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 29 May 2024

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.*
- Show all your working in calculations and include units where appropriate.

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.
- There is a Periodic Table on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

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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 Bromate(V) ions, BrO_3^-, react with bromide ions, Br^-, in aqueous acid.

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The rate equation for the reaction is shown.

$$\text{rate} = k\,[BrO_3^-]\,[Br^-]\,[H^+]^2$$

(a) Which **continuous** monitoring method could be used to obtain kinetics data for this reaction?

(1)

☐ A colorimetry

☐ **B** mass change

☐ **C** titration with sodium thiosulfate

☐ **D** volume of gas evolved

(b) What are the units of the rate constant, *k*, for this reaction?

(1)

☐ A $\text{mol dm}^{-3}\,\text{s}^{-1}$

☐ **B** $\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$

☐ **C** $\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}$

☐ **D** $\text{dm}^9\,\text{mol}^{-3}\,\text{s}^{-1}$

(c) The concentrations of **all** reactants are halved.

By what factor does the rate of reaction change?

(1)

☐ A $\frac{1}{2}$

☐ **B** $\frac{1}{4}$

☐ **C** $\frac{1}{8}$

☐ **D** $\frac{1}{16}$

(d) The first four steps in the reaction mechanism are shown.

Step **1** $BrO_3^- + H^+ \rightarrow BrO_3H$

Step **2** $BrO_3H + H^+ \rightarrow BrO_3H_2^+$

Step **3** $BrO_3H_2^+ + Br^- \rightarrow Br_2O_2 + H_2O$

Step **4** $Br_2O_2 + Br^- \rightarrow BrO_2^- + Br_2$

Which is the rate-determining step?

(1)

☒ A Step **1**

☐ B Step **2**

☐ C Step **3**

☐ D Step **4**

(Total for Question 1 = 4 marks)

2 Some data on lattice energies are shown.

Compound	Experimental lattice energy / $kJmol^{-1}$	Theoretical lattice energy / $kJmol^{-1}$
NaI	–705	–687
AgBr	–891	–816
Rb_2S	–1944	–1904
Li_2O	–2814	–2799

Which compound has the greatest degree of covalency within its ionic bonds?

☐ **A** NaI

☐ **B** AgBr

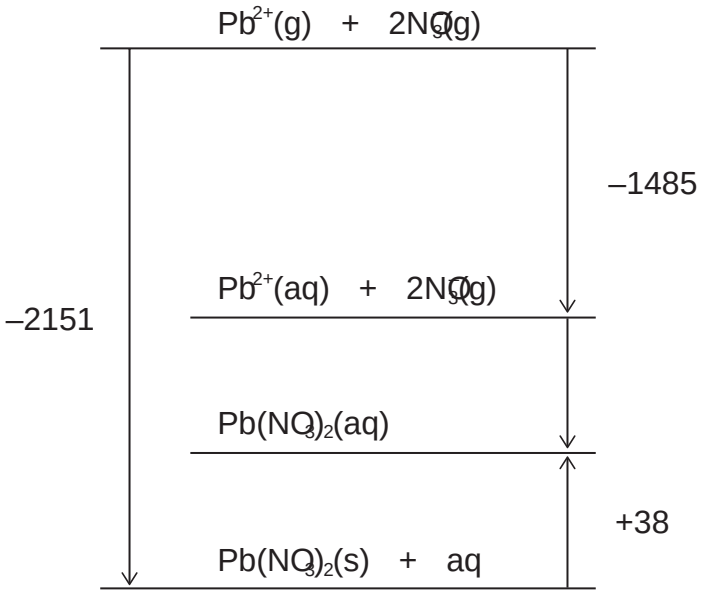
☐ **C** Rb_2S

☐ **D** Li_2O

(Total for Question 2 = 1 mark)

3 An enthalpy cycle for lead(II) nitrate is shown.

All values are in kJ mol^{-1}. The cycle is **not** to scale.



(a) Which of these statements is **true**?

(1)

- ☒ A the enthalpy change of formation of lead(II) nitrate is –2151 kJ mol^{-1}
- ☐ **B** the enthalpy change of solution of lead(II) nitrate is exothermic
- ☐ **C** the enthalpy change of hydration of a lead(II) ion is more exothermic than that of a nitrate ion
- ☐ **D** the entropy change of the surroundings for dissolving lead(II) nitrate is positive

(b) Using the enthalpy cycle, it can be calculated that the enthalpy change of hydration of a nitrate ion, in kJ mol^{-1}, is

(1)

- ☐ A –3598
- ☐ **B** –1799
- ☐ **C** –628
- ☐ **D** –314

(Total for Question 3 = 2 marks)

4 Ammonia is produced from nitrogen and hydrogen in the presence of a solid catalyst in an equilibrium reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\,kJ\,mol^{-1}$$

(a) 10 mol of $N_2(g)$ is heated with 30 mol of $H_2(g)$ in a sealed container. At equilibrium, 8.0 mol of $NH_3(g)$ is present.

What is the **total** amount of gas, in mol, in the equilibrium mixture?

(1)

☒ A 8.0

☒ **B** 20

☒ **C** 32

☒ **D** 48

(b) What is the expression for the equilibrium constant, K_p, for this reaction?

(1)

☒ A $\dfrac{p(N_2) + p(H_2)^3}{p(NH_3)^2}$

☒ **B** $\dfrac{p(NH_3)^2}{p(N_2) + p(H_2)^3}$

☒ **C** $\dfrac{p(NH_3)^2}{p(N_2) \times p(H_2)^3}$

☒ **D** $\dfrac{p(N_2) \times p(H_2)^3}{p(NH_3)^2}$

(c) Which change would increase the value of K_p for this reaction?

(1)

☒ A decreasing the temperature

☒ **B** decreasing the particle size of the catalyst

☒ **C** increasing the total pressure

☒ **D** increasing the concentration of hydrogen molecules

(Total for Question 4 = 3 marks)

5 For all chemical reactions, the equilibrium constant, K, is related to the total entropy change, ΔS_{total}, by the expression shown.

$$\Delta S_{total} = R \ln K$$

ΔS_{total} for a reaction is negative.

Which statement is true?

- ☒ **A** the value of K is less than 1
- ☐ **B** the value of K is greater than 1
- ☐ **C** the value of K is negative
- ☐ **D** the position of equilibrium lies to the right

(Total for Question 5 = 1 mark)

6 A buffer solution contains CH_3COOH and CH_3COONa in the ratio, 1 : 4.

What is the pH of this buffer solution?

[$K_a(CH_3COOH) = 1.7 \times 10^{-5}$ mol dm^{-3}]

- ☐ **A** 2.4
- ☐ **B** 4.2
- ☐ **C** 4.8
- ☐ **D** 5.4

(Total for Question 6 = 1 mark)

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

7 The accumulation of carbon dioxide during exercise reduces the pH in cells and in blood.

Which of these reactions is **most** important in buffering the decrease in pH that occurs?

- ☒ **A** $H_2CO_3 \rightarrow H^+ + HCO_3^-$
- ☐ **B** $HCO_3^- + H^+ \rightarrow H_2CO_3$
- ☐ **C** $HCO_3^- \rightarrow H^+ + CO_3^{2-}$
- ☐ **D** $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

(Total for Question 7 = 1 mark)

8 How many chiral centres are in the molecule shown?

- ☒ **A** 4
- ☐ **B** 5
- ☐ **C** 6
- ☐ **D** 7

(Total for Question 8 = 1 mark)

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

9 The rate equation for the hydrolysis of a halogenoalkane, RX, in aqueous alkali is shown.

$$\text{rate} = k\,[\text{RX}]$$

Which of these statements is **true**?

- **A** the mechanism involves a carbocation intermediate
- **B** the reaction has an S_N2 mechanism
- **C** the halogenoalkane could be 1-bromobutane
- **D** the main nucleophile in this reaction is H_2O

(Total for Question 9 = 1 mark)

10 Propanone reacts with HCN in the presence of KCN.

Which of these statements is **incorrect**?

- **A** CN^- acts as a nucleophile in the reaction
- **B** a racemic mixture is formed
- **C** the product is **not** optically active
- **D** the product is 2-hydroxy-2-methylpropanenitrile

(Total for Question 10 = 1 mark)

11 Which statement(s) is/are correct?

CH_3CH_2COCl reacts with

1 CH_3NH_2 to form $CH_3CH_2CONHCH_3$

2 $(CH_3)_2NH$ to form $CH_3CH_2CON(CH_3)_2$

3 $(CH_3)_3N$ to form $CH_3CH_2CON(CH_3)_3$

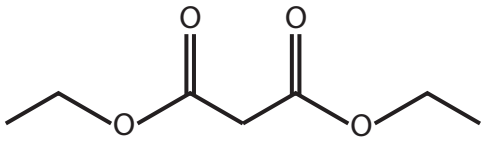
- **A** 1, 2 and 3
- **B** 1 and 2 only
- **C** 2 and 3 only
- **D** 1 only

(Total for Question 11 = 1 mark)

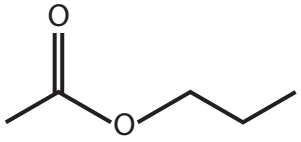
12 An ester is hydrolysed in excess dilute hydrochloric acid to form ethanol and propanedioic acid.

What is the skeletal formula of this ester?

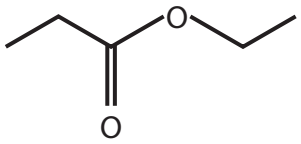
☒ **A**



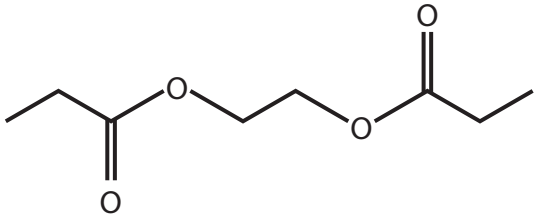
☐ **B**



☒ **C**



☒ **D**



(Total for Question 12 = 1 mark)

13 Which compound has **most** peaks in its ^{13}C NMR spectrum?

☒ **A** CH_3COCH_3

☐ **B** $CH_3COCH_2CH_3$

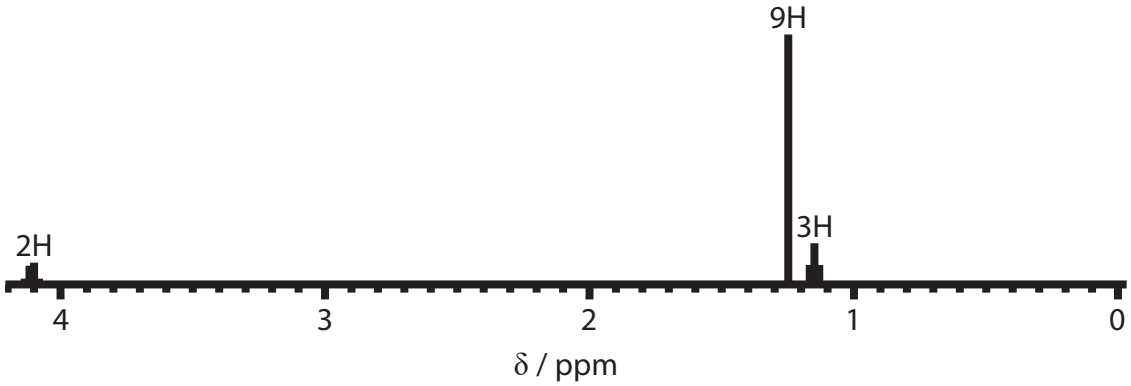
☐ **C** $CH_3CH_2COCH_2CH_3$

☐ **D** $CH_3COCH_2CH_2COCH_3$

(Total for Question 13 = 1 mark)

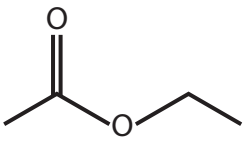
Use this space for any rough working. Anything you write in this space will gain no credit.

14 The high resolution ^{1}H NMR spectrum of an ester is shown.

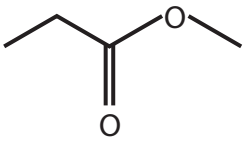


What is the skeletal formula of this ester? Use the Data Booklet as a source of information.

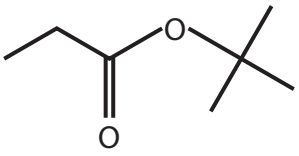
☒ **A**



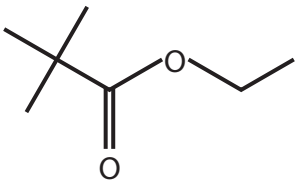
☒ **B**



☒ **C**



☒ **D**



(Total for Question 14 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 This question is about some compounds of silicon.

(a) Silicon dioxide and magnesium react when heated strongly.

Reaction **1** $SiO_2(s) + 4Mg(s) \rightarrow Mg_2Si(s) + 2MgO(s)$

(i) Complete the table, indicating the type of bonding in the reactants and products of this reaction.

(2)

Substance	SiO_2	Mg	Mg_2Si	MgO
Bonding type			covalent	

(ii) The entropy change of the system, ΔS_{system}, for Reaction **1** is $-43.8\,J\,K^{-1}\,mol^{-1}$.

Suggest, with reference to the equation, why ΔS_{system} for this reaction is negative.

(2)

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(iii) The enthalpy change, ΔH, for Reaction **1** is $-370\,kJ\,mol^{-1}$.

Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, in $J\,K^{-1}\,mol^{-1}$, for Reaction **1** at 23.0 °C.

(2)

(iv) Calculate the total entropy change, ΔS_{total}, for Reaction **1** at 23.0 °C.

Give your answer to an appropriate number of significant figures, and in units of $JK^{-1}\,mol^{-1}$.

(2)

(v) Reaction **1** does not occur at room temperature due to its very high activation energy.

Suggest why the activation energy for Reaction **1** is very high.

(1)

.....

.....

.....

(b) Magnesium silicide, Mg_2Si, reacts with hydrochloric acid forming silane, SiH_4, and magnesium chloride.

(i) Write an equation for this reaction.

State symbols are **not** required.

(1)

(ii) Silane has a molecular structure.

Complete the table, giving the shape of a molecule of SiH_4 and its bond angle.

(2)

Name of shape	
Bond angle	

(c) Silane spontaneously combusts in air at room temperature.

Reaction **2** $SiH_4(g) + 2O_2(g) \rightarrow SiO_2(s) + 2H_2O(l)$

Entropy data for this reaction are shown.

Species	$SiH_4(g)$	$O_2(g)$	$SiO_2(s)$	$H_2O(l)$
$S^\ominus$ / $JK^{-1}mol^{-1}$	204.5	205.0	41.8	69.9

(i) Calculate the entropy change of the system, ΔS_{system}, in $J\,K^{-1}\,mol^{-1}$, for Reaction **2**.

(2)

(ii) State why the entropy change of the surroundings for Reaction **2** is highly positive, in terms of the bond strengths of the reactants and products.

(1)

.....

.....

.....

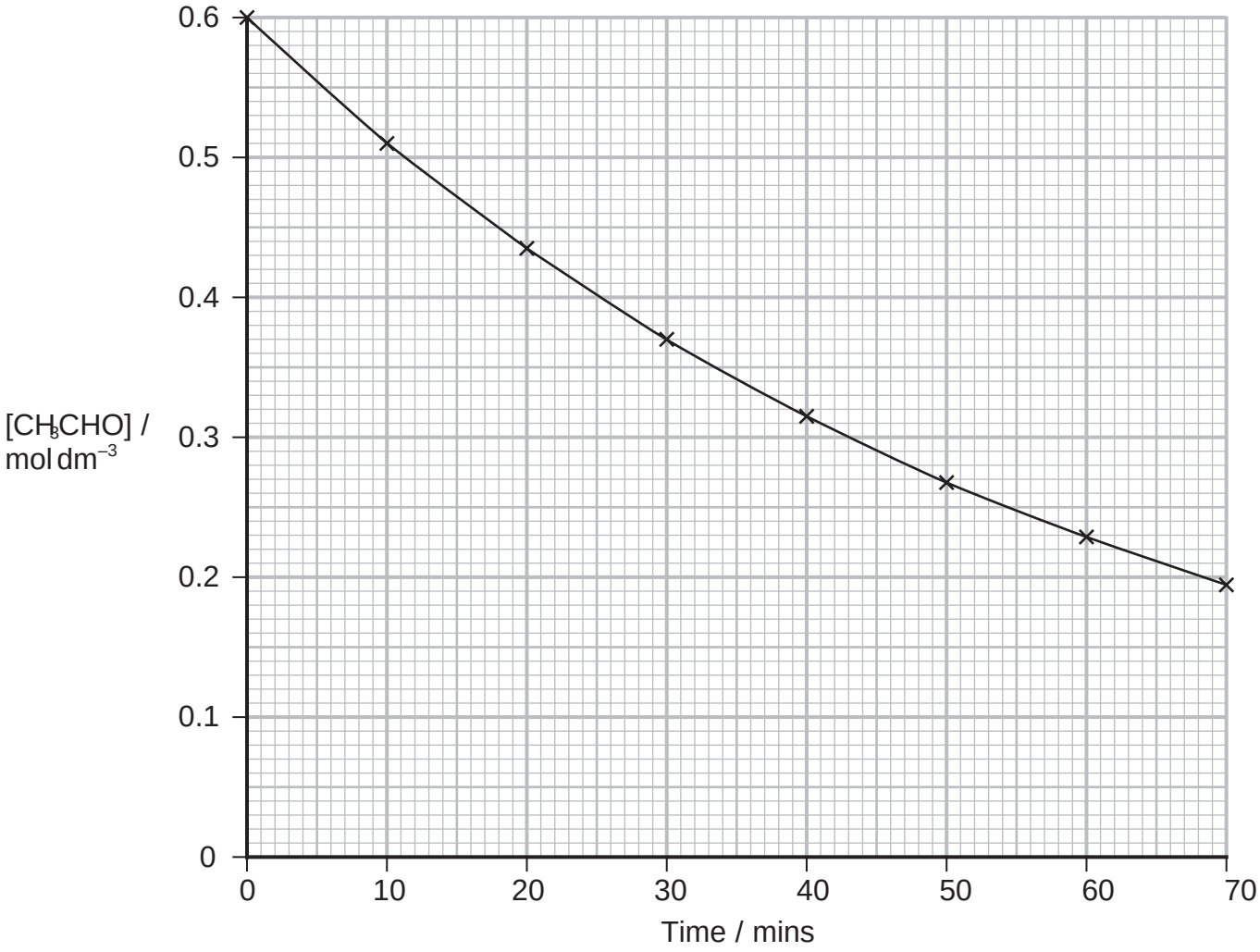
.....

(Total for Question 15 = 15 marks)

16 This question is about the kinetics of the gas phase decomposition of CH_3CHO.

$$CH_3CHO \rightarrow CH_4 + CO$$

(a) A concentration-time graph for this reaction at 1000 K is shown.



(i) Calculate the initial rate of reaction, in **mol dm^{-3} s^{-1}**, at 1000 K.

You must show your working on the graph.

(3)

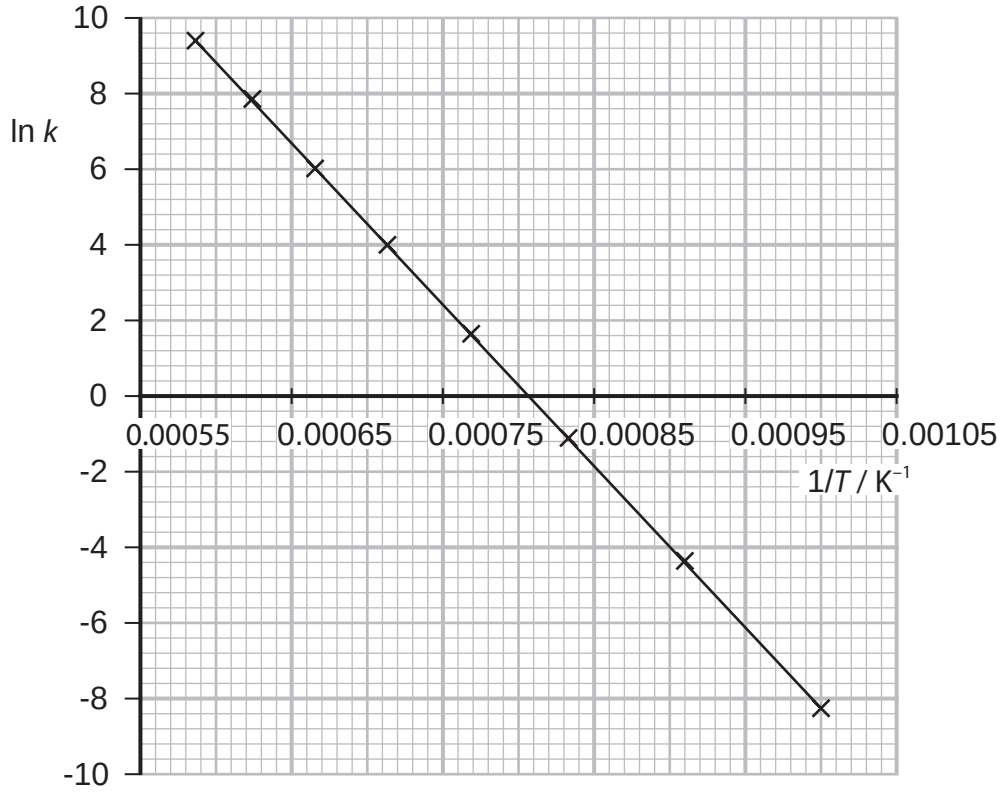
(ii) Deduce the rate equation for this reaction at 1000 K, by determining two half-lives.

You must show your working on the graph.

(2)

(b) The rate constant, k, for the decomposition of CH_3CHO was determined between 1000 K and 1700 K.

The results are plotted on the graph of ln k against $1 / T$.



Determine the activation energy, E_a, for this reaction.

Give your answer to **three** significant figures and include units.

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \qquad R = 8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$$

(4)

(Total for Question 16 = 9 marks)

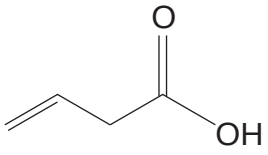
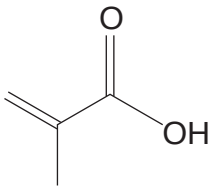
17 This question is about carboxylic acids and their derivatives.

(a) There are five carboxylic acids with the formula $C_4H_6O_2$.
Four are structural isomers.

One of these structural isomers has two stereoisomers.

(i) Name the two structural isomers shown.

(2)

Isomer		
Name		

(ii) The third structural isomer has two stereoisomers.

Draw these stereoisomers.

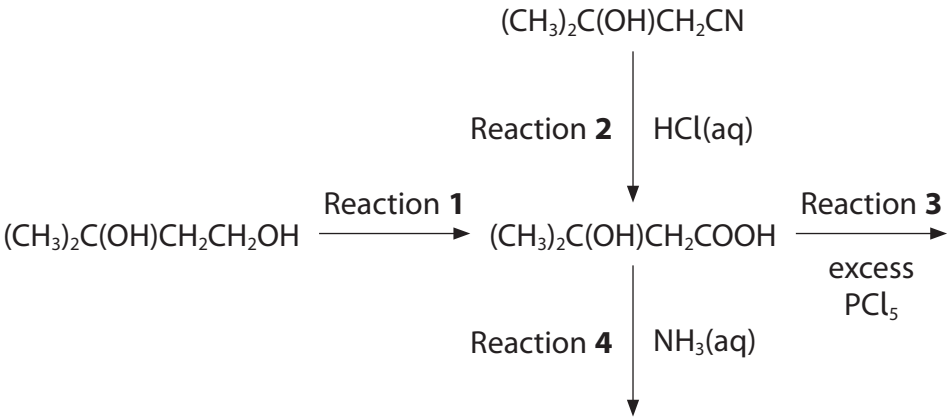
(2)

Stereoisomer **1**	Stereoisomer **2**

(iii) Draw the fourth structural isomer.

(1)

(b) Some reactions involving 3-hydroxy-3-methylbutanoic acid, $(CH_3)_2C(OH)CH_2COOH$, are shown.



(i) Give the **e**agents and conditions for Reaction **1**.

(1)

.....

.....

(ii) Write the equation for Reaction **2**. State symbols are **not** required.

(2)

(iii) Give the structure of the organic product formed in Reaction **3**.

(2)

(iv) Give the structure of the organic product formed in Reaction **4**.

(1)

(Total for Question 17 = 11 marks)

18 This question is about some reactions of propanal, CH_3CH_2CHO, and propanone, CH_3COCH_3.

(a) Propanal and propanone react similarly with lithium tetrahydridoaluminate(III).

Complete the table about these reactions.

(4)

Formula of lithium tetrahydridoaluminate(III)	
Essential reaction conditions	
Type of reaction	
Name of organic product with propanal	
Name of organic product with propanone	

(b) State what would be **seen** when separate samples of propanal and propanone are warmed with Tollens' reagent.

(2)

.....

.....

.....

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.....

.....

(c) When propanone reacts with iodine in the presence of aqueous sodium hydroxide, a yellow precipitate is observed.

Write an equation for this reaction.

Include state symbols.

(3)

(d) Propanal and propanone both react with 2,4-dinitrophenylhydrazine.

The products of these reactions may be used to distinguish between separate samples of propanal and propanone.

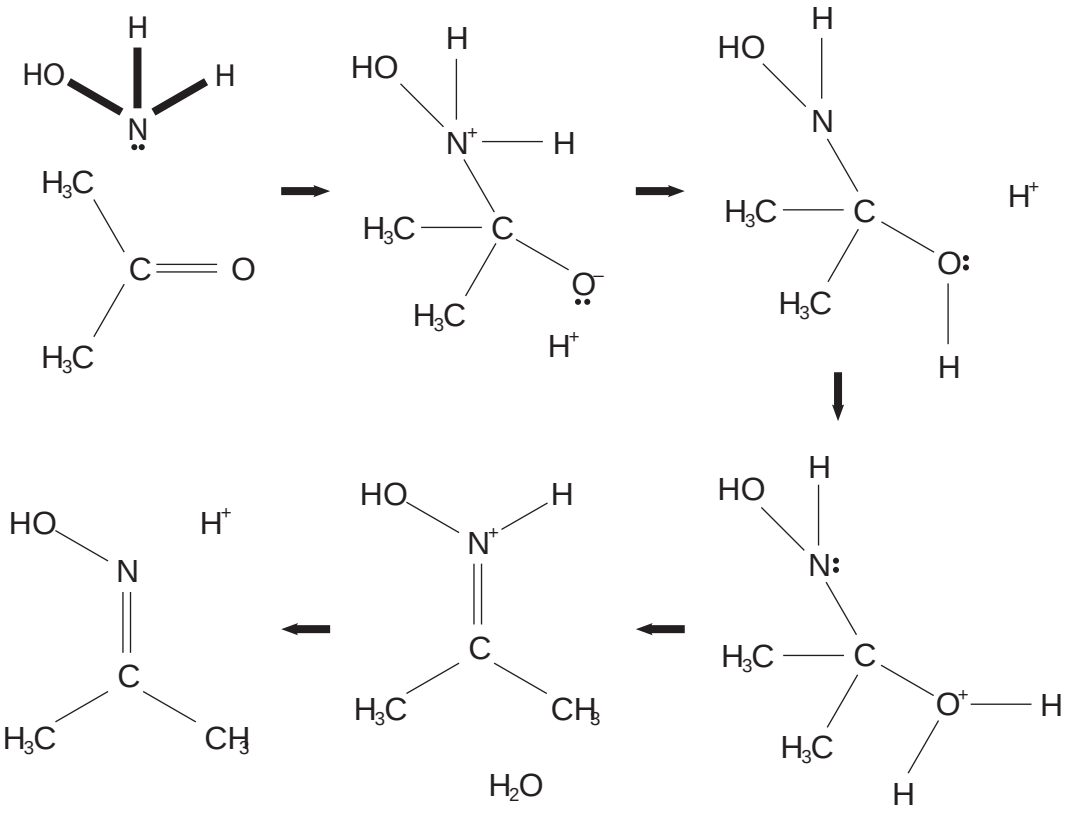
Describe, in outline, the laboratory procedure for doing this.

(3)

(e) Propanone, CH_3COCH_3, reacts with hydroxylamine, NH_2OH, under mildly acidic conditions.
The first stage of the reaction is a nucleophilic addition.

Add curly arrows to complete the mechanism for this reaction.

(4)



(Total for Question 18 = 16 marks)

TOTAL FOR SECTION B = 51 MARKS

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SECTION C

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

19 This question is about acids and bases.

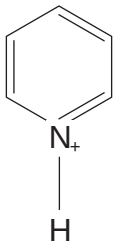
(a) Some K_a and pK_a values for several weak acids are shown.

Weak acid	K_a / mol dm^{-3}	pK_a
$C_5H_5NH^+$		5.25
CH_3CH_2COOH	1.3×10^{-5}	4.88
HCOOH	1.8×10^{-4}	3.75
$CH_2ClCOOH$	1.4×10^{-3}	2.85
$CHCl_2COOH$	4.5×10^{-2}	

(i) Complete the table.

(2)

(ii) The structure of $C_5H_5NH^+$ is shown.



Write the K_a expression for this weak acid.

(1)

(iii) When methanoic acid is added to propanoic acid, an equilibrium is set up containing two acid-base pairs.

Complete the equilibrium, labelling the acid-base pairs as **A1**, **B1** and **A2**, **B2**.

(2)

CH_3CH_2COOH + HCOOH $\rightleftharpoons$ ..... + ...

....

*(iv) A student measured the pH of separate 0.050 mol dm^{-3} solutions of $CH_2ClCOOH$ and of $CHCl_2COOH$, using a pH meter.

The student also calculated the pH of these solutions, making two assumptions:

- $[H^+] = [A^-]$
- $[HA]_{equilibrium} = [HA]_{initial}$

The measured and calculated pH values are shown.

	0.050 mol dm^{-3} $CH_2ClCOOH$	0.050 mol dm^{-3} $CHCl_2COOH$
Measured pH value	2.11	1.52
Calculated pH value	2.08	1.32

Discuss the differences between the student's measured and calculated pH values.

(6)

In your answer, you should

- show how the student calculated their pH values

  [$K_a(CH_2ClCOOH) = 1.4 \times 10^{-3}$ mol dm^{-3}; $K_a(CHCl_2COOH) = 4.5 \times 10^{-2}$ mol dm^{-3}]

- explain, with reference to the assumptions made, why there is a difference between the calculated and measured pH values
- suggest why the measured pH values are higher than the calculated pH values.

(b) 4-Hydroxybenzoic acid, HOC_6H_4COOH, is a diprotic acid, which dissociates in two stages. Each stage has a different pK_a value.

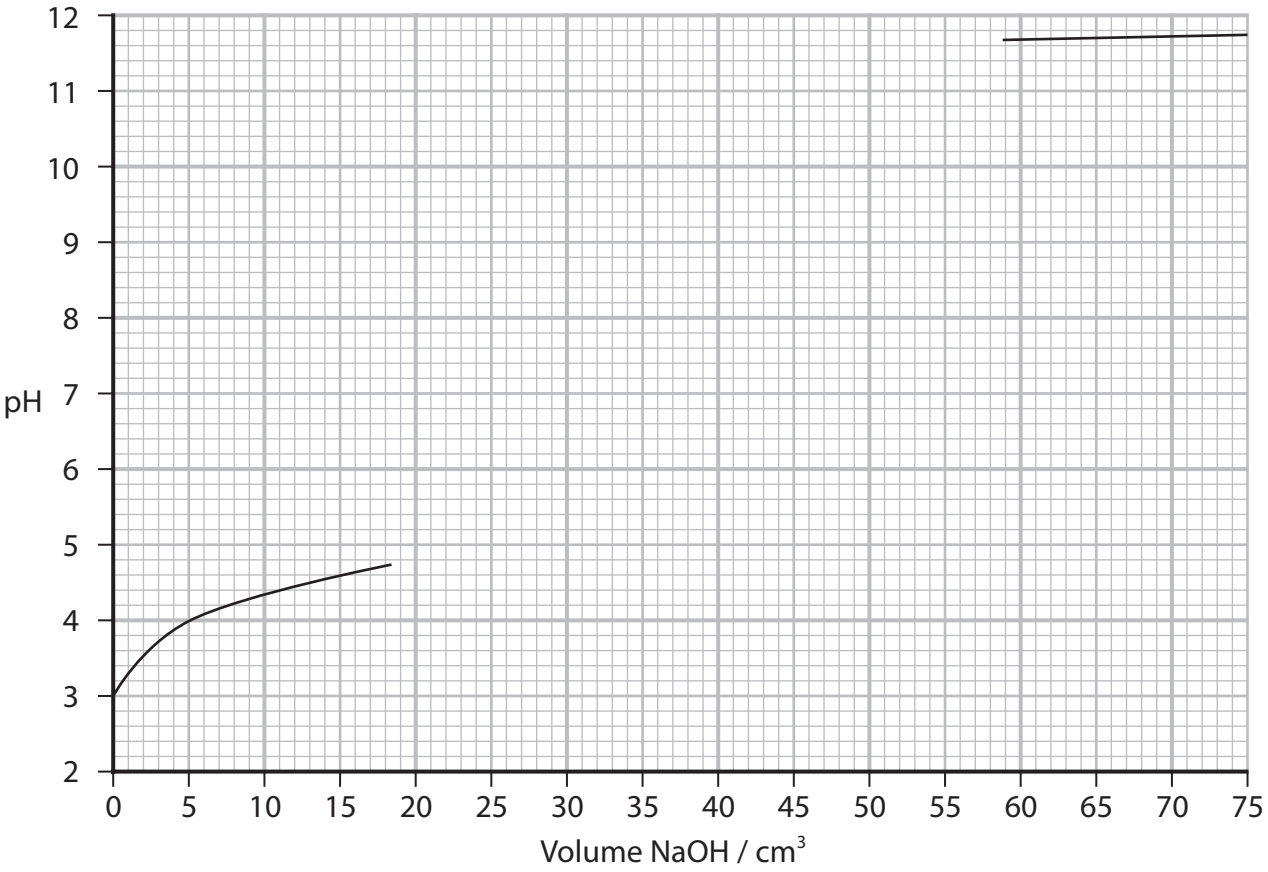
Stage **1** $HOC_6H_4COOH \rightleftharpoons H^+ + HOC_6H_4COO^-$ pK_{a1} = 4.5

Stage **2** $HOC_6H_4COO^- \rightleftharpoons H^+ + {}^-OC_6H_4COO^-$ pK_{a2} = 9.3

In a titration, 75.0 cm^3 of 0.025 mol dm^{-3} NaOH was added to 25.0 cm^3 of 0.025 mol dm^{-3} HOC_6H_4COOH.

Complete the titration curve.

(3)



(c) A student was given 50.0 cm^3 of a solution of sodium hydroxide.

The pH of this solution was 12.43.

The student was asked to adjust the pH to 12.00, by dilution with deionised water. The student did **not** have access to a pH meter.

Calculate the volume of deionised water, **in cm^3**, the student should add to the original solution.

(5)

(Total for Question 19 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 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