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)

Wednesday 27 January 2010 – Morning
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 ▶

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7/7/5/5/2/

N 3 6 2 8 9 A 0 1 2 8

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SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 Consider the equilibrium

$$Cl_2(g) + PCl_3(g) \rightleftharpoons PCl_5(g)$$

Which of the following is true when the total pressure of the system is increased at constant temperature?

		Value of K_p	Mole fraction of $PCl_5(g)$
☒	**A**	decreases	decreases
☒	**B**	unaltered	increases
☒	**C**	decreases	increases
☒	**D**	unaltered	unaltered

(Total for Question 1 = 1 mark)

2 In which of the following reactions is nitric acid acting as a base?

☒ **A** $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

☒ **B** $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

☒ **C** $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$

☒ **D** $HNO_3 + NaHCO_3 \rightarrow NaNO_3 + H_2O + CO_2$

(Total for Question 2 = 1 mark)

3 Why does phenolphthalein, which is colourless in acidic solutions, turn pink in alkaline solutions?

☒ **A** It is oxidized to a pink compound by hydroxide ions.

☒ **B** It forms a pink anion by loss of H^+ ions.

☒ **C** It forms a pink anion by gain of H^+ ions.

☒ **D** It forms a pink cation by gain of H^+ ions.

(Total for Question 3 = 1 mark)

4 The dissociation of ethanoic acid in aqueous solution is represented by

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Which of the following statements is true for this equilibrium?

☒ **A** CH_3COOH is an acid and its conjugate base is CH_3COO^-.

☒ **B** H_2O is an acid and its conjugate base is OH^-.

☒ **C** At equilibrium, the concentrations of each substance are the same.

☒ **D** At equilibrium, the reaction from left to right and the reaction from right to left have stopped.

(Total for Question 4 = 1 mark)

5 Why are aqueous solutions of sodium ethanoate slightly alkaline?

☒ **A** The sodium ions react with water to give an alkali.

☒ **B** The ethanoate ions react with water to give hydroxide ions.

☒ **C** All sodium salts give alkaline solutions.

☒ **D** The sodium ethanoate is fully ionized in solution.

(Total for Question 5 = 1 mark)

6 When ammonium nitrate crystals dissolve in water, the entropy of the system

☒ **A** remains the same.

☒ **B** falls, because the hydrated ions are more ordered than the solid.

☒ **C** rises, because the ions in the crystal become hydrated in the solution.

☒ **D** rises, because the ions are arranged more randomly in the solution than in the crystal.

(Total for Question 6 = 1 mark)

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

7 Which of the following molecules is a methyl ester?

☒ **A** $CH_3COOCH_2CH_3$

☒ **B** $HCOOCH_3$

☒ **C** $CH_3COCH_2CH_3$

☒ **D** CH_3COCl

(Total for Question 7 = 1 mark)

8 During the preparation of a liquid compound, samples were taken of the product at various stages in the purification procedure. Which of the following techniques would be most suitable for showing the change in composition of these samples during the purification procedure?

☒ **A** Gas-liquid chromatography

☒ **B** Fractional distillation

☒ **C** Filtration

☒ **D** Distillation

(Total for Question 8 = 1 mark)

9 Which of the following compounds would react with lithium tetrahydridoaluminate (lithium aluminium hydride) **and** also with phosphorus(V) chloride (phosphorus pentachloride)?

☒ **A** $CH_3CH_2CH_2COOH$

☒ **B** $CH_3CH_2COCH_3$

☒ **C** $CH_3CH{=}CHCH_3$

☒ **D** $CH_2{=}CHCH_2CH_2OH$

(Total for Question 9 = 1 mark)

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

10 In the synthesis of an ester, the use of an acyl chloride and an alcohol gives a better yield than the use of a carboxylic acid and an alcohol.

This is because the reaction between

☒ **A** an acyl chloride and an alcohol is an equilibrium.

☒ **B** an acid and an alcohol goes to completion.

☒ **C** an acid and an alcohol requires a catalyst.

☒ **D** an acyl chloride and an alcohol goes to completion.

(Total for Question 10 = 1 mark)

11 Not all molecules will absorb infrared radiation. Those that do

☒ **A** change their dipole moment when their bonds stretch or bend.

☒ **B** undergo homolytic fission.

☒ **C** must be polar.

☒ **D** are always organic substances.

(Total for Question 11 = 1 mark)

12 Which of the following methods may be used **in a single step** to make carboxylic acids?

☒ **A** Hydrolysis of an ester with an alkali.

☒ **B** Reaction of acidified potassium manganate(VII) with an alkene.

☒ **C** Hydrolysis of a nitrile with hydrochloric acid.

☒ **D** Reaction of an acyl chloride with ammonia.

(Total for Question 12 = 1 mark)

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

13 A solution of a weak acid cannot be titrated with a weak base using an indicator to find the end-point because

☒ **A** the pH change is too gradual close to the equivalence point.

☒ **B** there are too few H^+ ions to affect the indicator.

☒ **C** there are too few OH^- ions to affect the indicator.

☒ **D** the pH change occurs outside the range of any indicator.

(Total for Question 13 = 1 mark)

14 Which of the following reagents could be used to produce propanamide, $CH_3CH_2CONH_2$?

☒ **A** Ammonia and 1-chloropropane

☒ **B** Ammonia and propanoyl chloride

☒ **C** Methylamine and 1-chloropropane

☒ **D** Methylamine and propanoyl chloride

(Total for Question 14 = 1 mark)

15 The radio waves used in proton nmr

☒ **A** must not be absorbed by the sample.

☒ **B** cause electron transitions in the hydrogen atom.

☒ **C** can only be used with organic substances.

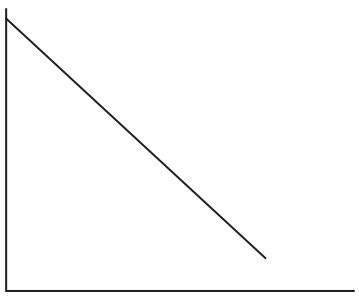
☒ **D** cause the hydrogen nucleus to change its spin state.

(Total for Question 15 = 1 mark)

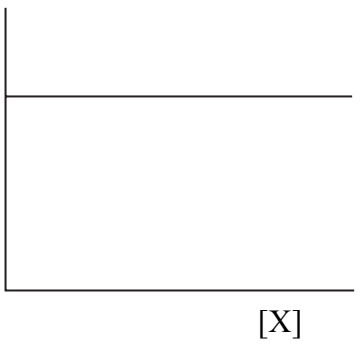
Use this space for any rough working. Anything you write in this space will gain no credit.

16 Which of the following graphs shows that a reaction is first order with respect to reactant **X**?

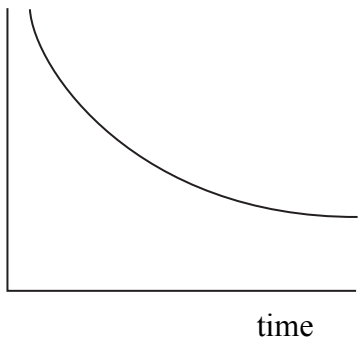
☒ **A**



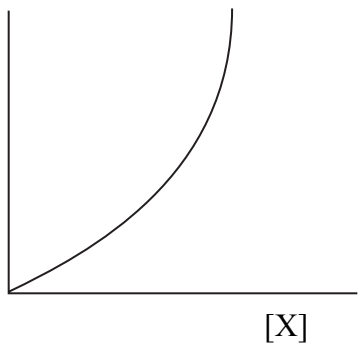
☒ **B**



☒ **C**



☒ **D**



(Total for Question 16 = 1 mark)

17 Which of the following changes will lead to the greatest increase in the **rate** of the following endothermic reaction?

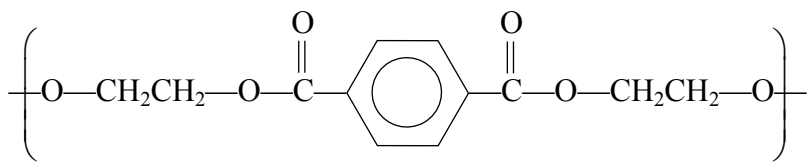
$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H \text{ +ve}$$

		Temperature	Initial concentration of N_2 and O_2
☒	**A**	decrease by 15%	decrease by 15%
☒	**B**	increase by 15%	stay the same
☒	**C**	decrease by 15%	increase by 15%
☒	**D**	increase by 15%	increase by 15%

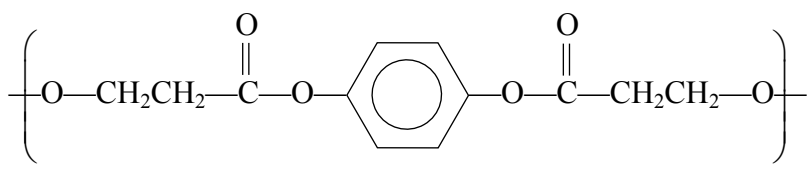
(Total for Question 17 = 1 mark)

18 The repeat unit of the polyester formed from ethane-1,2-diol, $HOCH_2CH_2OH$, and benzene-1,4-dicarboxylic acid, HOOC—C$_6$H$_4$—COOH, is

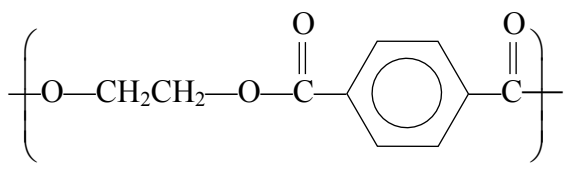
☒ **A**



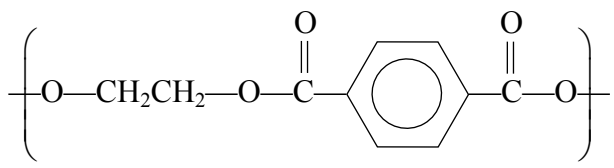
☒ **B**



☒ **C**



☒ **D**



(Total for Question 18 = 1 mark)

19 Iron and steam at high temperature react in a closed vessel to give an equilibrium mixture

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Which of the following is the correct expression for K_p?

☒ **A** $K_p = \dfrac{P_{H_2}}{P_{H_2O}}$

☒ **B** $K_p = \dfrac{P_{Fe_3O_4} P_{H_2}^4}{P_{Fe}^3 P_{H_2O}^4}$

☒ **C** $K_p = \dfrac{P_{H_2}^4}{P_{H_2O}^4}$

☒ **D** $K_p = P_{H_2}^4$

(Total for Question 19 = 1 mark)

20 At 100 °C, pure water has a pH of 6, whereas at 25 °C it has a pH of 7. This is because

☒ **A** the dissociation of water is endothermic, so the concentration of hydrogen ions is lower at 100 °C than it is at 25 °C.

☒ **B** the dissociation of water is exothermic, so the concentration of hydrogen ions is lower at 100 °C than it is at 25 °C.

☒ **C** the dissociation of water is endothermic, so the concentration of hydrogen ions is higher at 100 °C than it is at 25 °C.

☒ **D** at 100 °C, water has a higher concentration of hydrogen ions than of hydroxide ions.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

21 (a) (i) Define **pH**.

(1)

.....

(ii) Calculate the pH of 0.0100 mol dm^{-3} hydrochloric acid, which is a strong acid.

(1)

(b) Ethanoic acid is a weak acid with an acid dissociation constant, K_a, of value 1.75×10^{-5} mol dm^{-3} at 25 °C.

(i) Calculate the pH of 0.0100 mol dm^{-3} ethanoic acid at 25 °C, stating any ONE assumption that you have made.

(4)

Assumption .....

.....

.....

(ii) The pH of hydrochloric and of ethanoic acid at two different concentrations is given in the table.

	pH of 0.00100 mol dm^{-3} solution	pH of 0.000100 mol dm^{-3} solution
Hydrochloric acid	3.0	4.0
Ethanoic acid	3.9	4.4

In the case of hydrochloric acid, dilution by a factor of 10 increases the pH by one unit. Suggest why ethanoic acid behaves differently.

(2)

(c) Orange marmalade usually contains sodium citrate as a preservative. Together with the fruit in the marmalade, it forms a buffer solution which, at a suitable pH, inhibits mould growth.

(i) Define the term **buffer solution**.

(2)

(ii) What is the substance in the fruit that produces a buffer with sodium citrate?

(1)

(iii) Explain how a buffer solution works using this system or any other of your choice. Support your explanation with equations.

(4)

(Total for Question 21 = 15 marks)

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22 ***(a)** Ethanol can be oxidized successively to ethanal and to ethanoic acid.

The boiling temperatures of these substances are:
ethanol 78 °C, ethanal 21 °C, ethanoic acid 118 °C.

Explain in terms of the intermolecular forces in the liquids why the order of the boiling temperature is

ethanal < ethanol < ethanoic acid

(3)

(b) State what tests you would perform in each case, and the result you would expect, to show that

(i) ethanal contains a carbonyl group.

(2)

(ii) ethanal is an aldehyde.

(2)

(c) Ethanal reacts with HCN, in the presence of a catalyst of cyanide ions from KCN, to give a cyanohydrin, $CH_3CH(OH)CN$.

(i) Give the mechanism for this reaction.

(3)

(ii) Explain why it is necessary to use HCN and KCN in this reaction, rather than HCN on its own.

(1)

*(iii) Explain why the product mixture from this reaction is **not** optically active.

(2)

(Total for Question 22 = 13 marks)

23 Iodine and propanone react in the presence of an aqueous acid catalyst as follows

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$$

To determine the rate equation for the reaction, propanone is reacted with iodine in the presence of aqueous hydrochloric acid at constant temperature. Samples are withdrawn at known times, quenched with sodium hydrogencarbonate solution, and the iodine remaining titrated with a standard solution of sodium thiosulfate.

The rate equation for the reaction is

$$\text{rate} = k[CH_3COCH_3]^1\,[H^+]^1\,[I_2]^0$$

(a) The graph of $[I_2]$ against time is a straight line, showing that the order of reaction with respect to iodine is zero.

(i) Explain why the propanone and the hydrogen ions must be in large excess in this experiment in order to give this straight line.

(2)

(ii) What further experiment could be done to show that the order of reaction with respect to propanone is one? State the effect of this change on the graph.

(2)

(iii) Explain why the minimum number of steps in the mechanism for this reaction is two.

(2)

.....

.....

.....

.....

(b) Sodium hydrogencarbonate stops the reaction by neutralizing the acid catalyst.

(i) Give the ionic equation for the reaction between sodium hydrogencarbonate and acid.

(1)

(ii) Sodium hydroxide cannot be used for neutralization because under very alkaline conditions a reaction occurs between propanone and iodine.

Write the equation for this reaction. State symbols are **not** required.

(3)

(Total for Question 23 = 10 marks)

24 Hydrogen is used in very large quantities as a fuel, as a reducing agent, and in the production of ammonia. Hydrogen is manufactured by steam reforming of methane from natural gas. Two reactions are involved, both being in equilibrium in closed systems.

Reaction I $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +210$ kJ mol^{-1}

Reaction II $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -42$ kJ mol^{-1}

(a) Write the expression for the equilibrium constant, K_p, for reaction **I**.

(1)

(b) Reaction **I** occurs at a temperature of 1000 K and a pressure of 30 atm over a nickel catalyst.

(i) State and explain the effect, if any, **on the value of K_p** of increasing the pressure on the reaction.

(1)

(ii) Explain, in terms of your answers to (a) and (b)(i), why an increase in the pressure leads to a decrease in yield in reaction **I**.

(2)

(iii) Increasing the pressure on this heterogeneously-catalysed reaction **I** has very little effect on the rate of the reaction. Suggest why this is so.

(2)

(c) The expression for K_p for reaction **II** is

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$$

At a particular temperature and 30 atm pressure, a mixture of equal amounts of carbon monoxide and steam react to give an equilibrium mixture where 75 % of the CO has reacted.

Calculate the value of K_p showing your working.

(3)

(d) Carbon dioxide and hydrogen are separated by washing the gas with potassium carbonate solution to give potassium hydrogencarbonate solution, leaving hydrogen in the gas stream. Potassium carbonate is expensive and is regenerated by heating the potassium hydrogencarbonate and liberating the carbon dioxide.

(i) Hydrogen is often claimed to be a non-polluting fuel as it only produces water on burning.

Explain why its manufacture using reactions **I** and **II** does **not** support this claim.

(1)

(ii) Write the equation for the thermal decomposition of potassium hydrogencarbonate.

State symbols are **not** required.

(1)

(e) Although industrial processes are often discussed in terms of equilibria, they are rarely allowed to reach equilibrium.

Suggest why, apart from insufficient reaction time, this is so.

(1)

(Total for Question 24 = 12 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

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

25 The oxidation of iron metal in the presence of oxygen is spontaneous.

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

(a) Explain the meaning of **spontaneous** in a thermodynamic context.

(1)

.....

.....

.....

(b) (i) Find the values of the standard molar entropies of iron and of iron(III) oxide from your data booklet.

(1)

.....

.....

(ii) The standard molar entropy at 298 K for oxygen molecules O_2 is +205 J mol^{-1} K^{-1}.

Calculate the standard entropy change of the system for the reaction between iron and oxygen. Include a sign and units in your answer.

(2)

(iii) The standard enthalpy change for the reaction at 25 °C is –1648 kJ mol^{-1}.

Calculate $\Delta S_{surroundings}$.

(1)

(iv) Use your answers to (b)(ii) and (iii) to calculate the total standard entropy change for the reaction. Include a sign and units in your answer.

(2)

*(v) The reaction is thermodynamically spontaneous.

Use your answers to (b)(ii), (iii) and (iv) to explain, in terms of the physical states of the substances in the reaction and the movement of the molecules in the surroundings, why this is so.

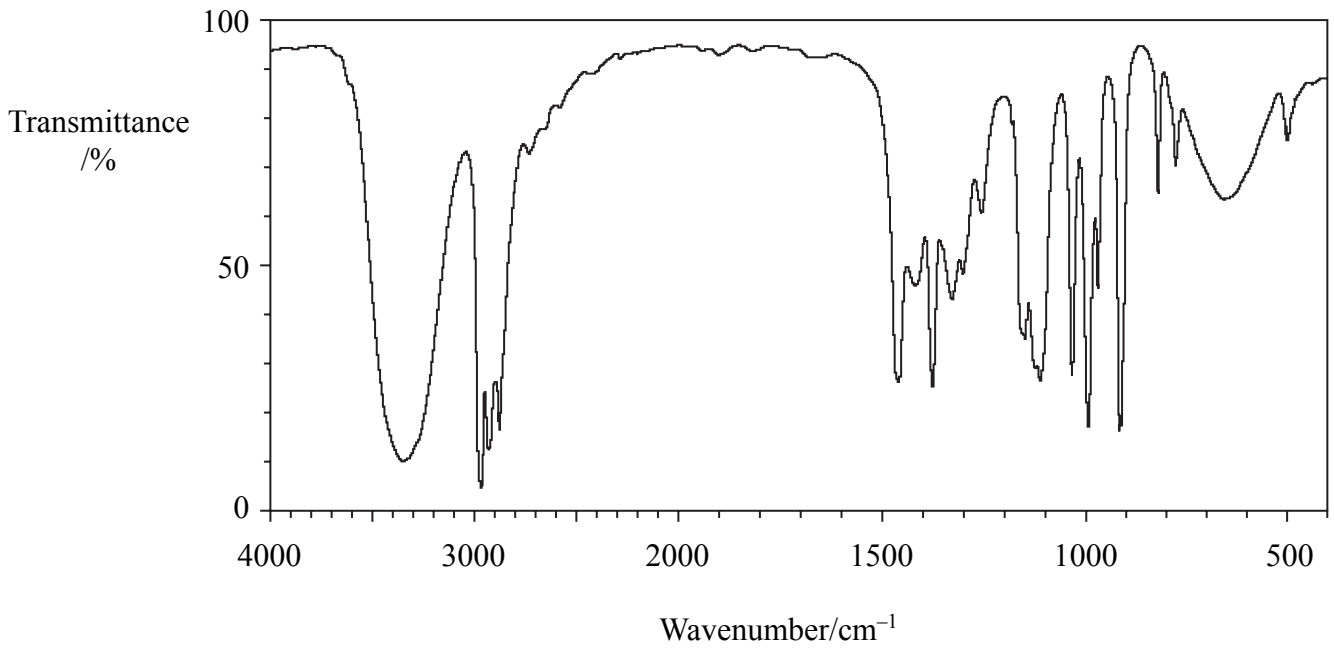
(3)

(Total for Question 25 = 10 marks)

26 This question is about compounds **X**, $C_4H_{10}O$, and **Y**, C_4H_8O.

(a) Compound **X**, $C_4H_{10}O$, can be oxidized to compound **Y**, C_4H_8O. The infrared spectrum of **X** is given below.

Infrared Spectrum of X

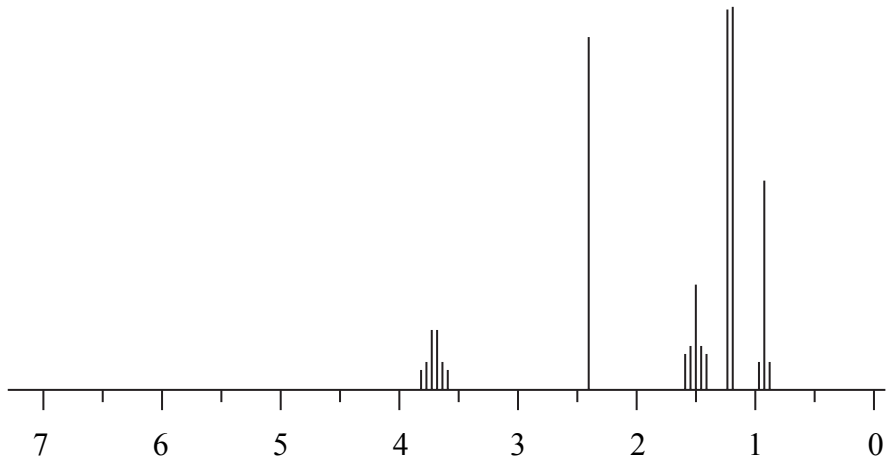


What can be deduced about the structures of **X** and **Y** using all this information and the data booklet? Justify your answer.

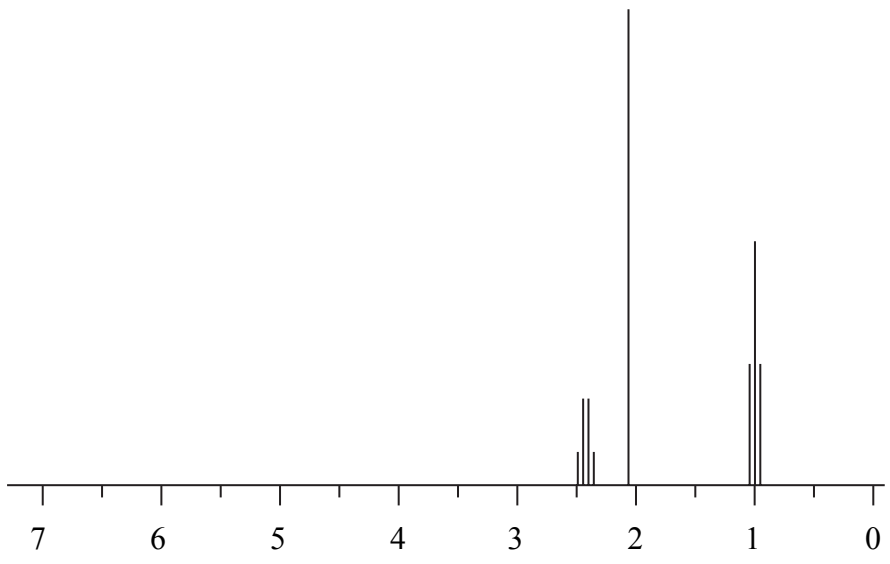
(4)

(b) Below are the nmr spectra of **X** and **Y**.

nmr spectrum of X



nmr spectrum of Y



*Use these nmr spectra and your answer to (a) to deduce the structural formulae of **X** and **Y**. Justify your answer and explain why **both** nmr spectra are consistent with these structures.

(6)

(Total for Question 26 = 10 marks)

TOTAL FOR SECTION C = 20 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)		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

* Actinide 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
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