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)

Thursday 26 January 2012 – 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 ▶

P39304A

7/7/5/3/3/3/

P 3 9 3 0 4 A 0 1 2 4

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 reaction between carbon monoxide and hydrogen reaches a dynamic equilibrium.

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

(a) Which of these statements about a dynamic equilibrium is **not** true?

(1)

☒ **A** The forward rate of reaction is equal to the backward rate of reaction.

☒ **B** The concentrations of the products and reactants do not change.

☒ **C** The concentrations of the products and reactants are equal.

☒ **D** The equilibrium can be approached from either direction.

(b) The K_c expression for the above reaction is

(1)

☒ **A** $K_c = \dfrac{[CH_3OH]}{[CO] \times [H_2]^2}$

☒ **B** $K_c = \dfrac{[CO] \times 2[H_2]}{[CH_3OH]}$

☒ **C** $K_c = \dfrac{[CO] \times [H_2]^2}{[CH_3OH]}$

☒ **D** $K_c = \dfrac{[CH_3OH]}{[CO] \times 2[H_2]}$

(Total for Question 1 = 2 marks)

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

2 Hydrogen and iodine, both with an initial concentration of 0.010 mol dm^{-3}, were allowed to react. At equilibrium, the concentration of hydrogen iodide was 0.0030 mol dm^{-3}.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

K_c is calculated using the values

		$H_2(g)$ / mol dm^{-3}	$I_2(g)$ / mol dm^{-3}	HI(g) / mol dm^{-3}
☒	**A**	0.0070	0.0070	0.0030
☒	**B**	0.0040	0.0040	0.0030
☒	**C**	0.0040	0.0040	0.0060
☒	**D**	0.0085	0.0085	0.0030

(Total for Question 2 = 1 mark)

3 The reaction below reached a dynamic equilibrium from an initial mixture of all four substances P, Q, R and S in aqueous solution.

$$P + Q \rightleftharpoons R + S$$

The following data were obtained.

Substance	Concentration at equilibrium / mol dm^{-3}
P	0.050
Q	0.040
R	0.020
S	0.010

K_c for the equilibrium is

☒ **A** 0.10

☒ **B** 0.33

☒ **C** 3.00

☒ **D** 10.0

(Total for Question 3 = 1 mark)

4 The Haber process is used to make ammonia from nitrogen and hydrogen at 450 °C.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.0 \text{ kJ mol}^{-1}$$

(a) If the partial pressures of these gases were measured in atm, the units of the equilibrium constant K_p will be

(1)

☒ **A** atm

☒ **B** atm^2

☒ **C** atm^{-2}

☒ **D** atm^{-1}

(b) When the temperature of the system is increased

(1)

☒ **A** K_p decreases.

☒ **B** K_p increases.

☒ **C** K_p stays the same.

☒ **D** K_p first decreases and then increases.

(Total for Question 4 = 2 marks)

5 In high performance liquid chromatography, HPLC, which of these factors does **not** affect the time taken for a component to pass through the column?

☒ **A** Type of detector

☒ **B** Material of stationary phase

☒ **C** Particle size of stationary phase

☒ **D** Temperature of column

(Total for Question 5 = 1 mark)

6 When equimolar amounts of the solutions below are mixed, which forms a buffer solution with a pH less than 7?

☒ **A** Hydrochloric acid and sodium chloride

☒ **B** Ethanoic acid and sodium ethanoate

☒ **C** Sodium hydroxide and sodium chloride

☒ **D** Ammonia and ammonium chloride

(Total for Question 6 = 1 mark)

7 The pH of a 1.5 mol dm^{-3} solution of hydrochloric acid, HCl(aq), is

☒ **A** −1.50

☒ **B** −0.18

☒ **C** 0.18

☒ **D** 1.50

(Total for Question 7 = 1 mark)

8 Which of these solid substances is likely to have the greatest standard entropy? Use of the data booklet is not required.

☒ **A** SnO

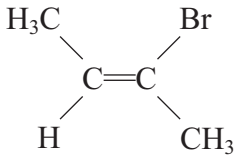
☒ **B** SnO_2

☒ **C** $SnBr_2$

☒ **D** $SnBr_4$

(Total for Question 8 = 1 mark)

9 What is the correct name for the molecule shown below?



☒ **A** *Z*-2-bromobut-2-ene

☒ **B** *E*-2-bromobut-2-ene

☒ **C** *E*-3-bromobut-2-ene

☒ **D** *Z*-3-bromobut-2-ene

(Total for Question 9 = 1 mark)

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

10 Ketones react with hydrogen cyanide, HCN, in the presence of cyanide ions, CN^-.

(a) Which of these ketones does **not** form a racemic mixture in this reaction?

(1)

☒ **A** $CH_3CH_2CH_2COCH_3$

☒ **B** $CH_3CH_2COCH_2CH_3$

☒ **C** $CH_3CH_2CH_2CH_2COCH_3$

☒ **D** $CH_3CH_2CH_2COCH_2CH_3$

(b) This type of reaction is classified as

(1)

☒ **A** nucleophilic substitution.

☒ **B** nucleophilic addition.

☒ **C** electrophilic addition.

☒ **D** electrophilic substitution.

(Total for Question 10 = 2 marks)

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11 Which of these is **not** observed when ethanoyl chloride reacts with water?

☒ **A** Misty fumes given off.

☒ **B** The gas given off turns damp blue litmus paper red.

☒ **C** The mixture gets hot.

☒ **D** A white precipitate forms.

(Total for Question 11 = 1 mark)

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12 UV light is useful in initiating some reactions because it

☒ **A** lowers the activation energy of the reaction.

☒ **B** causes bonds in molecules to stretch and bend.

☒ **C** causes molecules to form ions.

☒ **D** causes molecules to form free radicals.

(Total for Question 12 = 1 mark)

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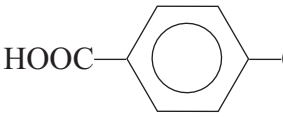
13 Butane-1,4-diol, $HO(CH_2)_4OH$, and benzene-1,4-dicarboxylic acid,

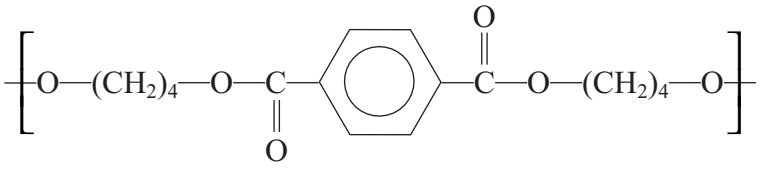


react to form a polyester.

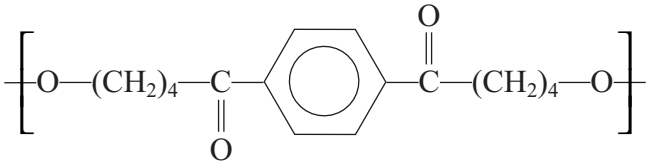
(a) The repeat unit of the polyester is

(1)

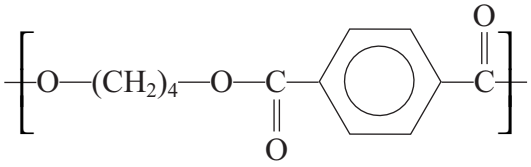
☒ **A**



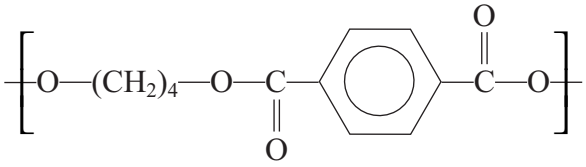
☒ **B**



☒ **C**



☒ **D**



(b) The type of reaction is

(1)

☒ **A** hydrolysis.

☒ **B** addition.

☒ **C** substitution.

☒ **D** condensation.

(Total for Question 13 = 2 marks)

14 The equation for the enthalpy of hydration for a magnesium ion is

☒ **A** $Mg^{2+}(s) + aq \rightarrow Mg^{2+}(aq)$

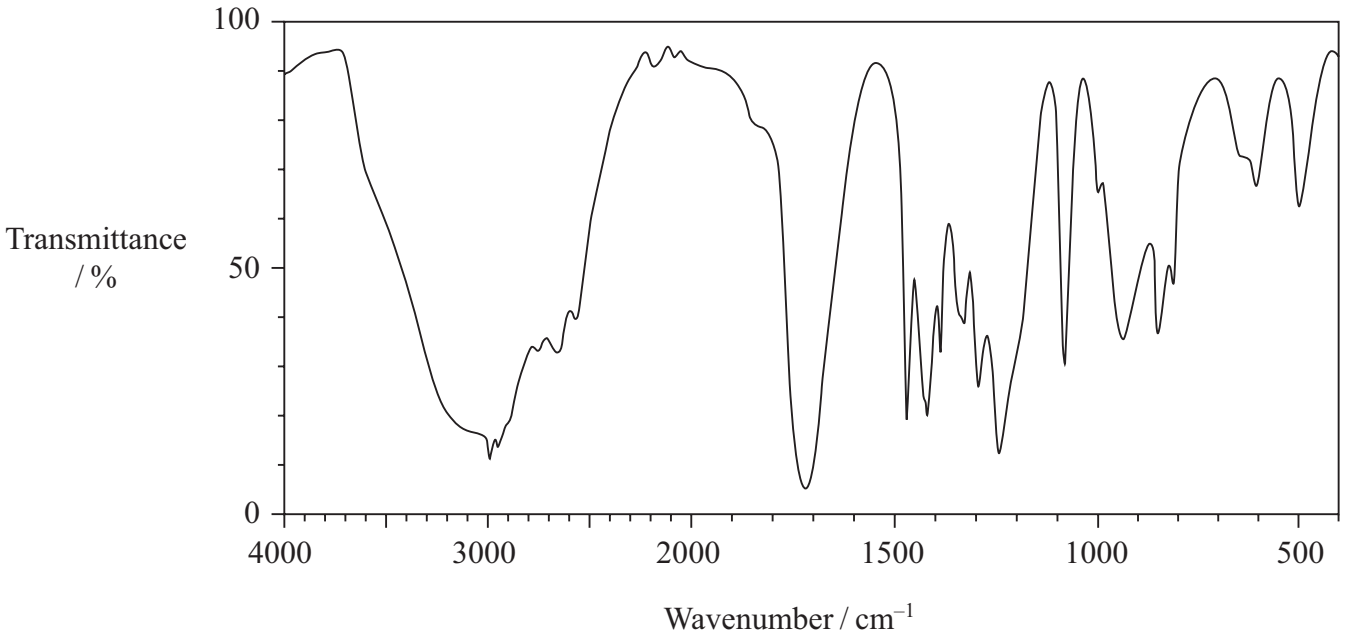
☒ **B** $Mg^{2+}(g) + aq \rightarrow Mg^{2+}(aq)$

☒ **C** $Mg^{2+}(aq) \rightarrow Mg^{2+}(g) + aq$

☒ **D** $Mg^{2+}(aq) \rightarrow Mg^{2+}(s) + aq$

(Total for Question 14 = 1 mark)

15 The IR spectrum of a substance is shown below.



Which of the following substances has this spectrum?

You may use the information on page 6 of the data booklet.

☒ **A** Propan-1-ol

☒ **B** Propanal

☒ **C** Propanone

☒ **D** Propanoic acid

(Total for Question 15 = 1 mark)

16 Two ketones, $CH_3COCH_2CH_2CH_3$ and $CH_3CH_2COCH_2CH_3$, both have $M_r = 86$. Which peak due to fragmentation into singly charged ions would you expect to be present in the mass spectrum of one but not the other?

☒ **A** 71

☒ **B** 57

☒ **C** 43

☒ **D** 29

(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 Two organic compounds, **X** and **Y**, both with the molecular formula C_4H_8O, contain a carbonyl group.

(a) Describe what you would see when 2,4-dinitrophenylhydrazine is added to either of these compounds.

(1)

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(b) It is suspected that **X** is a ketone and **Y** is an aldehyde. Outline a chemical test you could carry out to confirm this, describing the results in each case.

(3)

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(c) (i) Give the structural formulae of the two possible isomers of **Y** which are aldehydes.

(1)

(ii) Name the technique you would use to purify the product of the test with 2,4-dinitrophenylhydrazine.

(1)

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(iii) Other than by spectroscopic techniques, how would you use the purified product to identify compound **Y**? [Practical details are not required.]

(2)

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(Total for Question 17 = 8 marks)

18 Kits for manufacturing biodiesel from vegetable oils and methanol are sold for home use. The reaction which takes place may be represented by the following equation.

$$3CH_3OH + \begin{array}{l} CH_2OOCR \\ | \\ CHOOCR' \\ | \\ CH_2OOCR'' \end{array} \xrightarrow[50\,^{\circ}C,\ 98\%\ \text{yield}]{NaOH(s)} \begin{array}{ll} CH_2OH & + RCOOCH_3 \\ | & \\ CHOH & + R'COOCH_3 \\ | & \\ CH_2OH & + R''COOCH_3 \end{array}$$

*(a) Describe any two of the main hazards when carrying out this reaction. What precaution would you take to minimise the risk in each case?

(4)

Hazard .....

.....

Precaution .....

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Hazard .....

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Precaution .....

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(b) Suggest **two** environmental benefits of using these kits, despite the associated risks.

(2)

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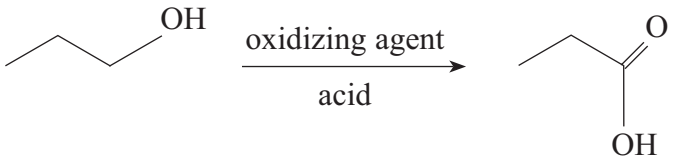
(Total for Question 18 = 6 marks)

19 The carboxylic acid, propanoic acid, can be prepared by oxidation of the alcohol, propan-1-ol.



propan-1-ol propanoic acid

(a) (i) Identify a suitable oxidizing agent you could use in this reaction.

(1)

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(ii) If you carried out this preparation in the laboratory, describe **two** measures you would take to ensure the maximum possible yield of propanoic acid is obtained.

(2)

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(iii) Propanoic acid can be made by the hydrolysis of a nitrile. Give the structural formula of the nitrile and write an equation for this reaction.

(3)

Structural formula .....

Equation

*(b) Propanoic acid reacts with methanol, CH_3OH, to form the ester, methyl propanoate.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

Even with the use of a catalyst, this reaction is quite slow and incomplete. Suggest a reagent, to replace the propanoic acid, which would form the ester at a faster rate. Suggest **two** reasons why your chosen reagent reacts faster.

(3)

(c) The structure of methyl propanoate can be investigated by using high resolution ^1H nuclear magnetic resonance (nmr) spectroscopy.

(i) What type of radiation interacts with ^1H nuclei in nmr spectroscopy?

(1)

(ii) Describe what happens to ^1H nuclei when they absorb this radiation.

(2)

(iii) Complete the table to show values for the chemical shift of the different ^1H nuclei in methyl propanoate and their splitting pattern. Page 7 of the data booklet gives information about chemical shifts.

(2)

^1H environment	Chemical shift, δ / ppm	Splitting pattern
$C\mathbf{H_3}O–$	3.7	Singlet
$–C\mathbf{H_2}–$	2.3	
$–C\mathbf{H_3}$		Triplet

(Total for Question 19 = 14 marks)

20 The exothermic reaction between carbon monoxide and hydrogen can be used industrially to make methanol. The process is carried out at 250 °C and between 50 and 100 atm.

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

(a) Explain why increasing the pressure increases the yield of methanol. Give **one** disadvantage of increasing the pressure.

(2)

(b) The reaction gives a greater equilibrium yield at 100 °C than at 250 °C.

(i) Explain, in terms of the entropy change of the surroundings and the total entropy change of the reaction, why this is so.

A calculation is **not** required.

(2)

(ii) Explain why the reaction is, nevertheless, carried out at 250 °C.

(1)

(c) Given that the reaction is an equilibrium, suggest **two** ways in which the atom economy of this process could be maximised without changing the temperature or pressure.

(2)

(Total for Question 20 = 7 marks)

21 This question is about the kinetics of the reaction between bromoethane and aqueous hydroxide ions.

(a) The results of an experiment to find the initial rate of the reaction are shown in the table below.

$[CH_3CH_2Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
0.100	0.150	1.54×10^{-6}

The rate equation for the reaction is

$$\text{rate} = k[CH_3CH_2Br][OH^-]$$

(i) Calculate the value of k. Give your answer to three significant figures and include units.

(3)

(ii) Calculate the initial rate if the concentrations of both reactants were changed to 0.020 mol dm^{-3}.

(1)

(b) (i) State the order of the reaction.

(1)

.....

(ii) The mechanism for this reaction can be inferred from the rate equation. Draw the transition state formed in the reaction between bromoethane and hydroxide ions.

(2)

(c) The rate constant for the reaction between bromoethane and hydroxide ions was determined at five different temperatures. The results are shown in the table below.

Temperature (T) / K	1/Temperature (1/T) / K^{-1}	Rate constant, k	ln k
293	3.41×10^{-3}	5.83×10^{-5}	−9.75
303	3.30×10^{-3}	1.67×10^{-4}	−8.70
313	3.19×10^{-3}	5.26×10^{-4}	−7.55
323	3.10×10^{-3}	1.36×10^{-3}	−6.60
333		3.77×10^{-3}	

(i) Complete the missing values in the table.

(2)

(ii) Plot a graph of ln k against 1/T. Calculate the gradient of your graph and use this to calculate the activation energy, E_A. The Arrhenius equation can be expressed as

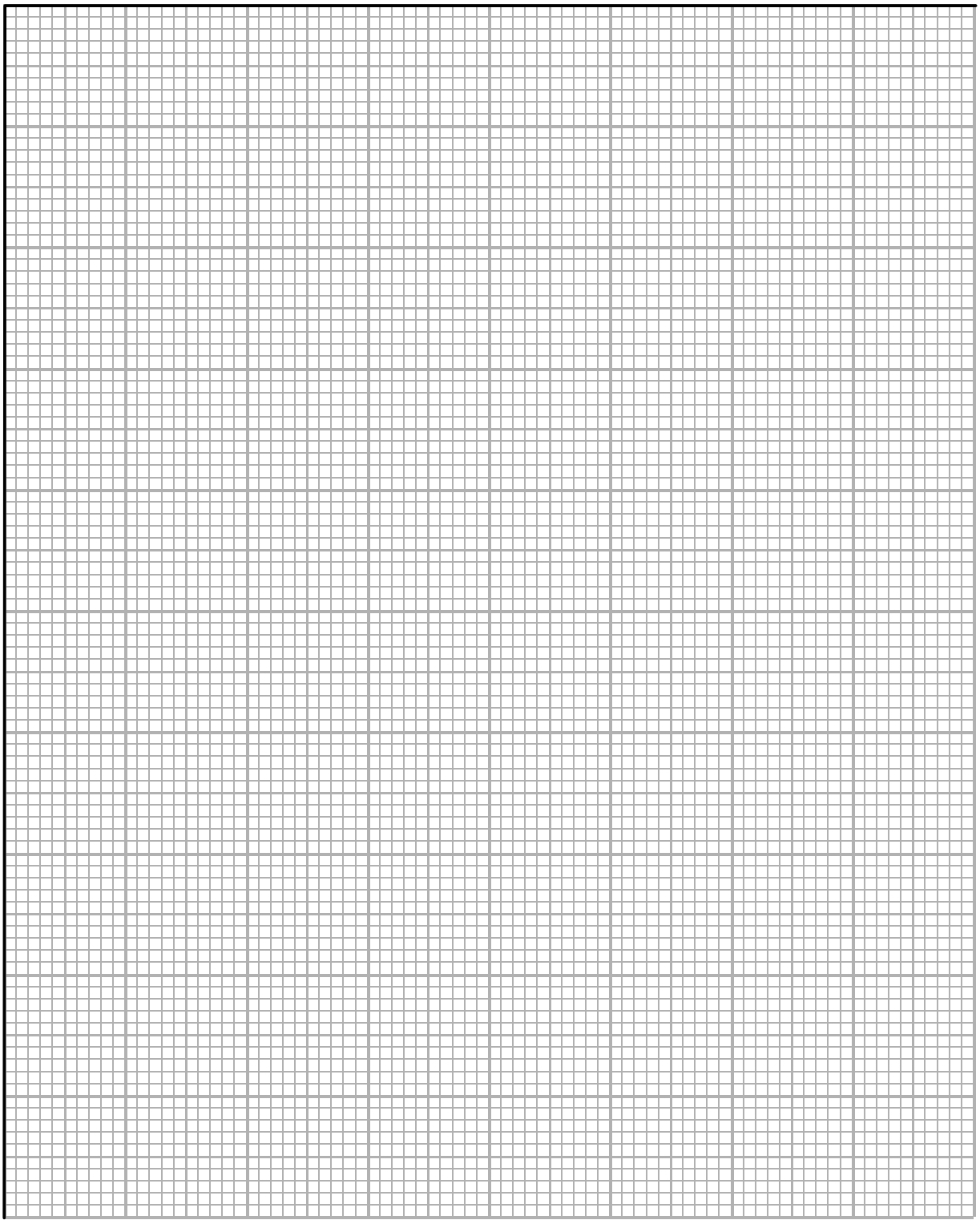
$$\ln k = \frac{-E_A}{R} \times \left(\frac{1}{T}\right) + \text{a constant}$$

[Gas constant, R = 8.31 J K^{-1} mol^{-1}]

(5)

$1/T/K^{-1}$

ln k



(Total for Question 21 = 14 marks)

TOTAL FOR SECTION B = 49 MARKS

SECTION C

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

22 The hydrocarbon butane can be cracked to form propene and methane by passing it over a heated aluminium oxide catalyst at a temperature of 700 K. The equation for the reaction is

$$C_4H_{10}(g) \rightarrow C_3H_6(g) + CH_4(g) \qquad \Delta H = +71.9 \text{ kJ mol}^{-1}$$

(a) (i) Use page 20 of the data booklet to complete the table below.

(1)

Hydrocarbon	$S^{\ominus}$/ J mol^{-1} K^{-1}
$C_4H_{10}(g)$	+310.1
$C_3H_6(g)$	+266.9
$CH_4(g)$	

(ii) Calculate the standard entropy change of the system, $\Delta S^{\ominus}_{system}$, for this reaction. Include a sign in your answer.

(2)

(iii) Was the sign for your answer as you expected? Fully justify your answer.

(2)

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(iv) Calculate the entropy change of the surroundings, $\Delta S_{surroundings}$, at 700 K.

Include a sign and units in your answer.

Use this value and your answer to (ii) to explain why butane cracks into propene and methane at this temperature.

(3)

(v) Calculate the minimum temperature needed for this reaction to be thermodynamically feasible.

(3)

(b) The aluminium oxide behaves as a heterogeneous catalyst. Explain both what is meant by the term **heterogeneous** and how, in terms of activation energy, the catalyst is able to speed up the reaction.

(3)

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(Total for Question 22 = 14 marks)

23 The bubble bath 'Colour Change Matey' has amongst its ingredients the weak acid benzoic acid, as well as the indicator bromocresol green. When it is added to bath water, its colour changes from yellow to blue.

(a) (i) Write the K_a expression for the dissociation of benzoic acid, C_6H_5COOH.

(1)

(ii) Use the data on page 18 of the data booklet to calculate the pH of a solution of benzoic acid, C_6H_5COOH, of concentration 0.0025 mol dm^{-3}.

(2)

*(b) Use the data on page 19 of the data booklet, and your answer to (a)(ii), to suggest why the bubble bath changes colour when it is diluted by being added to the bath water.

(4)

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(Total for Question 23 = 7 marks)

TOTAL FOR SECTION C = 21 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)											(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							

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

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