Please check the examination details below before entering your candidate information

Candidate surname	Other names

Centre Number

Candidate Number

Pearson Edexcel International Advanced Level

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 ▶

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 Two ways of writing an equation for the reaction between nitrogen monoxide and oxygen are shown.

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{Equation 1}$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad \text{Equation 2}$$

(a) Which **pair** of rate equations could be correct for this reaction?

(1)

		Equation 1	Equation 2
☒	**A**	rate = $k[NO]^2[O_2]$	rate = $k[NO]^2[O_2]$
☒	**B**	rate = $k[NO]^2[O_2]$	rate = $k[NO][O_2]^{½}$
☒	**C**	rate = $k[NO_2]^2$	rate = $k[NO_2]^2$
☒	**D**	rate = $k[NO_2]^2$	rate = $k[NO_2]$

(b) Which two methods can be used for **continuous** monitoring of the progress of this reaction?

(1)

☒ **A** colorimetry and titration

☒ **B** colorimetry and volume change

☒ **C** mass change and volume change

☒ **D** mass change and titration

(Total for Question 1 = 2 marks)

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

2 The half-life of a first order chemical reaction is

☒ **A** half the time taken for the reaction to be complete

☒ **B** the time taken for the value of the rate constant to halve

☒ **C** the time taken for the concentration of a reactant to halve

☒ **D** the time taken for the concentration of a product to double

(Total for Question 2 = 1 mark)

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3 Two chemicals, **E** and **F**, react to form products **G** and **H**.

$$\mathbf{E} + 2\mathbf{F} \rightarrow \mathbf{G} + \mathbf{H}$$

The mechanism for the reaction occurs in two steps via the formation of an intermediate **J**.

$$\mathbf{E} + \mathbf{F} \rightarrow \mathbf{J} \qquad \text{slow}$$

$$\mathbf{J} + \mathbf{F} \rightarrow \mathbf{G} + \mathbf{H} \qquad \text{fast}$$

What is the rate equation for the reaction?

☒ **A** rate = k[**E**][**F**]

☒ **B** rate = k[**E**][**F**]^2

☒ **C** rate = k[**F**][**J**]

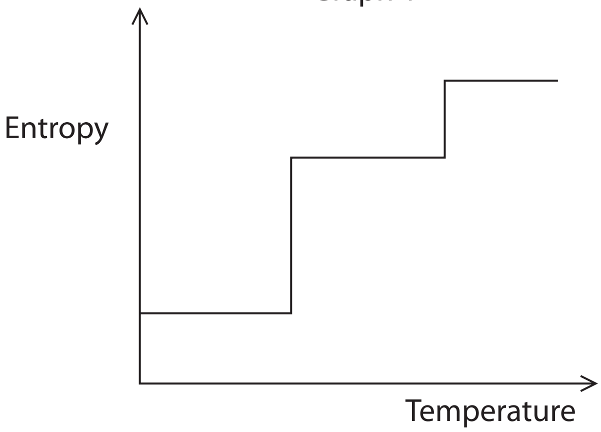
☒ **D** rate = k[**E**][**F**]^2[**J**]

(Total for Question 3 = 1 mark)

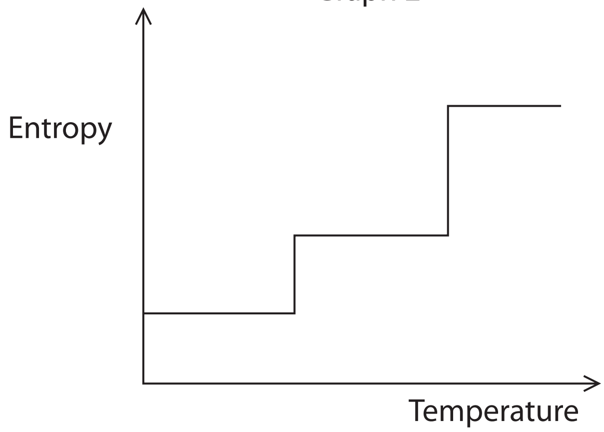
Use this space for any rough working. Anything you write in this space will gain no credit.

4 Which graph shows the entropy of a substance as it changes state from solid to liquid to gas?

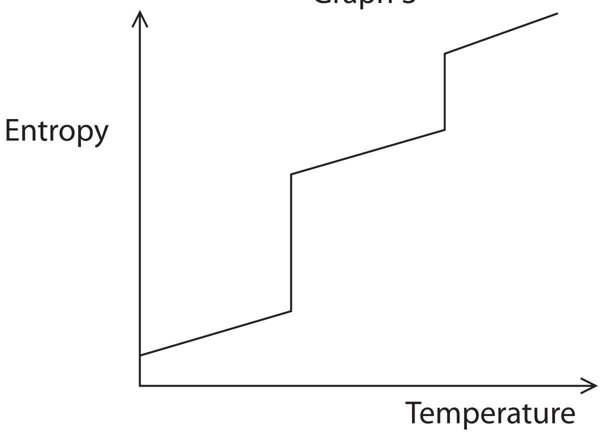
Graph 1



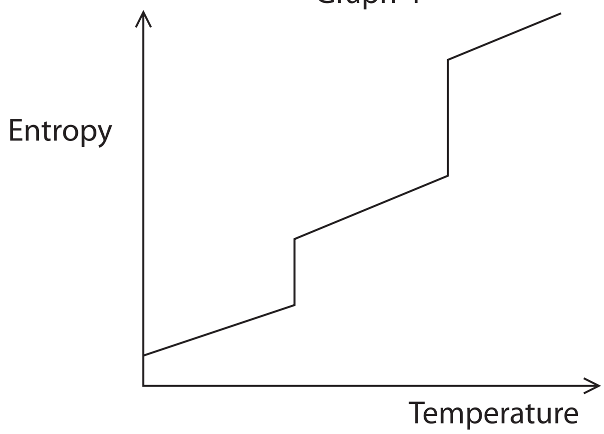
Graph 2



Graph 3



Graph 4



☒ **A** Graph 1

☒ **B** Graph 2

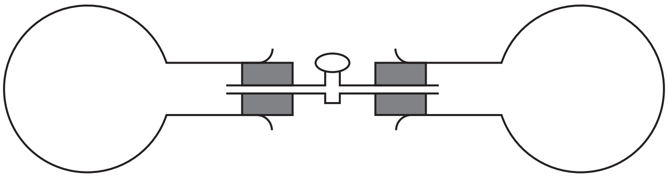
☒ **C** Graph 3

☒ **D** Graph 4

(Total for Question 4 = 1 mark)

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

5 Two flasks, **P** and **Q**, are connected by a tube fitted with a tap.



Flask **P** contains argon gas and flask **Q** is in vacuum.
Assume argon behaves as an ideal gas and therefore has no intermolecular forces between its atoms.

How do the entropy and energy of the system change when the tap is opened and the argon fills both flasks?

		Entropy of the system	Energy of the system
☒	**A**	increases	decreases
☒	**B**	decreases	decreases
☒	**C**	increases	unchanged
☒	**D**	decreases	unchanged

(Total for Question 5 = 1 mark)

6 When hydrogen and oxygen are mixed in a flask, there is no reaction.
When a platinum gauze is added to the flask, the mixture explodes.

It can be deduced that, in the absence of a platinum gauze, the mixture of hydrogen and oxygen is

☒ **A** kinetically stable and thermodynamically stable

☒ **B** kinetically stable and thermodynamically unstable

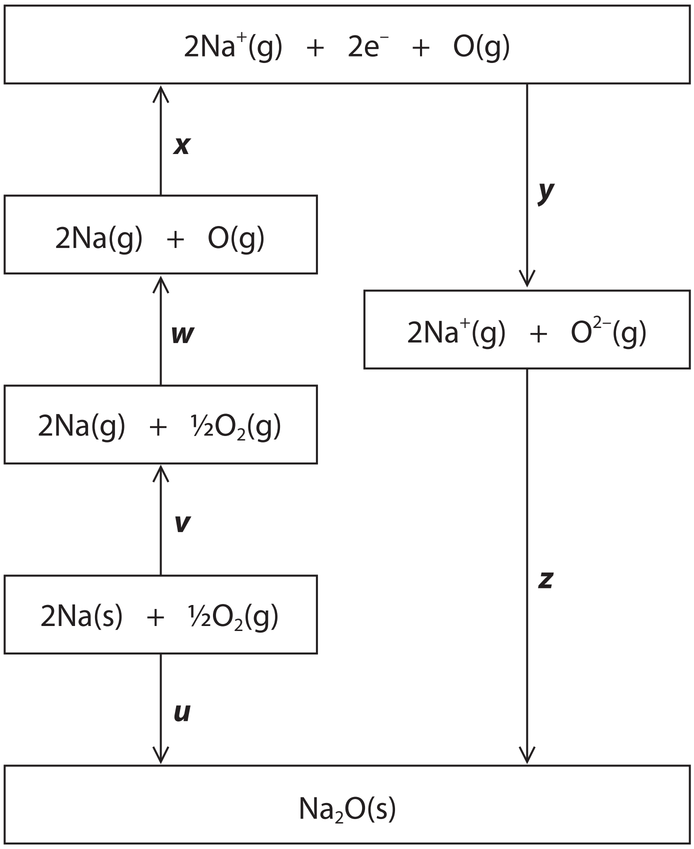
☒ **C** kinetically unstable and thermodynamically stable

☒ **D** kinetically unstable and thermodynamically unstable

(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 diagram shows the Born–Haber cycle for sodium oxide.



(a) Which energy change in the cycle does ***y*** represent?

(1)

- ☒ **A** the first electron affinity of oxygen
- ☒ **B** the second electron affinity of oxygen
- ☒ **C** the sum of the first and second electron affinities of oxygen
- ☒ **D** the sum of the enthalpy change of atomisation of oxygen and the first and second electron affinities of oxygen

(b) Which expression gives the enthalpy change of formation of sodium oxide, $\Delta_f H$?

(1)

- ☒ **A** $\Delta_f H = \boldsymbol{v} + \boldsymbol{w} + \boldsymbol{x} - \boldsymbol{y} - \boldsymbol{z}$
- ☒ **B** $\Delta_f H = \boldsymbol{v} + \boldsymbol{w} + \boldsymbol{x} + \boldsymbol{y} - \boldsymbol{z}$
- ☒ **C** $\Delta_f H = \boldsymbol{v} + \boldsymbol{w} + \boldsymbol{x} - \boldsymbol{y} + \boldsymbol{z}$
- ☒ **D** $\Delta_f H = \boldsymbol{v} + \boldsymbol{w} + \boldsymbol{x} + \boldsymbol{y} + \boldsymbol{z}$

(Total for Question 7 = 2 marks)

8 An ionic compound is found to have some degree of covalent bonding.

What will be the cause of the covalency and how will the lattice energy obtained from a Born–Haber cycle differ from the theoretical value obtained from electrostatic theory?

		Cause of covalency	Born–Haber lattice energy compared with theoretical value
☒	**A**	cation polarised by anion	Born–Haber more exothermic
☒	**B**	anion polarised by cation	Born–Haber less exothermic
☒	**C**	cation polarised by anion	Born–Haber less exothermic
☒	**D**	anion polarised by cation	Born–Haber more exothermic

(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 equation for the reaction between iron and steam is shown.

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g) \qquad \Delta H = -151.2\,kJ\,mol^{-1}$$

(a) What is the equilibrium constant expression for this reaction?

(1)

☒ **A** $K_c = \dfrac{[Fe_3O_4] \times [H_2]^4}{[Fe]^3 \times [H_2O]^4}$

☒ **B** $K_c = \dfrac{[Fe_3O_4] \times [H_2]^4}{[H_2O]^4}$

☒ **C** $K_c = \dfrac{[H_2]^4}{[Fe]^3 \times [H_2O]^4}$

☒ **D** $K_c = \dfrac{[H_2]^4}{[H_2O]^4}$

(b) What is the effect on the equilibrium constant for this reaction if small pieces of iron are replaced by iron powder and if the temperature is increased?

(1)

		Iron powder used	Temperature increased
☒	**A**	K_c increases	K_c increases
☒	**B**	K_c unchanged	K_c increases
☒	**C**	K_c increases	K_c decreases
☒	**D**	K_c unchanged	K_c decreases

(Total for Question 9 = 2 marks)

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

10 Equal amounts of ethanoic acid and methanoic acid are mixed.

[pK_a values: ethanoic acid = 4.8   methanoic acid = 3.8]

What are the conjugate acid-base pairs in the mixture?

		acid 1	base 1	acid 2	base 2
☒	**A**	HCOOH	$HCOO^-$	$CH_3COOH_2^+$	CH_3COOH
☒	**B**	CH_3COOH	CH_3COO^-	$HCOOH_2^+$	HCOOH
☒	**C**	HCOOH	CH_3COOH	$CH_3COOH_2^+$	$HCOO^-$
☒	**D**	CH_3COOH	HCOOH	$HCOOH_2^+$	CH_3COO^-

(Total for Question 10 = 1 mark)

11 A 1 mol dm^{-3} solution of ethanoic acid is gradually diluted by the addition of distilled water.

What happens to the degree of dissociation of the acid and the pH of the solution as the distilled water is added?

		Degree of dissociation	pH
☒	**A**	increases	increases
☒	**B**	increases	decreases
☒	**C**	decreases	increases
☒	**D**	decreases	decreases

(Total for Question 11 = 1 mark)

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

12 The solubility of magnesium hydroxide is 1.1×10^{-4} mol dm^{-3} at 25 °C and 4.0×10^{-3} mol dm^{-3} at 100 °C.

[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25 °C $K_w = 5.5 \times 10^{-14}$ mol^2 dm^{-6} at 100 °C]

(a) What is the pH of a saturated solution of magnesium hydroxide at 25 °C?

(1)

☒ **A** 9.7

☒ **B** 10.0

☒ **C** 10.3

☒ **D** 12.0

(b) Saturated solutions of magnesium hydroxide at 25 °C and 100 °C are compared.

How do the concentrations of hydroxide ions and the pH values of these solutions differ?

(1)

		Concentration of hydroxide ions at 100 °C	pH at 100 °C
☒	**A**	higher	lower
☒	**B**	higher	higher
☒	**C**	lower	higher
☒	**D**	lower	lower

(Total for Question 12 = 2 marks)

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

13 Propanal has a much higher boiling temperature than butane even though both compounds have the same molar mass.

The main reason for the difference in boiling temperature is that in the liquid state

☒ **A** propanal forms much stronger London forces than butane

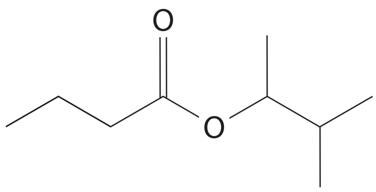
☒ **B** propanal forms permanent dipole-permanent dipole forces

☒ **C** propanal forms hydrogen bonds

☒ **D** propanal forms hydrogen bonds and permanent dipole-permanent dipole forces

(Total for Question 13 = 1 mark)

14 The structure of an ester is shown.



Which two compounds react to form this ester?

☒ **A** butanoyl chloride and 2-methylbutan-2-ol

☒ **B** butanoyl chloride and 3-methylbutan-2-ol

☒ **C** propanoyl chloride and 2-methylbutan-2-ol

☒ **D** propanoyl chloride and 3-methylbutan-2-ol

(Total for Question 14 = 1 mark)

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

15 Samples of ethanal and propanone are added to separate test tubes containing iodine dissolved in aqueous potassium hydroxide and the mixtures are heated gently.

A pale yellow precipitate will be formed with

☒ **A** ethanal and propanone

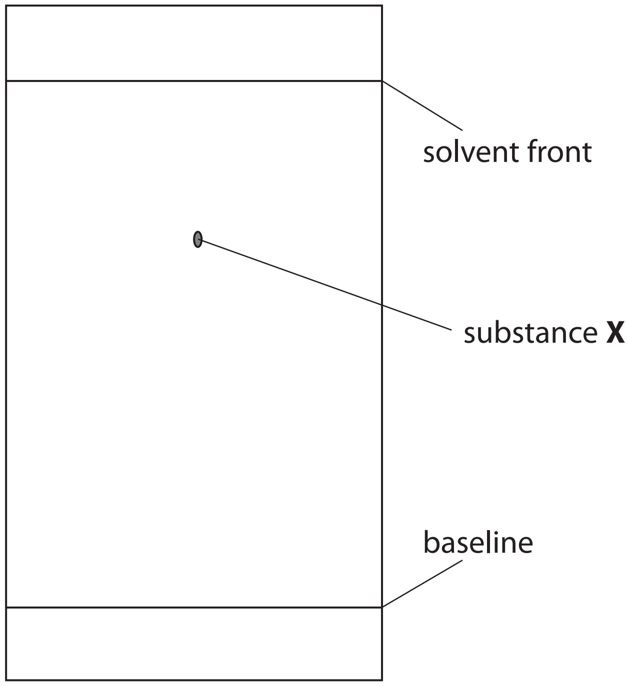
☒ **B** ethanal only

☒ **C** propanone only

☒ **D** neither ethanal nor propanone

(Total for Question 15 = 1 mark)

16 The chromatogram of a substance **X** is shown.



What is the R_f value for substance **X**?

☒ **A** 0.28

☒ **B** 0.62

☒ **C** 0.70

☒ **D** 0.86

(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 The reaction between hydrogen peroxide and iodide ions in acid conditions is known as the Harcourt–Esson reaction after the scientists who first studied its kinetics.

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

(a) A student carried out experiments to determine the rate equation for this reaction at 293 K.

(i) The rate of this reaction may be obtained by adding a fixed volume of sodium thiosulfate solution and a few drops of starch solution to the reaction mixture.

Explain how this method gives the rate of reaction.

(3)

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(ii) The student's results are shown.

Run	$[H_2O_2(aq)]$ / mol dm^{-3}	$[I^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.0210	0.0198	0.00105	0.00181
2	0.0105	0.0400	0.00105	0.00181
3	0.0105	0.0797	0.00099	0.00364
4	0.0210	0.0801	0.00201	0.00730

Deduce the rate equation for this reaction.

(3)

(iii) Calculate the rate constant for this reaction at 293 K, using the results from Run 1. Include units with your answer.

(3)

(b) The student carried out a second series of experiments with this reaction at 313 K. The rate of reaction was found to be 4.45 times faster at 313 K than at 293 K.

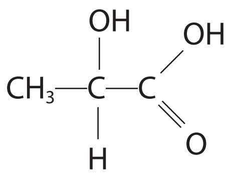
Calculate the activation energy, E_a, for this reaction, using the Arrhenius equation. Give your answer to an appropriate number of significant figures and include units.

$$\ln k = -\frac{E_a}{RT} + \text{constant}$$

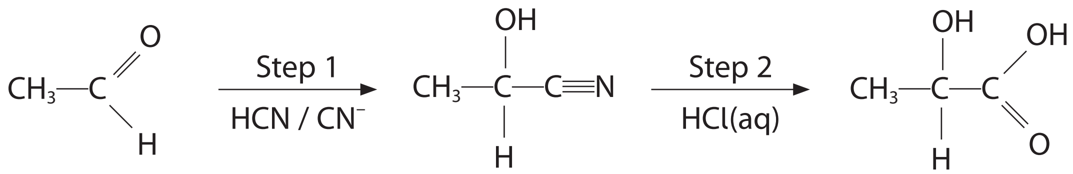
(4)

(Total for Question 17 = 13 marks)

18 Lactic acid is formed in muscles and in sour milk.



Lactic acid may be obtained from ethanal in the laboratory by the two-step synthesis shown.



*(a) Explain why lactic acid formed in muscles is optically active while lactic acid obtained using the laboratory synthesis is not.
You should define any terms you use.

(6)

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(b) Poly(lactic acid) is a polyester derived from lactic acid as the **only** monomer. Poly(lactic acid), which is often referred to as PLA, may be obtained from renewable resources and is also biodegradable.

(i) Draw the structure of a section of PLA showing **two** repeat units.

(2)

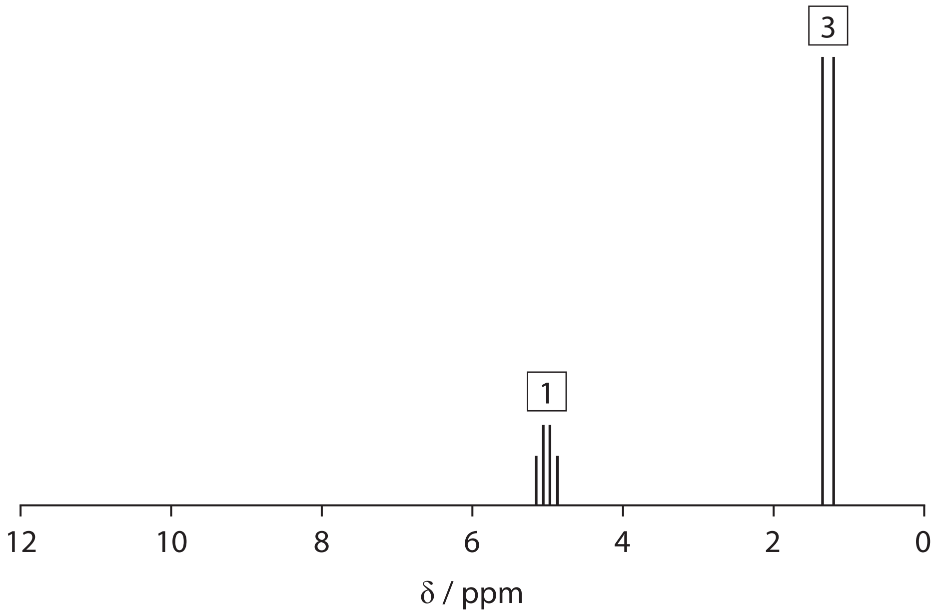
(ii) Lactic acid is converted into compound **X** which is then polymerised to form PLA.

The empirical formula of **X** is $C_3H_4O_2$ and its molar mass is 144 g mol^{-1}.

Determine the molecular formula of **X**.

(1)

(iii) A simplified high resolution proton NMR spectrum of **X** is shown.
The numbers above the peaks are the relative peak areas.
Note that the chemical shifts for **X** are different from the general values in the Data Booklet.



State what the number of peaks, their relative peak areas and splitting patterns show about the structure of **X**.

(3)

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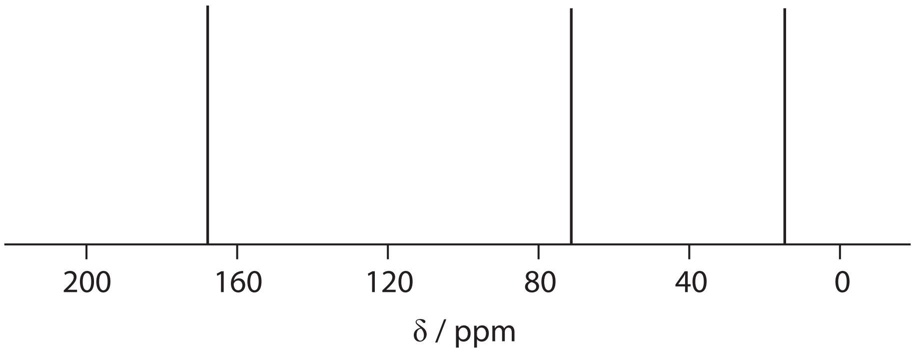
(iv) A simplified carbon-13 NMR spectrum of **X** is shown.



State what additional information about the structure of **X** is given by this spectrum.

(2)

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(v) Draw the structure of **X** using the information from (b)(ii) to (b)(iv).

(1)

(Total for Question 18 = 15 marks)

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19 Carbonyl compounds are usually reduced in the laboratory using complex metal hydrides such as lithium tetrahydridoaluminate(III), $LiAlH_4$.
The metal hydrides react by supplying hydride ions, H^-, which then react with the carbonyl group to form an intermediate.
The addition of a strong acid in aqueous solution to the intermediate produces the reduction product.

(a) State the essential condition for using $LiAlH_4$.

(1)

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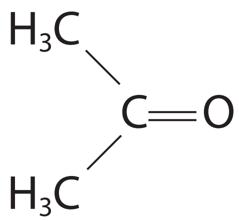
(b) Complete the mechanism for the reduction of propanone with $LiAlH_4$, showing the structure of the intermediate **and** of the final product.
Include curly arrows, and relevant lone pairs and dipoles.

(4)



H^-

(c) Explain why $LiAlH_4$ reduces carbonyl compounds but not alkenes, even though both types of compound have π bonds.

(3)

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(Total for Question 19 = 8 marks)

20 Cracking reactions are used to obtain more useful compounds from the alkanes found in crude oil. An equation for the cracking of butane is shown.

$$C_4H_{10}(g) \rightarrow C_2H_6(g) + C_2H_4(g)$$

Thermodynamic data for the compounds in this reaction are given in the table.

	$C_4H_{10}(g)$	$C_2H_6(g)$	$C_2H_4(g)$
Standard molar entropy $S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	310.1	229.5	219.5
Standard molar enthalpy change of formation $\Delta_f H^{\ominus}$ / $kJ\,mol^{-1}$	–126.5	–84.7	+52.2

(a) (i) Calculate the entropy change in the system, $\Delta S^{\ominus}_{system}$, for the cracking of butane.
Include a sign and units with your answer.

(2)

(ii) Calculate the enthalpy change of reaction, $\Delta_r H^{\ominus}$, for the cracking of butane.
Include a sign and units with your answer.

(2)

P 7 1 8 8 7 A 0 2 2 3 2

(iii) Calculate the entropy change in the surroundings, $\Delta S^{\ominus}_{\text{surroundings}}$, at 298 K for the cracking of butane, using your answer to (a)(ii).
Include a sign and units with your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{\text{total}}$, at 298 K for the cracking of butane, using your answers to (a)(i) and (a)(iii).
Include a sign and units with your answer.

(1)

(v) Calculate the temperature at which the cracking reaction becomes feasible.

(2)

(b) 5 mol of butane is cracked at 750 K. At equilibrium, 4.45 mol of ethene is formed and the total pressure is 1.20 atm.

$$C_4H_{10}(g) \rightleftharpoons C_2H_6(g) + C_2H_4(g)$$

(i) Give the expression for the equilibrium constant, K_p, for this reaction.

(1)

(ii) Calculate the value of K_p, including units if required.

(5)

(Total for Question 20 = 15 marks)

TOTAL FOR SECTION B = 51 MARKS

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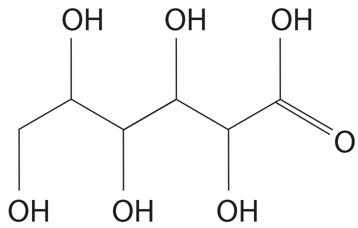
SECTION C

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

21 Gluconic acid is a weak acid which occurs in fruit and honey and is widely used as a food additive.



gluconic acid

(a) A solution of gluconic acid was prepared by dissolving 4.75 g of the solid in water and making the solution up to 250.0 cm^3 in a volumetric flask.

(i) Write the equation for the acid dissociation constant, K_a, of gluconic acid. Use RCOOH for gluconic acid.

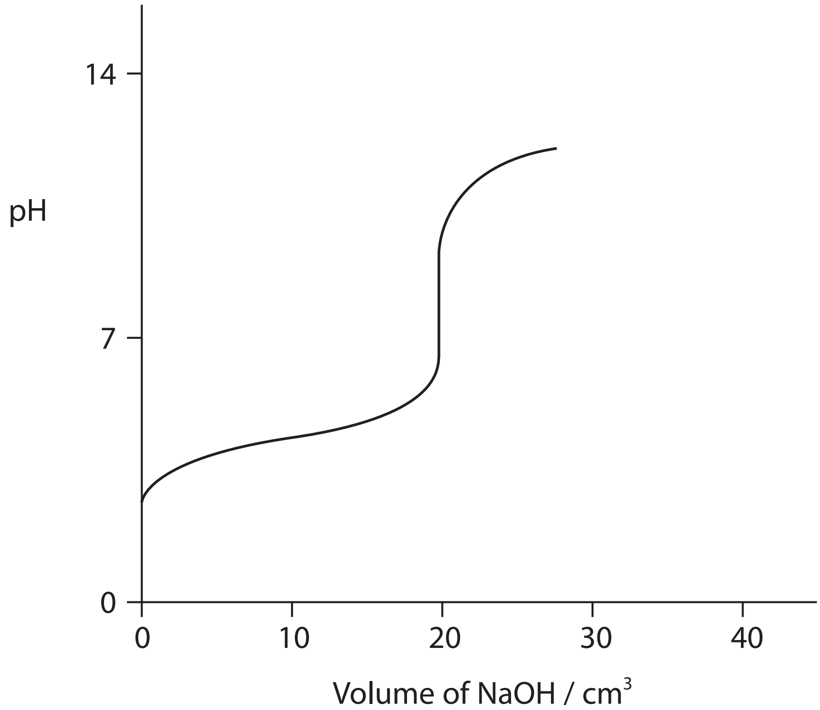
(1)

(ii) Calculate the pH of the solution of gluconic acid.

[M_r (gluconic acid) = 196 K_a (gluconic acid) = 1.38×10^{-4} mol dm^{-3}]

(4)

(b) A solution of 0.105 mol dm^{-3} sodium hydroxide was titrated against 25.0 cm^3 of the gluconic acid solution prepared in (a).
The titration curve is shown. The curve is **not** to scale.



(i) Explain why phenol red is an appropriate indicator for this titration.
Refer to the titration curve and the Data Booklet.

(2)

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(ii) Calculate the pH of the titration mixture after the addition of $35.0\,cm^3$ of sodium hydroxide solution.
The value required **cannot** be obtained from the titration curve in (b).

(5)

(c) Mixtures of gluconic acid and sodium gluconate are buffers.

(i) Explain how a solution that contains both gluconic acid and sodium gluconate acts as a buffer.
Use RCOOH for the formula of gluconic acid.

(4)

(ii) The concentration of a solution of gluconic acid is 1.55 mol dm^{-3}.

Calculate the number of moles of sodium gluconate that must be added to 1.00 dm^3 of this solution to give a buffer with pH = 3.71.
Assume that the volume of the solution is unchanged.

(3)

(Total for Question 21 = 19 marks)

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

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The Periodic Table of Elements

Key

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

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							

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