the reaction does not occur until the tablets are dissolved in water.

(3)

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(c) For the reaction at 25°C, the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings} = -234.9\,J\,K^{-1}\,mol^{-1}$.

Calculate the enthalpy change of the reaction.
Include a sign and units in your answer.

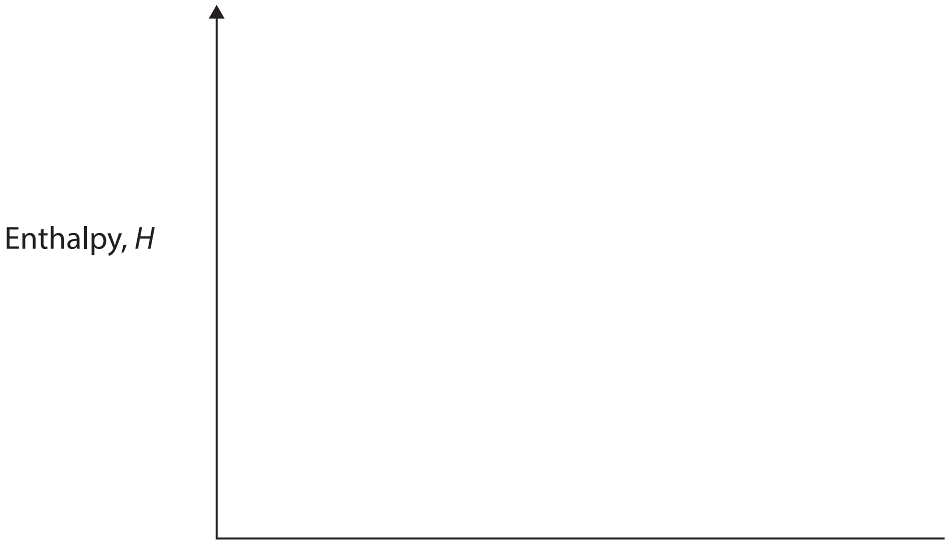
(2)

(d) The enthalpy change of solution, $\Delta_{sol}H$, of sodium hydrogencarbonate is $+18.6\,kJ\,mol^{-1}$.

Sketch the enthalpy level diagram to show the relationship between the enthalpy change of solution, lattice energy and enthalpies of hydration for the dissolving of sodium hydrogencarbonate in water.

Fully label your diagram.

(3)



(Total for Question 19 = 10 marks)

TOTAL FOR SECTION B = 49 MARKS

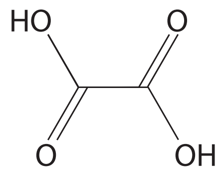
SECTION C

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

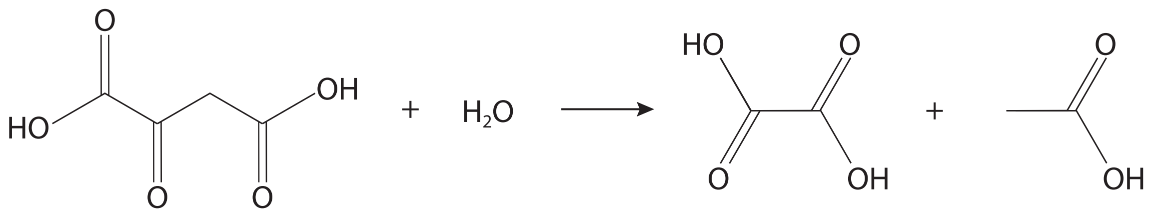
20

Oxalic acid

Oxalic acid has the IUPAC name ethanedioic acid and a molar mass = 90 g mol^{-1}.



The name oxalic acid originated from the fact that it was first isolated from plants of the genus *Oxalis*. The formation of oxalic acid in plants involves the hydrolysis of 2-oxobutanedioic acid.



Plants can also form oxalic acid from glycolic acid, $HOCH_2COOH$.

Oxalic acid can be manufactured by oxidising sucrose using nitric acid in the presence of a vanadium(V) oxide catalyst. Over 100,000 tonnes of oxalic acid are produced each year.

Much of the oxalic acid produced is used for cleaning or bleaching, because it converts insoluble iron compounds into soluble iron salts.

(a) Calculate the atom economy, by mass, for the formation of oxalic acid from the hydrolysis of 2-oxobutanedioic acid.

(2)

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(b) Give the laboratory reagents and conditions required to convert glycolic acid, $HOCH_2COOH$, to oxalic acid.

Do not consider nitric acid.

(2)

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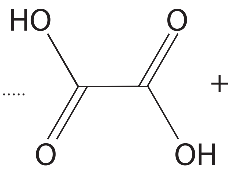
(c) Sucrose is oxidised by concentrated nitric acid to form oxalic acid.

(i) Complete the equation for the reaction of one mole of sucrose with nitric acid.

(2)

$C_{12}H_{22}O_{11}$ + $36HNO_3$ ⟶ .... 

+ .... NO_2 + ... H_2O

(ii) Give **one** observation that would be seen during this reaction.

(1)

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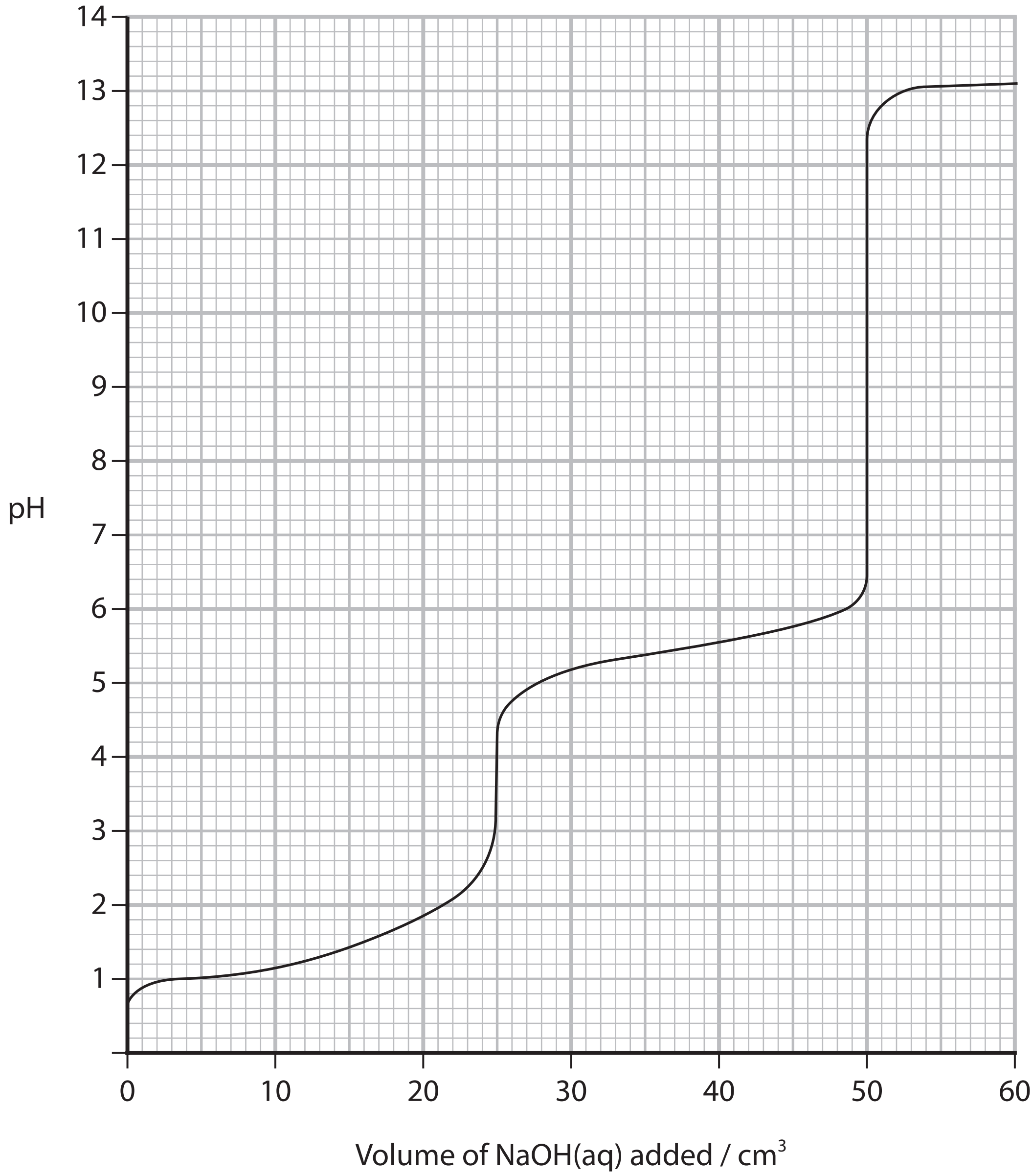
(d) A solution of sodium hydroxide was titrated against 25.0 cm^3 of oxalic acid solution. Both solutions were of equal concentrations.

(i) A student sketched a curve to show the changing pH during the titration.



Select **one** indicator for each equivalence point from this titration graph.
Include the colour at the end-point for each indicator.
Use your Data Booklet.

(2)

First indicator

....

Colour at the end-point

....

Second indicator

....

Colour at the end-point

....

(ii) Suggest a difficulty that would occur if both indicators were present in the same mixture.

(1)

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(iii) Determine, by using the graph, the **two** K_a values for oxalic acid.
You **must** show your working on the graph.

(5)

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(e) Spinach is one plant source of oxalic acid. Approximately 700 mg of oxalic acid can be extracted from 100 g of spinach.

(i) High-performance liquid chromatography, HPLC, is used for analysis in the extraction process. The HPLC equipment is connected to a detector which records peaks when substances pass through the HPLC column.

Suggest how a pure sample of oxalic acid would be used to identify the oxalic acid peak in the chromatogram of the spinach extract.

(1)

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(ii) A 0.558 mol dm^{-3} solution of oxalic acid is used for cleaning.

Calculate the mass of spinach required to make 500 cm^3 of this oxalic acid cleaning solution.
[Data: M_r oxalic acid = 90]

(3)

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(f) Write the equation for the reaction of oxalic acid with **excess** phosphorus(V) chloride.

(2)

(Total for Question 20 = 21 marks)

TOTAL FOR SECTION C = 21 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

Key

relative atomic mass **atomic symbol** name atomic (proton) number

1.0 **H** hydrogen 1

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
																	4.0 **He** helium 2
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											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							

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

DO NOT WRITE IN THIS AREA
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P 7 8 4 5 8 R A 0 3 2 3 2