Write your name here

Surname	Other names

Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Monday 14 January 2013 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
6CH04/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or ball-point pen.
- **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.*
- Questions labelled with an **asterisk** (*) are ones where the quality of your written communication will be assessed
  – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

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

Turn over ▶

P41214A

7/6/5/5/4/

P 4 1 2 1 4 A 0 1 2 8

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 Methods for investigating reaction rates include

A colorimetry

B collecting and measuring the volume of a gas

C quenching, followed by titration with acid

D quenching, followed by titration with iodine solution.

Which method would be most suitable to investigate the rate of the following reactions?

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

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) $C_4H_9Br(l) + OH^-(aq) \rightarrow C_4H_9OH(l) + Br^-(aq)$

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 1 = 2 marks)

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

2 For a given initial reactant pressure, the half-life for a first order gaseous reaction was found to be 30 minutes.

If the experiment were repeated at half the initial reactant pressure, the half-life would be

☒ **A** 15 minutes.

☒ **B** 30 minutes.

☒ **C** 45 minutes.

☒ **D** 60 minutes.

(Total for Question 2 = 1 mark)

3 To determine the activation energy (E_a) for a reaction, the variation of reaction rate with temperature is investigated.

The rate constant, k, for the reaction is related to the absolute temperature, T, by the expression

$$\ln k = -\frac{E_a}{R} \times \left(\frac{1}{T}\right) + \text{constant}$$

where R is the gas constant.

The activation energy for the reaction could be obtained by plotting a graph of

	vertical axis	**horizontal axis**
☒ **A**	k	T
☒ **B**	k	$\frac{1}{T}$
☒ **C**	$\ln k$	T
☒ **D**	$\ln k$	$\frac{1}{T}$

(Total for Question 3 = 1 mark)

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

4 Energy is evolved when one mole of gaseous calcium ions is hydrated.

$$Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq)$$

This reaction is more exothermic than the corresponding value for barium ions, Ba^{2+}, because the

☒ **A** ionization energy of calcium is greater than that of barium.

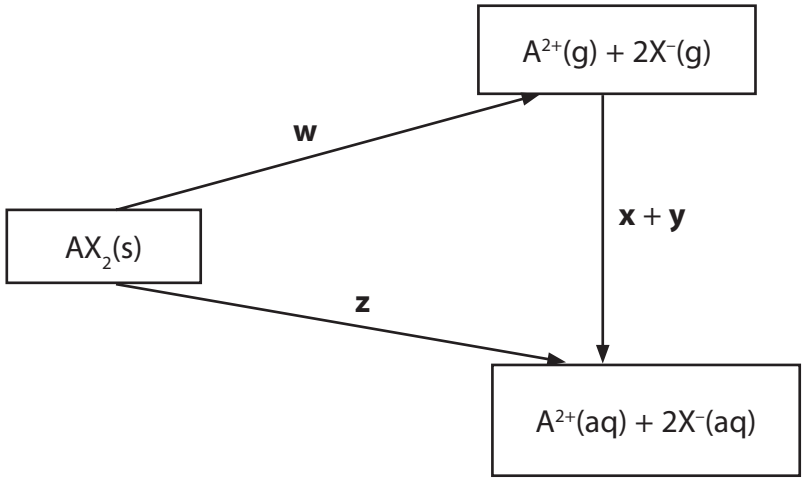
☒ **B** lattice energy of calcium oxide is more exothermic than that of barium oxide.

☒ **C** solubility of calcium hydroxide in water is less than that of barium hydroxide.

☒ **D** ionic radius of Ca^{2+} is less than that of Ba^{2+}.

(Total for Question 4 = 1 mark)

5 The following cycle represents the enthalpy changes **w**, **x**, **y** and **z**, occurring when an ionic solute, $AX_2(s)$, dissolves in water.



Which of the changes is the lattice energy of $AX_2(s)$?

☒ **A** ½ **w**

☒ **B** − **w**

☒ **C** **z**

☒ **D** **z** − **x** − **y**

(Total for Question 5 = 1 mark)

6 The equation for the synthesis of methanol is

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

At equilibrium, when the temperature is 340 K, the total pressure is 20 atm. The moles of each component present at equilibrium are shown in the table below.

Formula	Equilibrium moles / mol	Mole fraction
CO	0.15	0.23
H_2	0.32	
CH_3OH	0.18	0.28

(a) The mole fraction of hydrogen in the equilibrium mixture is

(1)

☒ **A** 0.23

☒ **B** 0.46

☒ **C** 0.49

☒ **D** 0.92

(b) The numerical value for the equilibrium partial pressure of the carbon monoxide, in atmospheres, is

(1)

☒ **A** 3.0

☒ **B** 4.6

☒ **C** 5.0

☒ **D** 9.2

(c) Units for the equilibrium constant, K_p, for this reaction are

(1)

☒ **A** no units

☒ **B** atm

☒ **C** atm^{-1}

☒ **D** atm^{-2}

(Total for Question 6 = 3 marks)

7 An aqueous solution of ammonium chloride, NH_4Cl, has a pH of less than 7 because

☒ **A** the ammonium ions donate protons to water molecules giving rise to oxonium ions, $H_3O^+(aq)$.

☒ **B** the chloride ions combine with hydrogen ions from water to form hydrochloric acid, HCl(aq).

☒ **C** an aqueous solution of ammonium chloride is unstable and evolves ammonia gas, $NH_3(g)$, leaving dilute hydrochloric acid.

☒ **D** the ammonium chloride reacts with carbon dioxide from the atmosphere giving ammonium carbonate, $(NH_4)_2CO_3(aq)$, and hydrochloric acid, HCl(aq).

(Total for Question 7 = 1 mark)

8 Which one of the following indicators is most suitable for titrating ethanoic acid with 0.1 mol dm^{-3} sodium hydroxide?

(Refer to page 19 of your data booklet.)

☒ **A** Thymol blue (acid)

☒ **B** Bromothymol blue

☒ **C** Thymol blue (base)

☒ **D** Alizarin yellow R

(Total for Question 8 = 1 mark)

9 What is the conjugate base of the acid, HCO_3^-?

☒ **A** H_2CO_3

☒ **B** CO_3^{2-}

☒ **C** OH^-

☒ **D** CO_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 What is the approximate pH of a buffer solution containing 0.20 mol of a weak acid, HA, (pK_a = 4.8) and 0.20 mol of the sodium salt of the acid, NaA, in a total volume of 1 dm^3 of solution?

☒ **A** 7.0

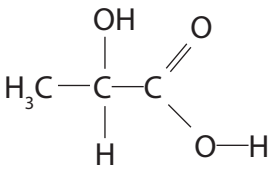
☒ **B** 5.8

☒ **C** 4.8

☒ **D** 3.8

(Total for Question 10 = 1 mark)

11 Ethanal, CH_3CHO, can be converted by a two-step synthesis into 2-hydroxypropanoic acid.



2-hydroxypropanoic acid

The reagents and conditions are

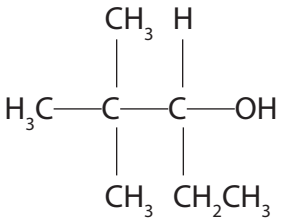
	1st step	2nd step
☒ **A**	$Na_2Cr_2O_7$ and dilute H_2SO_4, heat under reflux	NaOH(aq), heat under reflux
☒ **B**	Cl_2, UV light	NaOH(aq), heat under reflux
☒ **C**	$LiAlH_4$ in dry ether	CO_2, room temperature
☒ **D**	HCN, in presence of KCN(aq)	dilute HCl(aq), heat under reflux

(Total for Question 11 = 1 mark)

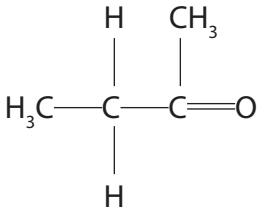
Use this space for any rough working. Anything you write in this space will gain no credit.

12 Questions (a) to (d) concern the following organic compounds.

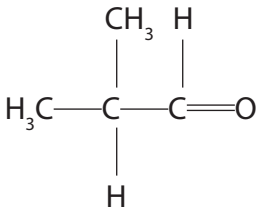
Compound A



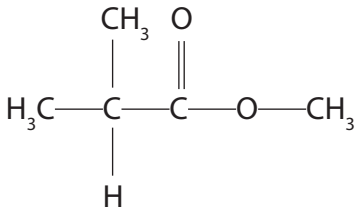
Compound B



Compound C



Compound D



Select from **A** to **D** the compound that

(a) forms iodoform with iodine in the presence of alkali.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(b) is chiral.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(c) reacts with Tollens' reagent.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(d) can be oxidized to form a ketone.

(1)

☒ **A**

☒ **B**

☒ **C**

☒ **D**

(Total for Question 12 = 4 marks)

13 Ethanoic acid, CH_3COOH, can be converted into ethanoyl chloride, CH_3COCl, by the action of

☒ **A** phosphorus(V) chloride.

☒ **B** chlorine.

☒ **C** dilute hydrochloric acid.

☒ **D** concentrated hydrochloric acid.

(Total for Question 13 = 1 mark)

14 A compound, **Q**, gives an orange precipitate with 2,4-dinitrophenylhydrazine.
Compound **Q** is resistant to oxidation.
On reduction, **Q** gives a product made up of a pair of optical isomers.

Which of the following compounds could be compound **Q**?

☒ **A** $CH_3CH_2CH_2COCH_3$

☒ **B** $CH_3CH{=}CHCH(OH)CH_3$

☒ **C** $CH_3CH_2CH_2CH_2CHO$

☒ **D** $CH_3CH_2COCH_2CH_3$

(Total for Question 14 = 1 mark)

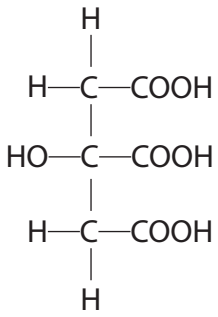
TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 Citric acid is found in lemon juice.

The structure and formula of citric acid are shown below.



$C_6H_8O_7$

(a) In the presence of a small amount of moisture, citric acid reacts with sodium hydrogencarbonate as shown in the equation below.

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

Use the structural formula of citric acid to explain why one mole of citric acid neutralizes three moles of sodium hydrogencarbonate.

(1)

.....

.....

.....

(b) You will need to refer to the data booklet in the calculations which follow.

You should also use the values given below.

compound	$S^{\ominus}$ / J mol^{-1} K^{-1}
$Na_3C_6H_5O_7(s)$	200.5
$C_6H_8O_7(s)$	199.9

(i) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for the following reaction at 298 K. Include a sign and units in your answer.

(2)

$$C_6H_8O_7(s) + 3NaHCO_3(s) \rightarrow Na_3C_6H_5O_7(s) + 3CO_2(g) + 3H_2O(l)$$

*(ii) Explain how the sign of your answer to (b)(i) could be predicted from the equation for the reaction between citric acid and sodium hydrogencarbonate.

(2)

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.....

(iii) Given that $\Delta H^{\ominus}_{298}$ for the reaction shown in (b)(i) is +70 kJ mol^{-1}, calculate the standard entropy change of the surroundings, $\Delta S^{\ominus}_{surroundings}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(iv) Calculate the total entropy change, $\Delta S^{\ominus}_{total}$, for this reaction at 298 K.

(1)

(v) What does the sign of $\Delta S^{\ominus}_{total}$ suggest about this reaction at 298 K?

(1)

.....

.....

(Total for Question 15 = 9 marks)

16 Methanoic acid, HCOOH, is present in ant stings.

A scientist analyzed 25.0 cm^3 of an aqueous solution of methanoic acid, solution **Z**, by titrating it with dilute sodium hydroxide, NaOH(aq).

- 20.0 cm^3 of sodium hydroxide was required to neutralize the methanoic acid
- The equation for the neutralization of methanoic acid is

$$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$$

(a) (i) Give the expression for K_w, the ionic product of water.

(1)

(ii) The concentration of the sodium hydroxide, NaOH(aq), used in the titration was 0.00750 mol dm^{-3}.

Calculate the pH of the sodium hydroxide solution.

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

(2)

(b) Use the equation for the reaction and the data from the titration to show that the concentration of the methanoic acid in solution **Z** was 6.00×10^{-3} mol dm^{-3}.

(2)

(c) Methanoic acid is a weak acid.

(i) Explain the term **weak acid**.

(2)

Weak .....

.....

Acid .....

.....

(ii) The equation for the dissociation of methanoic acid in aqueous solution is shown below.

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq)$$

Write the expression for the acid dissociation constant, K_a, for methanoic acid.

(1)

*(iii) At 298 K, the acid in ant stings has a concentration of 6.00×10^{-3} mol dm^{-3} and a pH of 3.01.

Calculate the value of K_a for methanoic acid at 298 K.

State clearly any assumptions that you have made.

(4)

Calculation:

Assumption(s):

.....

.....

.....

.....

(Total for Question 16 = 12 marks)

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20			

(iii) Explain why K_c for this reaction has no units.

(1)

.....

.....

(iv) Calculate the numerical value of K_c.

(1)

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

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.....

(c) (i) Identify which bonds are broken and which bonds are made in the esterification reaction.

(2)

Bonds broken:

Bonds made:

(ii) Explain why ΔH for this reaction is not **exactly** zero.
(A calculation is not required.)

(1)

.....

.....

(d) (i) State the relationship between ΔS_{total} and the equilibrium constant, K, of a reaction.

(1)

*(ii) Use entropy considerations and your answer to (d)(i) to predict any effect of an increase in temperature on the value of the equilibrium constant of a reaction for which ΔH is zero. Assume that ΔS_{system} does not change with temperature.

(3)

(e) An alternative method for preparing ethyl ethanoate is to react ethanoyl chloride with ethanol.

(i) Give the equation for the reaction.

(1)

(ii) Draw the **skeletal** formula of ethyl ethanoate.

(1)

(iii) Ethanoyl chloride also reacts with concentrated ammonia. Draw the **displayed** formula of the organic product of this reaction.

(1)

(f) (i) Complete the equation below for the alkaline hydrolysis of ethyl ethanoate using sodium hydroxide. State symbols are **not** required.

(1)

$CH_3COOCH_2CH_3 + NaOH \rightarrow$

(ii) Explain why the reaction in (f)(i) gives a better yield of the alcohol compared with acid hydrolysis of the ethyl ethanoate.

(1)

.....

.....

.....

.....

(Total for Question 17 = 19 marks)

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18 Bromate(V) ions, BrO_3^-, oxidize bromide ions, Br^-, in the presence of dilute acid, H^+, as shown in the equation below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Three experiments were carried out using different initial concentrations of the three reactants.

The initial rate of reaction was calculated for each experiment.

The results are shown in the table below.

Experiment number	$[BrO_3^-(aq)]$ / mol dm^{-3}	$[Br^-(aq)]$ / mol dm^{-3}	$[H^+(aq)]$ / mol dm^{-3}	Initial rate of reaction / mol dm^{-3} s^{-1}
1	0.050	0.25	0.30	1.68×10^{-5}
2	0.050	0.25	0.60	6.72×10^{-5}
3	0.15	0.50	0.30	1.01×10^{-4}

*(a) (i) This reaction is first order with respect to $BrO_3^-(aq)$. State, with reasons, including appropriate experiment numbers, the order of reaction with respect to

(5)

$H^+(aq)$

.....

.....

.....

$Br^-(aq)$

.....

.....

.....

.....

(ii) Write the rate equation for the reaction.

(1)

(iii) Use the data from experiment 1 and your answer to (a)(ii) to calculate the value of the rate constant. Include units in your answer.

(3)

(b) What evidence suggests that this reaction proceeds by more than one step?

(1)

(c) The initial rate of reaction was obtained from measurements of the concentration of bromine at regular time intervals. How is the **initial** rate of formation of bromine calculated from a concentration-time graph?

(2)

(Total for Question 18 = 12 marks)

TOTAL FOR SECTION B = 52 MARKS

SECTION C

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

19 An organic compound, **X**, was analyzed in a laboratory.

(a) Compound **X** was found to have the following percentage composition by mass:

carbon, C = 54.5%

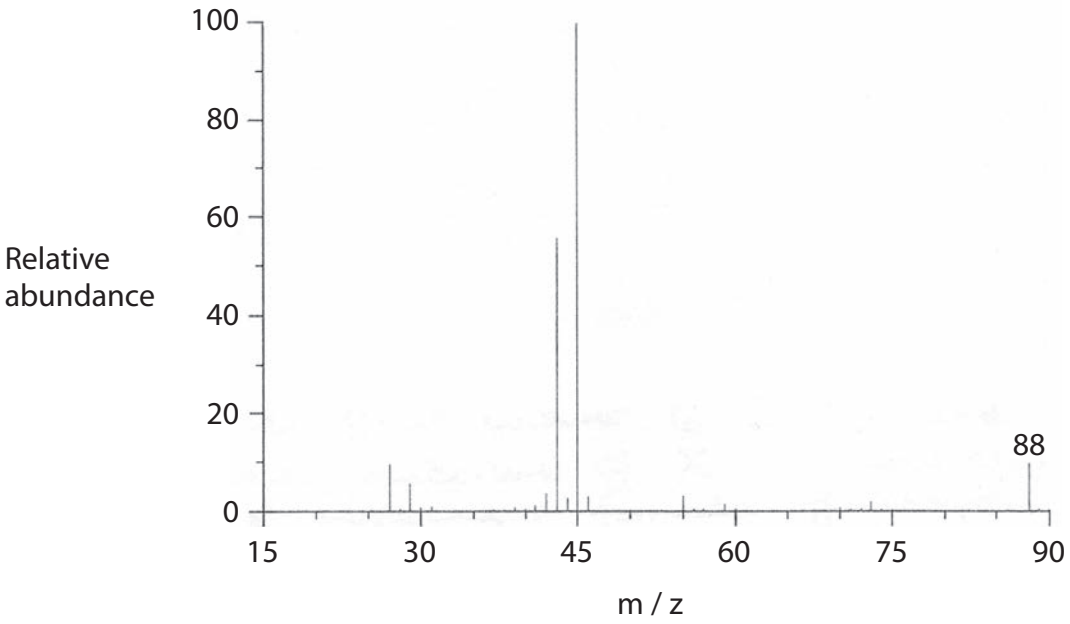
hydrogen, H = 9.1%

oxygen, O = 36.4%

(i) Use these data to calculate the empirical formula of compound **X**, showing your working.

(2)

(ii) The mass spectrum of **X** is shown below.



Use your answer to (a)(i), and the mass spectrum of **X**, to show that the molecular formula of compound **X** is $C_4H_8O_2$.

(2)

(b) The infrared spectrum of **X** has a broad peak at approximately 3500 cm^{-1} and a sharp peak at approximately 1700 cm^{-1}. Identify the **bond** responsible for the peak at

(2)

3500 cm^{-1}

1700 cm^{-1}

(c) (i) Some chemical information about compound **X** is given below.

- **X** is a neutral organic compound.
- **X** has no effect on Tollens' reagent.
- **X** turns hot acidified potassium dichromate(VI) solution from orange to green.

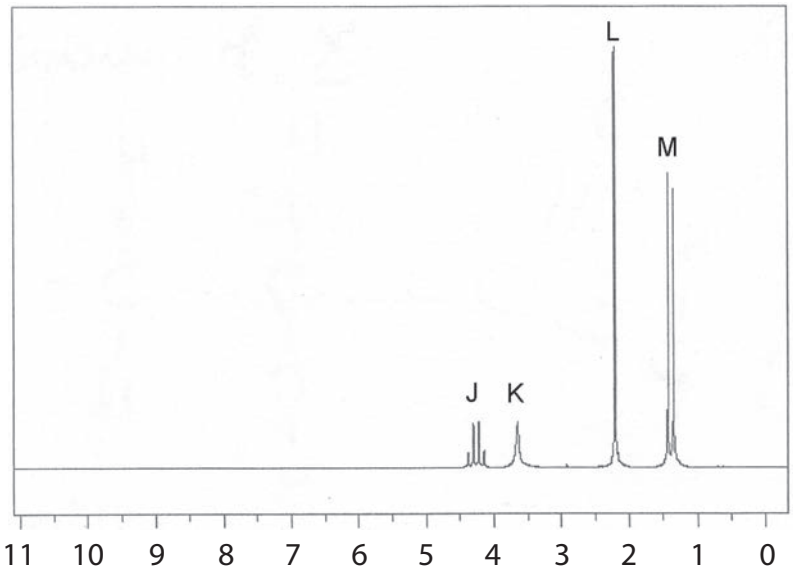
What does each of these three pieces of information suggest about the nature of **X**?

(4)

(ii) Use your answers to parts (b) and (c)(i) to name the two functional groups present in **X**.

(1)

*(d) The high resolution proton nmr spectrum of **X** is shown below.



The relative number of protons causing the peaks shown are: J = 1, K = 1, L = 3 and M = 3.

Use the information above to determine the structural formula of **X**.

In your answer, you should refer to the number of peaks, their relative sizes and their splitting patterns.

(7)

(Total for Question 19 = 18 marks)

TOTAL FOR SECTION C = 18 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									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

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
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

* Lanthanide series

* Actinide series