Write your name here

Surname	Other names

Pearson Edexcel
International
Advanced Level

Centre Number | | | | | |

Candidate Number | | | | |

Chemistry

Advanced

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

Thursday 12 January 2017 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH04/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or **black** 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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6/6/5/5/1/1/

P 4 8 3 7 2 R 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 The rate equation for the reaction in which carbon disulfide, CS_2, decomposes is

$$\text{rate} = k[CS_2]$$

The units of the rate constant, k, are

☒ **A** s

☒ **B** s^{-1}

☒ **C** $mol\ dm^{-3}\ s^{-1}$

☒ **D** $dm^3\ mol^{-1}\ s^{-1}$

(Total for Question 1 = 1 mark)

2 The chemical equation and the rate equation for the reaction between nitrogen monoxide and bromine are

$$2NO(g) + Br_2(g) \rightarrow 2NOBr$$

$$\text{rate} = k[NO]^2[Br_2]$$

When the concentration of nitrogen monoxide is halved and the concentration of bromine is doubled, the rate is

☒ **A** unchanged.

☒ **B** doubled.

☒ **C** halved.

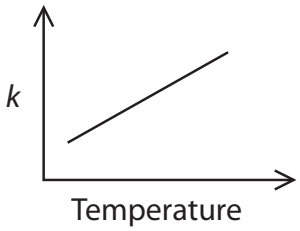
☒ **D** quartered.

(Total for Question 2 = 1 mark)

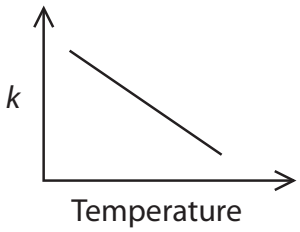
Use this space for any rough working. Anything you write in this space will gain no credit.

3 Which graph shows how the rate constant of a reaction, *k*, changes with temperature?

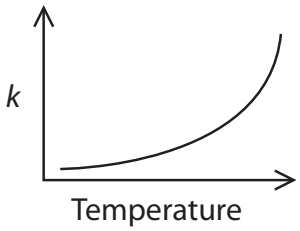
☒ **A**



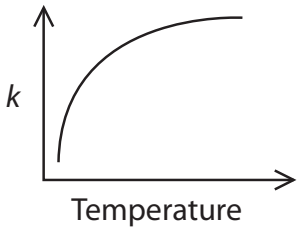
☒ **B**



☒ **C**



☒ **D**



(Total for Question 3 = 1 mark)

4 When solid sodium hydrogencarbonate is added to dilute hydrochloric acid, the mixture starts fizzing and the temperature drops.

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Which statement about this reaction is **not** true?

☒ **A** ΔH is positive.

☒ **B** $\Delta S_{surroundings}$ is positive.

☒ **C** ΔS_{system} is positive.

☒ **D** ΔS_{total} is positive.

(Total for Question 4 = 1 mark)

5 There is a **decrease** in the entropy of the system when

☒ **A** a gaseous molecule decomposes into two smaller gaseous molecules.

☒ **B** a solid decomposes to form a gas.

☒ **C** a vapour condenses.

☒ **D** a solid melts.

(Total for Question 5 = 1 mark)

6 What is the enthalpy change for dissolving sodium chloride in water?

$$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$$

$\Delta H_{sol} = \Delta H_{solution}$ $\Delta H_{hyd} = \Delta H_{hydration}$

☒ **A** $\Delta H_{sol} = +$ Lattice energy of NaCl $+ \Delta H_{hyd}\, Na^+ + \Delta H_{hyd}\, Cl^-$

☒ **B** $\Delta H_{sol} = +$ Lattice energy of NaCl $- \Delta H_{hyd}\, Na^+ - \Delta H_{hyd}\, Cl^-$

☒ **C** $\Delta H_{sol} = -$ Lattice energy of NaCl $- \Delta H_{hyd}\, Na^+ - \Delta H_{hyd}\, Cl^-$

☒ **D** $\Delta H_{sol} = -$ Lattice energy of NaCl $+ \Delta H_{hyd}\, Na^+ + \Delta H_{hyd}\, Cl^-$

(Total for Question 6 = 1 mark)

7 Energy is given out when one mole of gaseous sodium ions is hydrated.

$$Na^+(g) + aq \rightarrow Na^+(aq)$$

This reaction is more exothermic than the corresponding reaction for potassium ions, $K^+(g)$, because

☒ **A** sodium compounds are more soluble than potassium compounds.

☒ **B** the first ionisation energy of sodium is greater than the first ionisation energy of potassium.

☒ **C** the lattice energies of sodium compounds are more exothermic than the lattice energies of corresponding potassium compounds.

☒ **D** the radius of the Na^+ ion is less than the radius of the K^+ ion.

(Total for Question 7 = 1 mark)

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

8 Silver oxide decomposes on heating.

$$Ag_2O(s) \rightarrow 2Ag(s) + \tfrac{1}{2}O_2(g)$$

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

☒ **A** $K_p = \dfrac{(pAg)^2 \quad (pO_2)^{1/2}}{(pAg_2O)}$

☒ **B** $K_p = \dfrac{(pAg_2O)}{(pAg)^2 \quad (pO_2)^{1/2}}$

☒ **C** $K_p = (pO_2)^{1/2}$

☒ **D** $K_p = \dfrac{1}{(pO_2)^{1/2}}$

(Total for Question 8 = 1 mark)

9 The dissociation of methanoic acid in aqueous solution is endothermic. When a sample of aqueous methanoic acid is warmed

☒ **A** the pH will decrease.

☒ **B** the pH does not change.

☒ **C** the concentration of undissociated HCOOH will increase.

☒ **D** the concentration of methanoate ions will decrease.

(Total for Question 9 = 1 mark)

10 Which solution has the highest pH?

☒ **A** 0.010 mol dm^{-3} sodium hydroxide solution

☒ **B** 0.100 mol dm^{-3} sodium hydroxide solution

☒ **C** 0.010 mol dm^{-3} aqueous ammonia

☒ **D** 0.100 mol dm^{-3} aqueous ammonia

(Total for Question 10 = 1 mark)

11 An indicator with a pH range 3.8 to 5.4 is suitable for the titration of

☒ **A** nitric acid with ammonia.

☒ **B** ethanoic acid with sodium hydroxide.

☒ **C** ethanoic acid with ammonia.

☒ **D** sodium thiosulfate with iodine.

(Total for Question 11 = 1 mark)

12 The reaction between concentrated nitric acid and concentrated sulfuric acid is

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$

The Brønsted-Lowry acids in this equilibrium are

☒ **A** HNO_3 and H_2SO_4

☒ **B** $H_2NO_3^+$ and HSO_4^-

☒ **C** HNO_3 and HSO_4^-

☒ **D** $H_2NO_3^+$ and H_2SO_4

(Total for Question 12 = 1 mark)

13 When one of the optical isomers of 2-bromobutane reacts with aqueous hydroxide ions by an S_N2 mechanism, butan-2-ol is formed.

Which of the following is correct?

☒ **A** There are two steps in the reaction.

☒ **B** The butan-2-ol which forms is optically active.

☒ **C** A racemic mixture forms.

☒ **D** A planar intermediate forms.

(Total for Question 13 = 1 mark)

14 Ethanamide, CH_3CONH_2, is formed in **one** step by the reaction of

☒ **A** ethanoic acid with ammonia.

☒ **B** ethanoyl chloride with ammonia.

☒ **C** ethanal with hydrogen cyanide.

☒ **D** methanol with methylamine.

(Total for Question 14 = 1 mark)

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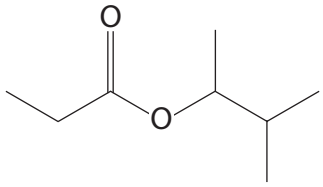
15 The ester



can be made by reacting

- ☒ **A** ethanoic acid with 2-methylbutan-2-ol.
- ☒ **B** propanoic acid with 2-methylbutan-2-ol.
- ☒ **C** ethanoic acid with 3-methylbutan-2-ol.
- ☒ **D** propanoic acid with 3-methylbutan-2-ol.

(Total for Question 15 = 1 mark)

16 Propanoic acid can be obtained by the

- ☒ **A** oxidation of propanone with potassium dichromate(VI) and sulfuric acid.
- ☒ **B** reduction of propanal with lithium tetrahydridoaluminate(III).
- ☒ **C** hydrolysis of methyl propanoate with hydrochloric acid.
- ☒ **D** hydrolysis of propyl methanoate with hydrochloric acid.

(Total for Question 16 = 1 mark)

17 Which pair of compounds can be easily distinguished by their infrared spectra **outside** the fingerprint region?

- ☒ **A** C_2H_4 from C_2H_6
- ☒ **B** C_4H_{10} from C_5H_{12}
- ☒ **C** $CH_3CH_2CH_2OH$ from $CH_3CH(OH)CH_3$
- ☒ **D** $CH_3COOC_2H_5$ from $C_2H_5COOCH_3$

(Total for Question 17 = 1 mark)

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18 Which of the following statements about gas chromatography (GC) is true?

☒ **A** It is only carried out at room temperature.

☒ **B** It can be used for samples which decompose when they are vaporised.

☒ **C** It can be used for non-volatile substances.

☒ **D** It can be used to measure the amount of each component in a mixture.

(Total for Question 18 = 1 mark)

19 The mass spectrum of dichloroethene, $C_2H_2Cl_2$, has large peaks at m/e values of 61 and 63 due to fragmentation when a C—Cl bond breaks.

The only isotopes present in the fragment forming the peak at $m/e = 63$ are

☒ **A** ^{12}C, ^{1}H and ^{35}Cl.

☒ **B** ^{14}C, ^{1}H and ^{35}Cl.

☒ **C** ^{12}C, ^{2}H and ^{37}Cl.

☒ **D** ^{12}C, ^{1}H and ^{37}Cl.

(Total for Question 19 = 1 mark)

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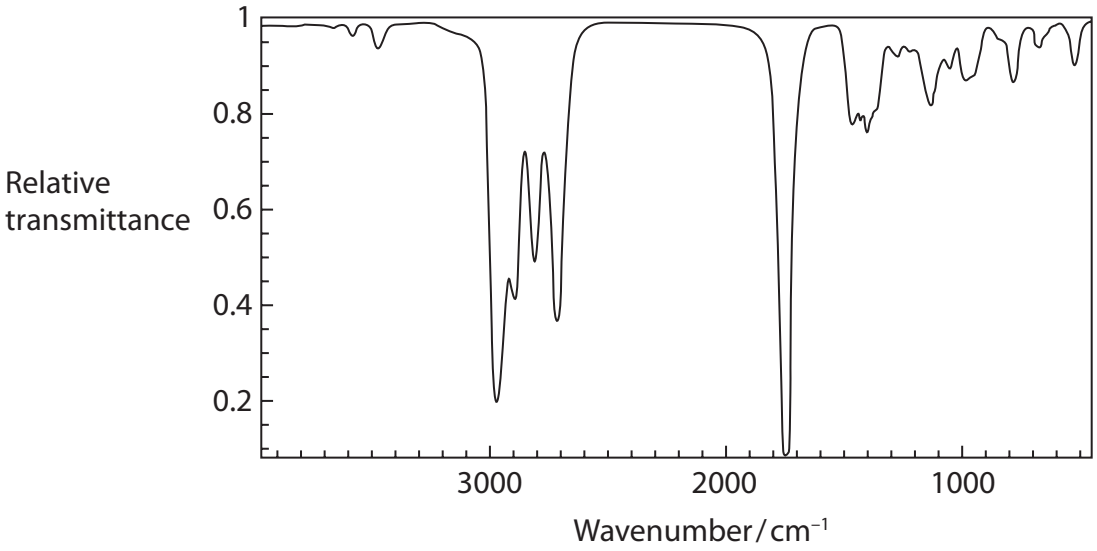
20 The infrared spectrum of a compound is shown.



Use the information on pages 5 and 6 of your Data Booklet to identify which compound produced this spectrum.

☒ **A** C_3H_7CHO

☒ **B** $CH_3COC_2H_5$

☒ **C** $CH_3CH{=}CHCH_2OH$

☒ **D** C_5H_{12}

(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 Crystal violet is an indicator which is coloured in solutions of acids, and colourless in alkalis.

The kinetics of the reaction of crystal violet with sodium hydroxide were investigated. Using the abbreviation CV^+ for the formula of crystal violet, a simplified equation for the reaction is

$$\underset{\text{violet}}{CV^+(aq)} + OH^-(aq) \rightarrow \underset{\text{colourless}}{CVOH(aq)}$$

(a) Equal volumes of 0.100 mol dm^{-3} sodium hydroxide and 5.00×10^{-5} mol dm^{-3} crystal violet were mixed.

(i) Explain why very different concentrations of sodium hydroxide and crystal violet were used in the experiment to find the order with respect to crystal violet.

(1)

.....

.....

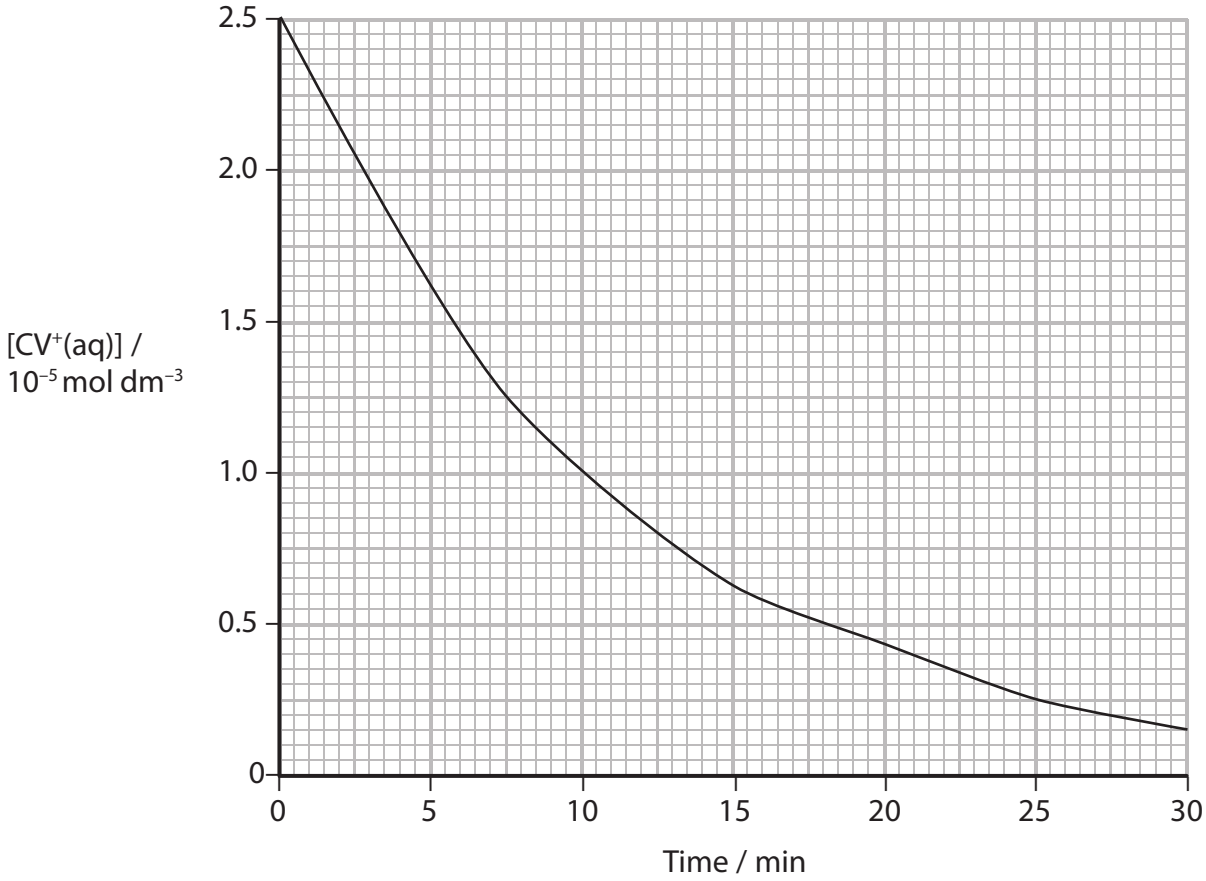
.....

(ii) Suggest a method which could be used in this experiment to continuously monitor the change in concentration of crystal violet with time.

(1)

.....

(iii) The graph shows how the concentration of crystal violet changes with time.



Measure **two** half-lives for this reaction showing your working on the graph.
Give the half-lives below.

(2)

(iv) Use your half-lives to deduce the order with respect to CV^+.

Justify your answer.

(2)

(b) In another series of experiments the rate constant was determined at different temperatures.

The table shows the values of the rate constant, k, at different temperatures.
Some of the corresponding values for the reciprocal of temperature and ln k are also shown.

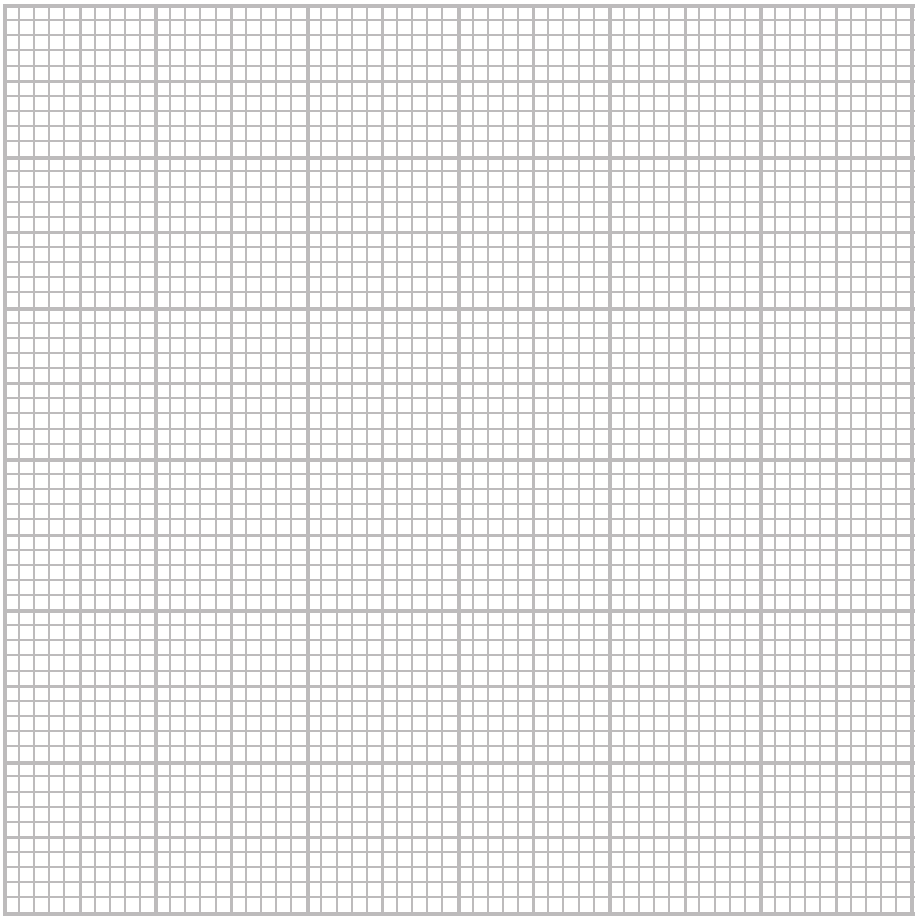
(i) Complete the table by calculating the missing values.

(1)

T/K	k	$\frac{1}{T}$ / K^{-1}	ln k
285	3.35×10^{-3}	3.51×10^{-3}	–5.70
288	4.30×10^{-3}	3.47×10^{-3}	–5.45
291	5.19×10^{-3}	3.44×10^{-3}	–5.26
294	6.67×10^{-3}	3.40×10^{-3}	–5.01
297	7.91×10^{-3}		

(ii) Plot a graph of ln k on the vertical axis against $1/T$ on the horizontal axis and calculate the gradient.

(5)



Gradient .....

(iii) Use your value of the gradient in (b)(ii) to calculate the activation energy, E_a, of the reaction.

Remember to include units with your answer, which should be given to **two** significant figures.

The Arrhenius equation is

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

(2)

(Total for Question 21 = 14 marks)

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22 This question is about the isomers **P** and **Q**.

$CH_3COCH(CH_3)_2$ **P**

$CH_3CH_2COCH_2CH_3$ **Q**

(a) Identify the reagent used in a test to show that **P** and **Q** are both carbonyl compounds.

Give the positive result of the test.

(2)

Reagent .....

Result .....

(b) Identify the reagents used in a test which gives a positive result with **P** but not with **Q**.

Give the positive result of the test and identify the organic product which is observed.

(3)

Reagents .....

Result .....

Identity of organic product .....

(c) **Name** the organic product formed when **P** reacts under suitable conditions with lithium tetrahydridoaluminate(III).

(1)

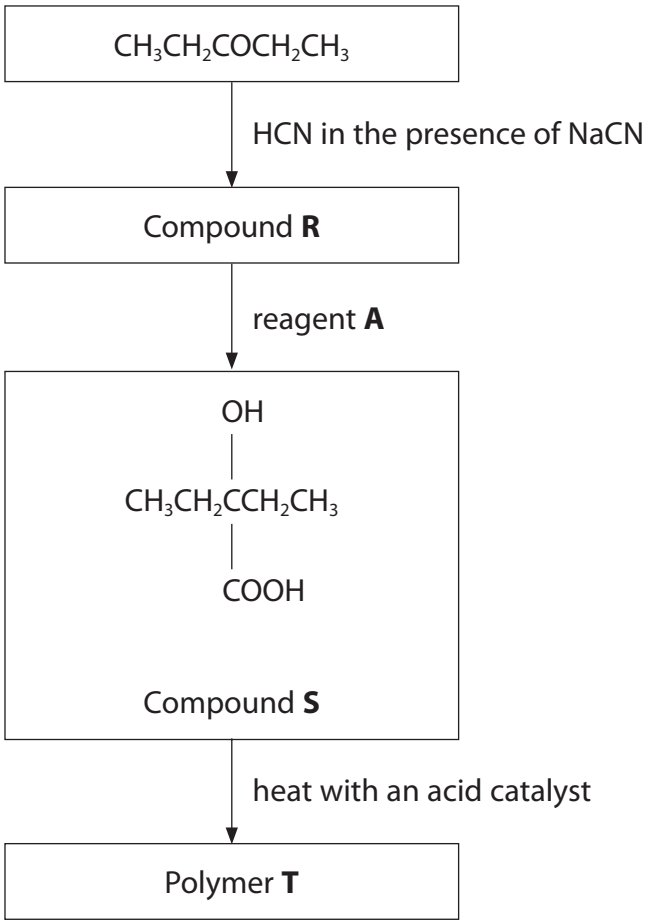
.....

(d) The proton nmr spectra of **P** and **Q** were compared. Complete the table.

(4)

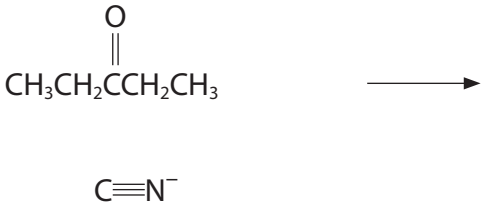
	P $CH_3COCH(CH_3)_2$	**Q** $CH_3CH_2COCH_2CH_3$
Number of peaks in the **low** resolution nmr spectrum		
Number of H atoms producing peak with the greatest area in **low** resolution nmr spectrum		
Splitting pattern of the peak with greatest area in the **high** resolution nmr spectrum		

(e) A sequence of reactions was carried out with **Q**.



(i) Complete the mechanism for the reaction of **Q** with HCN in the presence of NaCN, showing relevant curly arrows, lone pairs, charges and dipoles.

(4)



(ii) Identify the reagent **A** used to convert compound **R** to compound **S**.

(1)

.....

(iii) Draw the displayed formula of **two** repeat units of polymer **T**.

(2)

(Total for Question 22 = 17 marks)

23 This question is about lactic acid, $CH_3CH(OH)COOH$

(a) Give the IUPAC name for lactic acid.

(1)

.....

(b) Write the equation for the reaction of lactic acid with **excess** phosphorus(V) chloride, PCl_5, showing the structural formula of the organic product.

State symbols are not required.

(3)

(c) The acid dissociation constant, K_a, of lactic acid is 1.38×10^{-4} mol dm^{-3}.

(i) Write the expression for the acid dissociation constant of lactic acid.

(1)

(ii) State whether lactic acid is a stronger or weaker acid than ethanoic acid.

Quote data from page 18 of your Data Booklet to justify your answer.

(1)

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(iii) Calculate the pH of a 0.150 mol dm^{-3} solution of lactic acid, giving your answer to **two** decimal places. State **two** assumptions you have made.

(4)

Assumptions

.....

.....

.....

(iv) A buffer solution with a pH of 4.00 is prepared using lactic acid and sodium lactate, $CH_3CH(OH)COONa$.

Calculate the mass of sodium lactate that should be dissolved in 1.00 dm^3 of 0.150 mol dm^{-3} solution of lactic acid to make a buffer solution of pH 4.00.

Sodium lactate has molar mass of 112 g mol^{-1}.

(4)

*(v) A small volume of hydrochloric acid is added to the buffer solution made in (c) (iv).

Explain why the pH of the solution does not change significantly.
Include an equation when you refer to any reaction which occurs.

(3)

(Total for Question 23 = 17 marks)

TOTAL FOR SECTION B = 48 MARKS

SECTION C

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

24 Nitrosyl chloride, NOCl, is a yellow gas which decomposes on heating.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(a) A sample of 2.00 mol of NOCl was heated in a sealed vessel to a certain temperature, *T*. The volume of the vessel was 5.00 dm^3. When equilibrium was reached, 0.220 mol of NO had been formed.

(i) Write the expression for the equilibrium constant, K_c, for this reaction.

(1)

*(ii) Calculate the value of K_c under these conditions. Include units in your answer.

(4)

*(iii) The volume of the vessel containing the equilibrium mixture in (a) was doubled to 10 dm^3, keeping the temperature constant.

State the effect of this change in volume on the value of K_c and on the number of moles of NO at equilibrium. A calculation is not required but justify your answers.

(2)

(b) (i) Some data about nitrosyl chloride is given in the table.

Complete the table with the data for nitrogen(II) oxide and chlorine, using the Data Booklet where appropriate.

(2)

Substance	Standard enthalpy change of formation, $\Delta H_f^{\ominus}{}_{298}$ / kJ mol^{-1}	Standard molar entropy, $S^{\ominus}_{298}$ / J mol^{-1} K^{-1}
NOCl(g)	+51.7	261.7
NO(g)		
Cl_2(g)		165.0

(ii) Calculate the standard enthalpy change of the reaction, $\Delta H^{\ominus}$, at 298 K.

$$2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$$

(2)

(iii) Use your answer to (b)(ii) to explain why ΔS_{total} becomes less negative as temperature increases.

(2)

(iv) Give the expression relating the equilibrium constant to the total entropy change and hence explain how the equilibrium constant changes as the temperature increases.

(2)

(c) (i) The standard molar entropies of the substances, $S^{\ominus}$, in the reaction are given at 800 K.

Substance	Standard molar entropy, $S^{\ominus}_{800}$ / J mol^{-1} K^{-1}
NOCl(g)	305.5
NO(g)	231.2
Cl_2(g)	189.3

Explain why the value for the standard molar entropy of all these substances is greater at 800 K than at 298 K.

(2)

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, at 800 K.

Include a sign and units with your answer.

(2)

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(iii) The standard enthalpy change of the reaction, $\Delta H^{\ominus}$ at 800 K is +53.2 kJ mol^{-1}.

Show by calculation whether or not the reaction is thermodynamically spontaneous at 800 K.

(3)

(Total for Question 24 = 22 marks)

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

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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

* 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