Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number | Candidate Number

Pearson Edexcel International Advanced Level

Tuesday 22 October 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.*

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 ▶

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Pearson

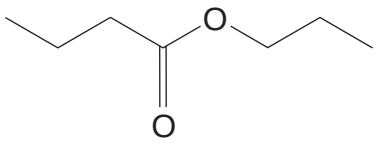
SECTION A

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 An ester has the structure shown.



Which pair of reactants would form this ester, under suitable conditions?

☒ **A** butanoic acid and propan-2-ol

☒ **B** butanoyl chloride and propan-1-ol

☒ **C** propanoic acid and butan-1-ol

☒ **D** propanoyl chloride and butan-2-ol

(Total for Question 1 = 1 mark)

2 Which compound will have the **highest** boiling temperature?

☒ **A** $CH_3CH_2CH_2CH_2CH_3$

☒ **B** $CH_3CH_2CH_2CHO$

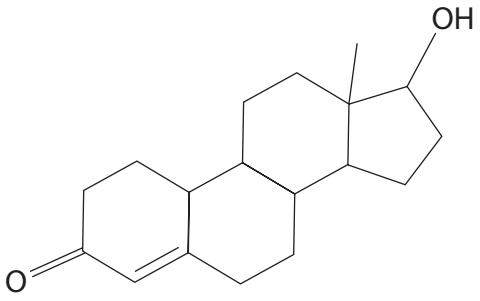
☒ **C** $CH_3COCH_2CH_3$

☒ **D** CH_3CH_2COOH

(Total for Question 2 = 1 mark)

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

3 The steroid nandrolone has the structure shown.

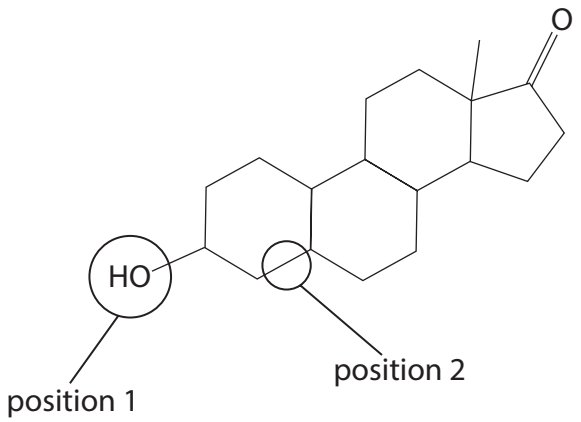


(a) How many chiral centres are present in nandrolone?

(1)

- ☒ **A** six
- ☒ **B** seven
- ☒ **C** eight
- ☒ **D** nine

(b) Nandrolone is broken down in the body into the compound shown.

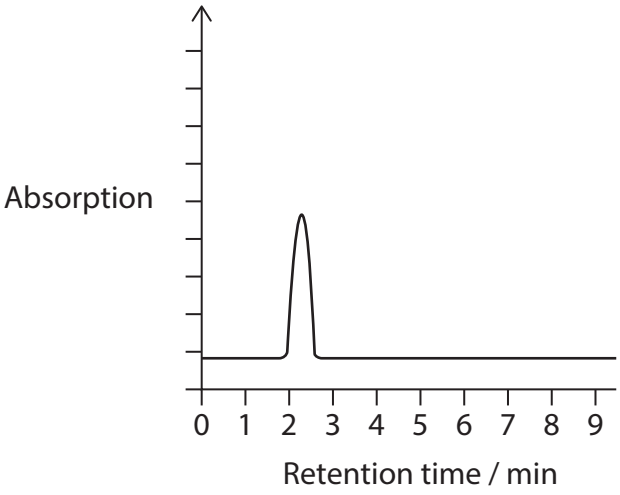


What reactions have taken place to form the new bonds at position 1 and position 2?

(1)

		Position 1	Position 2
☒	**A**	reduction	substitution
☒	**B**	reduction	addition
☒	**C**	oxidation	substitution
☒	**D**	oxidation	addition

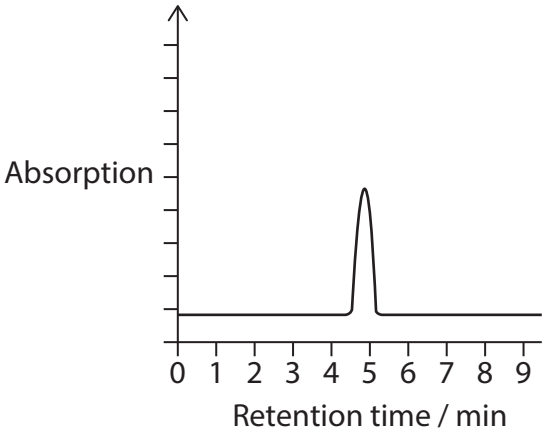
(c) A sample containing 2×10^{-9} g cm^{-3} of nandrolone was analysed using gas chromatography. The chromatogram produced is shown.



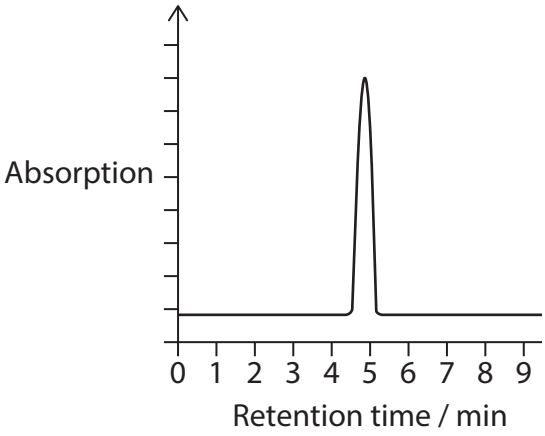
A second sample containing 4×10^{-9} g cm^{-3} of nandrolone was also analysed using gas chromatography, under the same conditions.

Which is the chromatogram produced by this second sample?

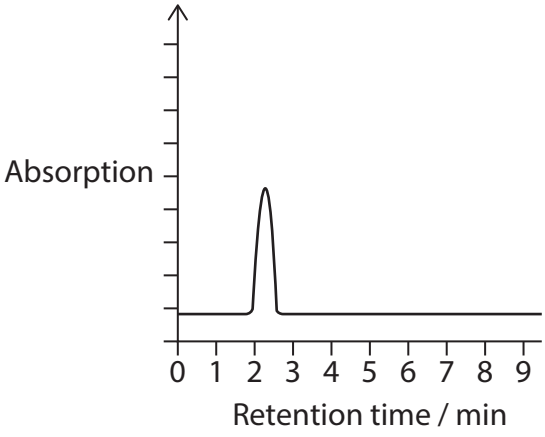
(1)



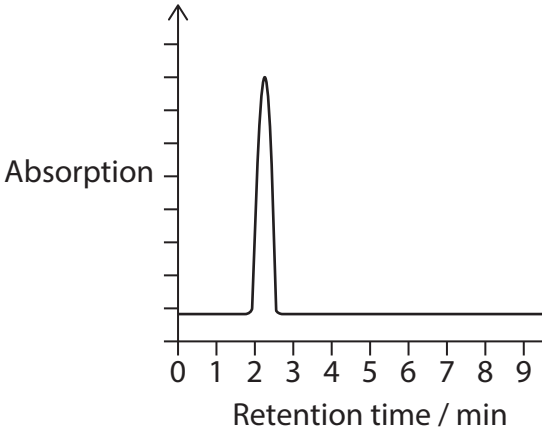
☒ **A**



☒ **B**



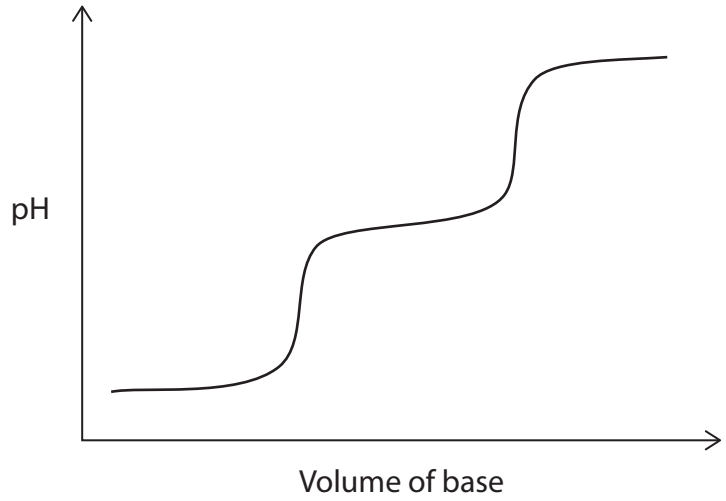
☒ **C**



☒ **D**

(Total for Question 3 = 3 marks)

4 A titration curve for the titration of an acid with a strong base is shown.



What could be the formula of the acid?

- ☒ **A** HX
- ☒ **B** HX_2
- ☒ **C** H_2X
- ☒ **D** H_3X

(Total for Question 4 = 1 mark)

5 Ethanoic acid, CH_3COOH, can react with a hydrogensulfite ion, HSO_3^-.

Which is a correct acid conjugate-base pair for this reaction?

[K_a for ethanoic acid = 1.7×10^{-5} mol dm^{-3}

K_a for hydrogensulfite ion = 6.2×10^{-8} mol dm^{-3}]

	Acid	Conjugate-base
☒ **A**	HSO_3^-	SO_3^{2-}
☒ **B**	HSO_3^-	H_2SO_3
☒ **C**	CH_3COOH	$CH_3CO_2^-$
☒ **D**	CH_3COOH	$CH_3COOH_2^+$

(Total for Question 5 = 1 mark)

6 Which indicator can be used to show the end-point of a titration between hydrochloric acid, HCl(aq), and ammonia solution, NH_3(aq)?

- ☒ **A** universal indicator
- ☒ **B** phenolphthalein
- ☒ **C** phenol red
- ☒ **D** methyl orange

(Total for Question 6 = 1 mark)

7 Phenolphthalein is a very weak acid and it forms a colourless solution under acidic conditions.

Sodium hydroxide is titrated against hydrochloric acid using phenolphthalein indicator. At the end-point, the solution is pink because phenolphthalein

- ☒ **A** accepts hydroxide ions and becomes a cation
- ☒ **B** accepts hydroxide ions and becomes an anion
- ☒ **C** donates hydrogen ions and becomes a cation
- ☒ **D** donates hydrogen ions and becomes an anion

(Total for Question 7 = 1 mark)

8 The dissociation of water is an endothermic reaction.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad \Delta H \text{ is positive}$$

[$K_w = 1.0 \times 10^{-14}\,mol^2\,dm^{-6}$ at 298 K $\quad K_w = 2.92 \times 10^{-14}\,mol^2\,dm^{-6}$ at 313 K]

What is the best **estimate** of the pH of water at 313 K?

- ☒ **A** 7.8
- ☒ **B** 7.0
- ☒ **C** 6.8
- ☒ **D** 5.8

(Total for Question 8 = 1 mark)

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

9 Magnesium nitrate decomposes on heating as shown.

$$Mg(NO_3)_2(s) \rightleftharpoons MgO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

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

☒ **A** $K_p = p(NO_2)^2 p(O_2)^{\frac{1}{2}}$

☒ **B** $K_p = p(NO_2)^4 p(O_2)$

☒ **C** $K_p = \dfrac{p(MgO)\, p(NO_2)^2\, p(O_2)^{\frac{1}{2}}}{p(Mg(NO_3)_2)}$

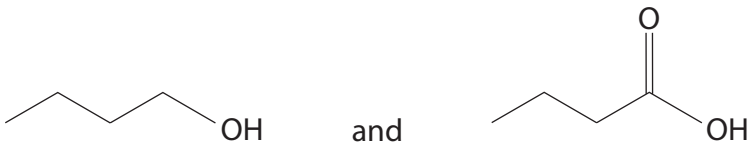
☒ **D** $K_p = \dfrac{p(MgO)^2\, p(NO_2)^4\, p(O_2)}{p(Mg(NO_3)_2)^2}$

(Total for Question 9 = 1 mark)

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

10 Which test can be used to distinguish between each of the pairs of compounds shown?

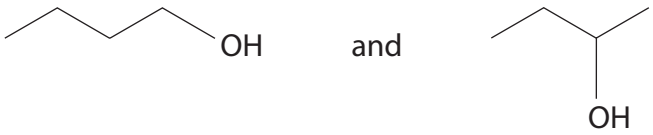
(a)



(1)

- ☒ **A** warm each compound with Tollens' reagent
- ☒ **B** add sodium carbonate solution to each compound
- ☒ **C** warm each compound with iodine under alkaline conditions
- ☒ **D** add phosphorus(V) chloride to each compound

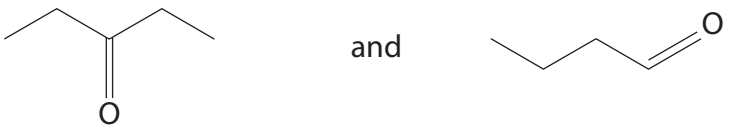
(b)



(1)

- ☒ **A** warm each compound with Tollens' reagent
- ☒ **B** add sodium carbonate solution to each compound
- ☒ **C** warm each compound with iodine under alkaline conditions
- ☒ **D** add phosphorus(V) chloride to each compound

(c)



(1)

- ☒ **A** warm each compound with Tollens' reagent
- ☒ **B** add sodium carbonate solution to each compound
- ☒ **C** warm each compound with iodine under alkaline conditions
- ☒ **D** add phosphorus(V) chloride to each compound

(Total for Question 10 = 3 marks)

11 Some thermodynamic information is shown for four reactions, W, X, Y and Z, at 298 K.

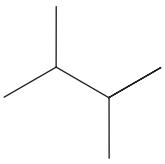
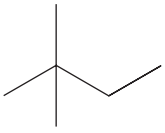
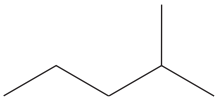
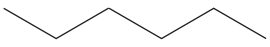
Reaction	ΔH	$T\Delta S_{system}$
W	negative and with a larger negative value than $T\Delta S_{system}$	negative
X	negative	positive
Y	positive	positive and with a smaller positive value than ΔH
Z	positive	negative

Which of these reactions are feasible at 298 K?

- ☒ **A** X only
- ☒ **B** W and X only
- ☒ **C** Y only
- ☒ **D** W and Z only

(Total for Question 11 = 1 mark)

12 Which isomer has the most peaks in its ^{13}C NMR spectrum?

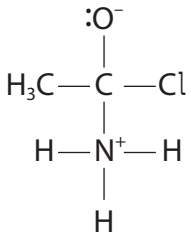
- ☒ **A** 
- ☒ **B** 
- ☒ **C** 
- ☒ **D** 

(Total for Question 12 = 1 mark)

13 Ethanoyl chloride reacts with ammonia, forming ethanamide.

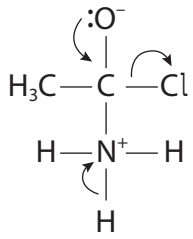
$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl$$

The first step of the mechanism forms the intermediate shown.

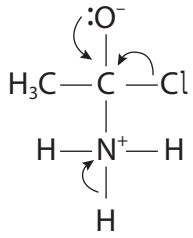


Which diagram shows the movements of electron pairs when ethanamide forms from this intermediate?

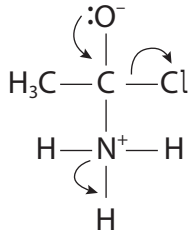
☒ **A**



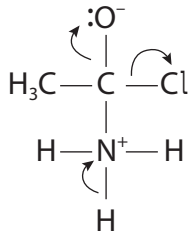
☒ **B**



☒ **C**

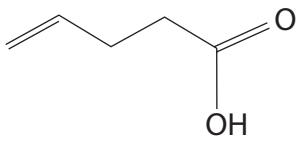


☒ **D**



(Total for Question 13 = 1 mark)

14 The compound shown reacts with **excess** $LiAlH_4$.



(a) What solvent is used in this reaction?

(1)

☒ **A** ethanol

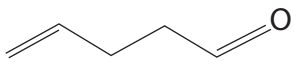
☒ **B** ether

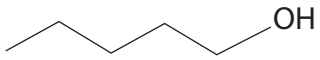
☒ **C** ethyl ethanoate

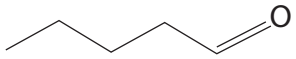
☒ **D** water

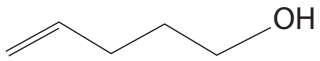
(b) What is the organic product that forms?

(1)

☒ **A**


☒ **B**


☒ **C**


☒ **D**


(Total for Question 14 = 2 marks)

15 Which monomer could form a condensation polymer without needing a second type of monomer?

☒ **A** $HO(CH_2)_4OH$

☒ **B** $HO(CH_2)_4COCl$

☒ **C** $HO(CH_2)_4CH{=}CH_2$

☒ **D** $HO(CH_2)_4CH_2Cl$

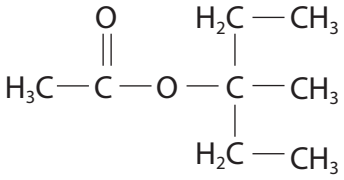
(Total for Question 15 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

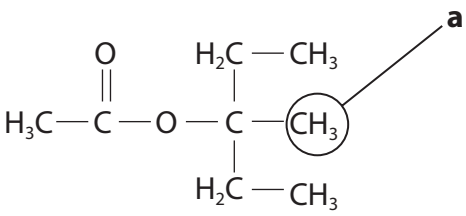
16 An ester, **X**, with the molecular formula $C_8H_{16}O_2$, has the structure shown.



(a) Deduce the name of the alcohol used to synthesise **X** in a reaction with ethanoyl chloride.

(1)

(b) One of the proton environments in **X** is labelled '**a**'.



(i) Complete the labelling of this structure to show each of the other proton environments in **X**, clearly linking any that are the same.

(2)

(ii) Describe **three** ways in which the high resolution ^{1}H NMR spectrum can be used to distinguish between the **methyl** groups in **X**, other than **a**.

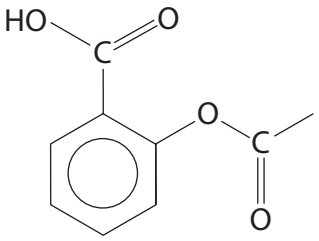
(3)

(c) An isomer of **X** is a carboxylic acid with five peaks in its ^{13}C NMR spectrum.

Draw a possible skeletal structure for this carboxylic acid.

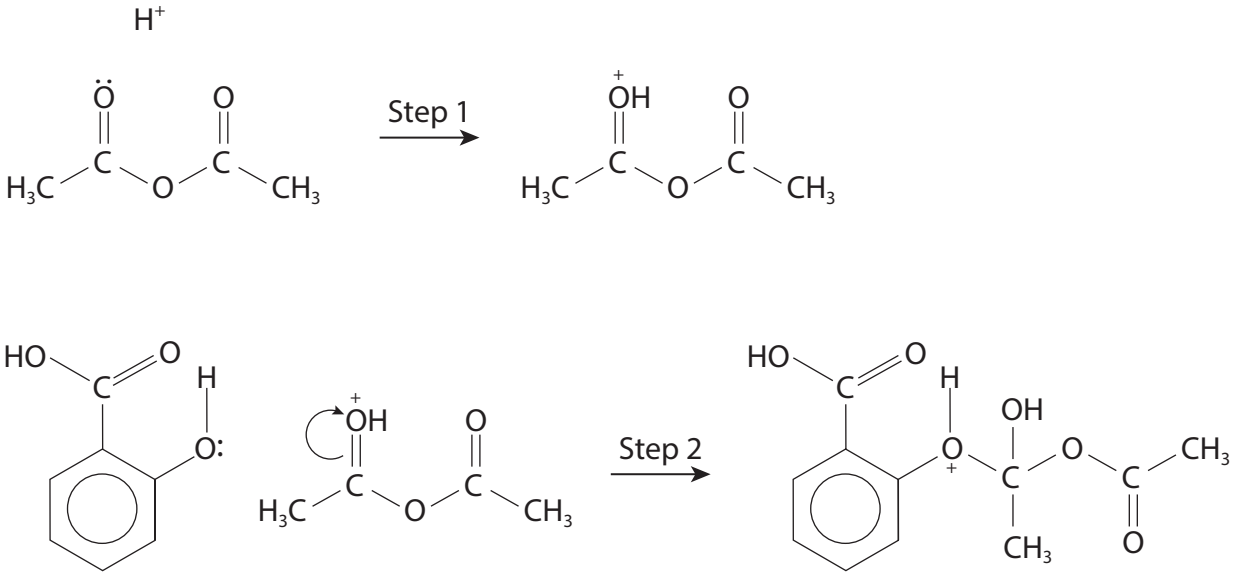
(1)

(d) The painkiller aspirin is also an ester, formed by the reaction of 2-hydroxybenzoic acid and ethanoic anhydride.



aspirin

Part of the mechanism for this reaction is shown.



(i) Add a single curly arrow to Step 1 and a single curly arrow to Step 2 to complete this part of the mechanism.

(2)

(ii) State the role of the H^+ ion in the synthesis of aspirin.

(1)

.....

(Total for Question 16 = 10 marks)

17 This question is about acids containing sulfur.

(a) Sulfuric acid reacts with sodium hydroxide solution as shown.

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

Calculate the pH of the solution formed when 20.0 cm^3 of sulfuric acid of concentration = 0.0720 mol dm^{-3} is mixed with 80.0 cm^3 of sodium hydroxide solution of concentration = 0.240 mol dm^{-3}.

Give your answer to one decimal place.

$$K_w = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$$

(6)

(b) Sulfurous acid, $H_2SO_3(aq)$, is a weak acid and dissociates as shown.

$$H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$

It forms a buffer solution when mixed with sodium hydrogensulfite, $NaHSO_3$.

(i) State what is meant by the term weak in this context.

(1)

.....

.....

.....

(ii) State what is meant by the term buffer solution.

(2)

.....

.....

.....

.....

(iii) Calculate the mass of sodium hydrogensulfite that should be added to 50.0 cm^3 of 0.0480 mol dm^{-3} sulfurous acid solution to form a buffer solution of pH = 2.18

[K_a (H_2SO_3) = 1.54×10^{-2} mol dm^{-3} Relative formula mass of $NaHSO_3$ = 104.1]

(5)

(Total for Question 17 = 14 marks)

18 This question is about carbonyl compounds such as ethanal, CH_3CHO.

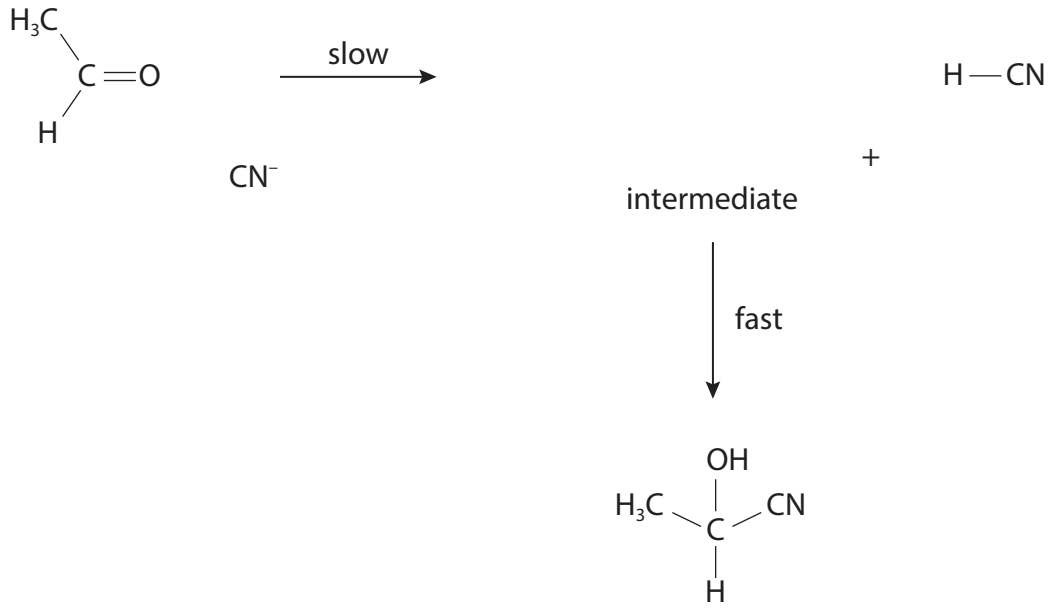
(a) Ethanal reacts with the weak acid hydrogen cyanide to form a racemic mixture of hydroxynitriles.

$$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$$

A small amount of sodium hydroxide solution, NaOH(aq), is also added to the reaction mixture.

(i) Complete the mechanism for the reaction.
Include curly arrows, the structure of the intermediate, and any relevant lone pairs and dipoles.

(4)



(ii) Explain why a small amount of sodium hydroxide solution is added to the reaction mixture, by considering the nature of the attacking species in the slow step.

(2)

.....

.....

.....

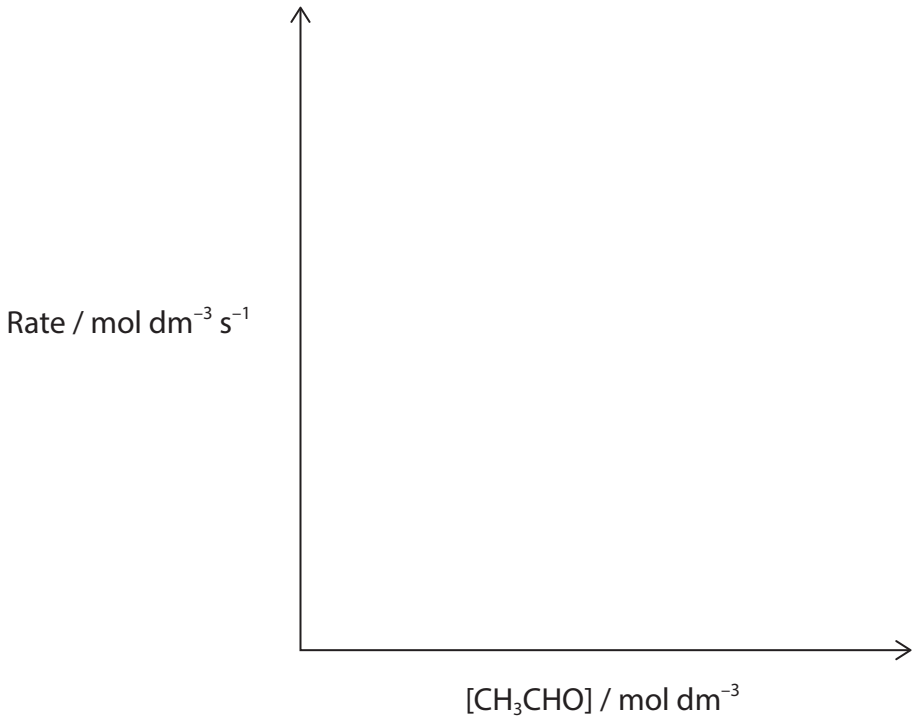
.....

(b) Deduce the rate equation for the reaction using the mechanism in (a)(i).

(1)

(c) Sketch a line on the axes to show how the concentration of ethanal affects the rate of this reaction.

(1)



*(d) Carbonyl compounds can be identified from their 2,4-dinitrophenylhydrazine derivatives.

Describe this process, including in your answer

- observations you would see in the formation of the 2,4-dinitrophenylhydrazine derivative
- an outline of the steps used to separate and purify the derivative, giving the purpose of each step
- how the derivative is used to identify the original carbonyl compound.

Detailed descriptions of practical techniques are not required.

(6)

(Total for Question 18 = 14 marks)

19 This question is about the hydrolysis of halogenoalkanes with hydroxide ions.

(a) The initial rates for the hydrolysis of 2-bromobutane, $CH_3CH_2CHBrCH_3$, were obtained for different initial concentrations of the reactants.
Both 2-bromobutane and the product formed in this reaction exist as pairs of stereoisomers.

$$CH_3CH_2CHBrCH_3 + OH^- \rightarrow CH_3CH_2CH(OH)CH_3 + Br^-$$

Experiment	Initial concentration of 2-bromobutane / mol dm^{-3}	Initial concentration of hydroxide ions / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
Experiment 1	0.150	0.150	0.027
Experiment 2	0.300	0.150	0.054
Experiment 3	0.450	0.300	0.162

All rates were determined at the same temperature.

(i) State what is meant by the term stereoisomer.

(1)

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(ii) Show that the data in the table are consistent with the S_N2 mechanism for this hydrolysis of 2-bromobutane.

(3)

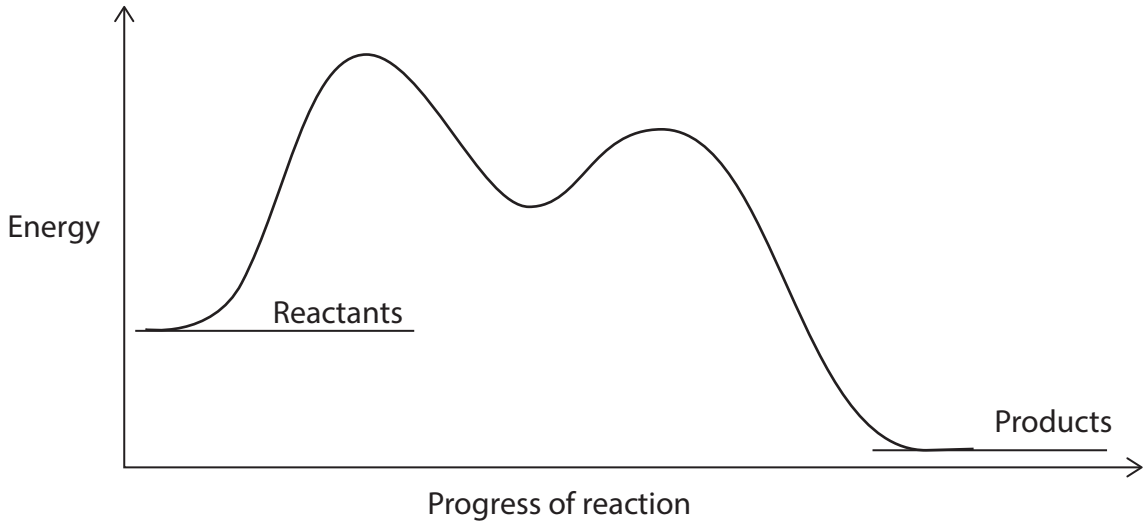
(iii) In one experiment, a single stereoisomer of 2-bromobutane was hydrolysed.

Explain the stereochemistry of the product of this reaction.

(3)

(b) 2-Bromo-2-methylbutane, $(CH_3)_2CBrCH_2CH_3$, can also be hydrolysed with hydroxide ions. The mechanism for the reaction is S_N1.

The reaction profile is shown.



Explain how all the features of this reaction profile are consistent with an S_N1 mechanism.

(3)

(Total for Question 19 = 10 marks)

TOTAL FOR SECTION B = 48 MARKS

SECTION C

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

20 This question is about Group 2 compounds.

(a) Barium carbonate, $BaCO_3$, decomposes at high temperatures as shown.

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

(i) Calculate the standard entropy change for the system, $\Delta S^{\ominus}_{system}$.

Compound	Standard molar entropy / $J\,K^{-1}\,mol^{-1}$
$BaCO_3$	112.1
BaO	70.4
CO_2	213.6

(2)

(ii) The lowest temperature at which barium carbonate, $BaCO_3$, decomposes is 712 °C.

Use this information and your answer from (a)(i) to calculate the standard enthalpy change of the reaction, in $kJ\,mol^{-1}$.
Give your answer to an appropriate number of significant figures.

(3)

(b) Magnesium chloride, $MgCl_2(s)$, is used in the manufacture of tofu from soya milk.

An experiment was carried out to determine the enthalpy change of solution, $\Delta_{sol}H$, of anhydrous magnesium chloride, $MgCl_2(s)$.
4.26 g of anhydrous magnesium chloride was added to 200 cm^3 of deionised water in a polystyrene cup. The mixture was stirred to ensure all the solid dissolved to form a solution.
The temperature of the solution rose by 6.8 °C.

Calculate the enthalpy change of solution, $\Delta_{sol}H$, of anhydrous magnesium chloride, $MgCl_2(s)$.
Include a sign and units with your answer.

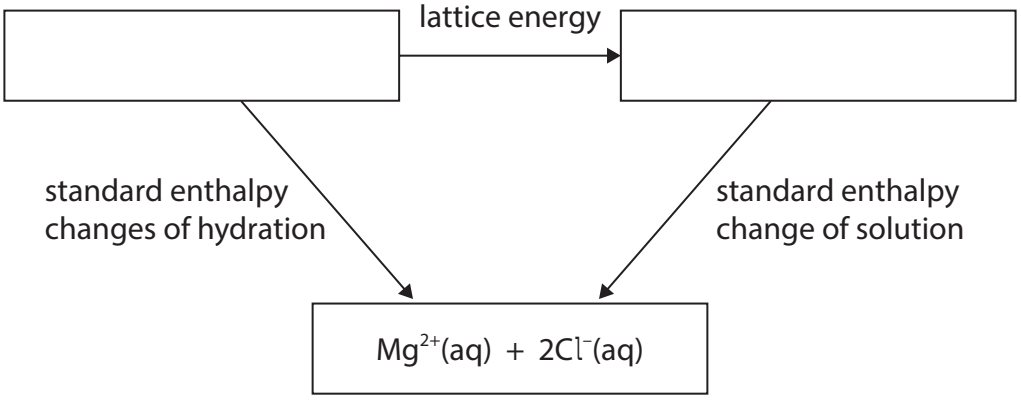
[Specific heat capacity of the solution = 4.18 $J\,g^{-1}\,°C^{-1}$]

(3)

(c) The standard enthalpy change of solution, $\Delta_{sol}H^{\ominus}$, of anhydrous $MgCl_2(s)$, can also be determined using a Hess Cycle.

(i) Complete the Hess Cycle shown by adding appropriate formulae, with state symbols, to the empty boxes.

(1)



[Lattice energy = −2526 $kJ\,mol^{-1}$
Standard enthalpy change of hydration of magnesium ions = −1920 $kJ\,mol^{-1}$]

(ii) Calculate the standard enthalpy change of hydration of chloride ions, $\Delta_{hyd}H^{\ominus}[Cl^-(g)]$, using the cycle and data in (c)(i) and your answer to (b).

[If you did not obtain a final answer to (b) use a value of $-155\,kJ\,mol^{-1}$. This is not the correct value.]

(3)

(d) The theoretical lattice energy for magnesium chloride, $MgCl_2(s)$, is $-2326\,kJ\,mol^{-1}$.

(i) Give **two** assumptions used in theoretical calculations of lattice energy.

(2)

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(ii) Explain the difference between the theoretical and experimental values for the lattice energy of magnesium chloride, $MgCl_2(s)$.

(3)

(e) Hydrated barium chloride is a soluble, toxic salt. It can be formed from the reaction of barium carbonate with hydrochloric acid as shown.

$$BaCO_3 + 2HCl + nH_2O \rightarrow BaCl_2 \cdot nH_2O + CO_2 + H_2O$$

A 5.00 g sample of barium carbonate reacted with 120 cm^3 of 0.500 mol dm^{-3} hydrochloric acid.

(i) Show that the hydrochloric acid is in excess in this reaction.

(2)

(ii) All of the barium carbonate reacted and produced 6.19 g of hydrated barium chloride.

Calculate the relative formula mass of $BaCl_2 \cdot nH_2O$ and hence deduce the value of n.

(3)

(Total for Question 20 = 22 marks)

TOTAL FOR SECTION C = 22 MARKS
TOTAL FOR PAPER = 90 MARKS

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

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