Write your name here

Surname	Other names

Pearson Edexcel GCE

Centre Number	Candidate Number

Chemistry

Advanced

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

Tuesday 13 June 2017 – Afternoon

Time: 1 hour 40 minutes

Paper Reference **6CH04/01**

You must have: Data Booklet
Scientific 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 ▶

P48082A

5/5/6/6/6/1/

P 4 8 0 8 2 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 Bromate(V) ions react with bromide ions in the presence of a dilute acid.

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

The rate of this reaction can be determined by measuring the change in colour intensity or the change in conductivity of the solution.

Which changes will occur?

	Change in colour intensity	Change in conductivity
☒ **A**	decreases	decreases
☒ **B**	decreases	increases
☒ **C**	increases	decreases
☒ **D**	increases	increases

(Total for Question 1 = 1 mark)

2 Substance **A** decomposes in a first order reaction.

The half-life for this reaction is 48 s.

In an experiment, the initial amount of **A** is 1.00 mol.

The amount, in moles, of **A** remaining at 144 s is

☒ **A** 0.500

☒ **B** 0.333

☒ **C** 0.250

☒ **D** 0.125

(Total for Question 2 = 1 mark)

3 Nitrogen dioxide, NO_2, reacts with carbon monoxide, CO.

$$NO_2 + CO \rightarrow NO + CO_2$$

The rate equation is rate = $k[NO_2]^2$.

(a) The concentration of nitrogen dioxide was doubled and the concentration of carbon monoxide was halved, while the temperature remained constant.

The rate constant, *k*, will

(1)

☒ **A** stay the same.

☒ **B** double.

☒ **C** triple.

☒ **D** quadruple.

(b) Which is a possible mechanism for the reaction that is consistent with the rate equation?

(1)

☒ **A** $2NO_2 + 2CO \rightarrow N_2 + O_2 + 2CO_2$ fast
$N_2 + O_2 \rightarrow 2NO$ slow

☒ **B** $2NO_2 + 2CO \rightarrow N_2 + O_2 + 2CO_2$ slow
$N_2 + O_2 \rightarrow 2NO$ fast

☒ **C** $2NO_2 \rightarrow 2NO + O_2$ fast
$2CO + O_2 \rightarrow 2CO_2$ slow

☒ **D** $2NO_2 \rightarrow 2NO + O_2$ slow
$2CO + O_2 \rightarrow 2CO_2$ fast

(Total for Question 3 = 2 marks)

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

4 The decomposition of a concentrated solution of hydrogen peroxide is slow at room temperature.

What does this indicate about the values for the activation energy and the rate constant for this decomposition?

	Activation energy	Rate constant
☒ **A**	high	high
☒ **B**	high	low
☒ **C**	low	high
☒ **D**	low	low

(Total for Question 4 = 1 mark)

5 Which process produces a **decrease** in the entropy of the system?

☒ **A** $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

☒ **B** $H_2O(s) \rightarrow H_2O(l)$

☒ **C** $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

☒ **D** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(Total for Question 5 = 1 mark)

6 Methane hydrate, $CH_4.6H_2O$, decomposes to form methane and water.

$$CH_4.6H_2O(s) \rightleftharpoons CH_4(g) + 6H_2O(l) \qquad \Delta H \text{ is positive}$$

Which conditions of temperature and pressure will give the highest equilibrium yield of methane?

	Temperature	Pressure
☒ **A**	high	high
☒ **B**	high	low
☒ **C**	low	high
☒ **D**	low	low

(Total for Question 6 = 1 mark)

7 Ethanoic acid, CH_3COOH, can react with methanoic acid, HCOOH.

pK_a of ethanoic acid = 4.8

pK_a of methanoic acid = 3.8

Which is a correct conjugate pair in the reaction between ethanoic acid and methanoic acid?

	Acid	Conjugate base
☒ **A**	HCOOH	$HCOO^-$
☒ **B**	HCOOH	$HCOOH_2^+$
☒ **C**	CH_3COOH	CH_3COO^-
☒ **D**	CH_3COOH	$CH_3COOH_2^+$

(Total for Question 7 = 1 mark)

8 What is the pH of water at 313 K?

$K_w = 2.92 \times 10^{-14}$ mol^2 dm^{-6} at 313 K

☒ **A** 6.8

☒ **B** 7.0

☒ **C** 7.2

☒ **D** 13.5

(Total for Question 8 = 1 mark)

9 What is the pH of 0.1 mol dm^{-3} propanoic acid at 298 K?

$K_a = 1.3 \times 10^{-5}$ mol dm^{-3} at 298 K

☒ **A** 2.4

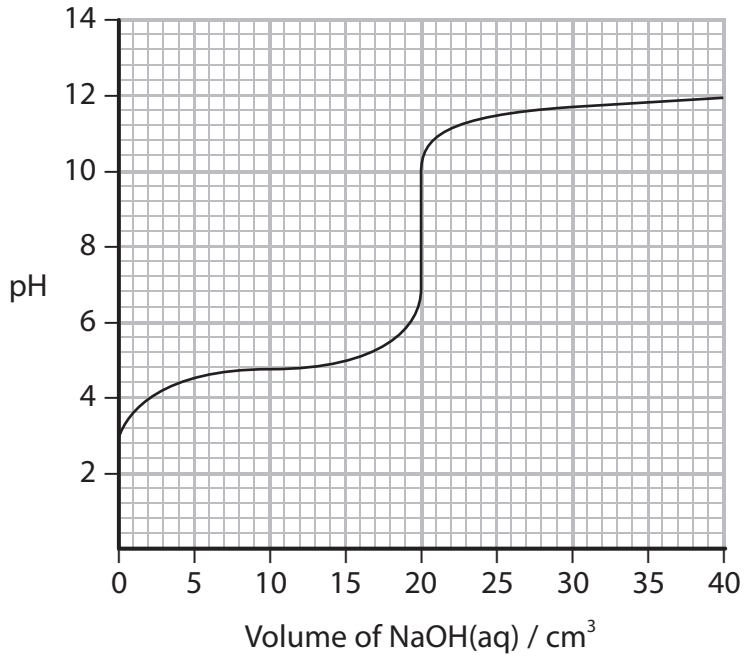
☒ **B** 2.9

☒ **C** 4.9

☒ **D** 5.9

(Total for Question 9 = 1 mark)

10 The titration curve shows the change in pH when 0.100 mol dm^{-3} sodium hydroxide solution is added to 25.0 cm^3 of a weak acid, HA.



(a) What is the pK_a value of the weak acid?

(1)

- ☒ **A** 2.9
- ☒ **B** 4.8
- ☒ **C** 7.0
- ☒ **D** 11.0

(b) What is the concentration, in mol dm^{-3}, of the weak acid?

(1)

- ☒ **A** 0.040
- ☒ **B** 0.080
- ☒ **C** 0.100
- ☒ **D** 0.125

(c) Which is the best indicator to use in a titration between the weak acid and the sodium hydroxide solution?

(1)

☒ **A** methyl orange ($pK_{in} = 3.7$)

☒ **B** methyl red ($pK_{in} = 5.1$)

☒ **C** bromothymol blue ($pK_{in} = 7.0$)

☒ **D** phenol red ($pK_{in} = 7.9$)

(d) The following volumes of 0.100 mol dm^{-3} sodium hydroxide solution were added to separate 25.0 cm^3 portions of the weak acid.

Which added volume, in cm^3, will result in the best buffer solution?

(1)

☒ **A** 2

☒ **B** 10

☒ **C** 20

☒ **D** 30

(Total for Question 10 = 4 marks)

11 Which compound has the highest boiling temperature?

☒ **A** CH_3CH_2CHO $M_r = 58$

☒ **B** CH_3COCH_3 $M_r = 58$

☒ **C** $CH_3CH_2CH_2OH$ $M_r = 60$

☒ **D** CH_3COOH $M_r = 60$

(Total for Question 11 = 1 mark)

12 Which compound reacts with iodine in an alkali to give a pale yellow precipitate with an antiseptic smell?

☒ **A** CH_3COCH_3

☒ **B** CH_3CH_2CHO

☒ **C** $CH_3CH_2COCH_2CH_3$

☒ **D** $CH_3CH_2CH_2CH_2CHO$

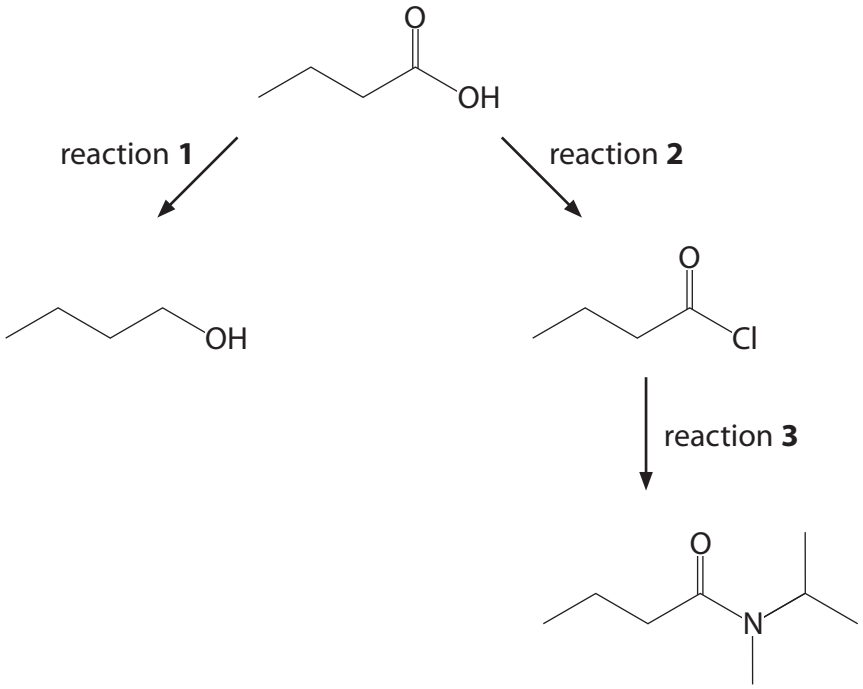
(Total for Question 12 = 1 mark)

13 The reaction that produces propanoic acid is

- ☒ **A** heating $CH_3CH_2CH_3$ with acidified potassium dichromate(VI).
- ☒ **B** heating CH_3COCH_3 with acidified potassium dichromate(VI).
- ☒ **C** refluxing CH_3CH_2CN with dilute hydrochloric acid.
- ☒ **D** refluxing $CH_3CH_2CH_2CN$ with dilute hydrochloric acid.

(Total for Question 13 = 1 mark)

14 Some reactions are shown in the scheme below.



(a) Which of these reagents is needed for reaction **1**?

(1)

- ☒ **A** Lithium tetrahydridoaluminate(III) in dry ether
- ☒ **B** Hydrogen with a nickel catalyst
- ☒ **C** Sodium in ethanol
- ☒ **D** Zinc in dilute acid

(b) Which reagent is needed in reaction **2**?

(1)

☒ **A** Aluminium chloride

☒ **B** Chlorine

☒ **C** Phosphorus(V) chloride

☒ **D** Sodium chloride

(c) Which reagent is needed in reaction **3**?

(1)

☒ **A** $CH_3CH_2CH_2CH_2NH_2$

☒ **B** $(CH_3)_2CHCH_2NH_2$

☒ **C** $CH_3NHCH(CH_3)_2$

☒ **D** $CH_3CH_2N(CH_3)_2$

(Total for Question 14 = 3 marks)

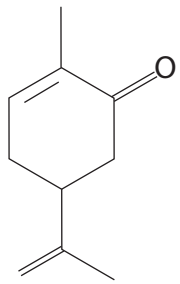
TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

15 This question is about carbonyl compounds.

(a) Carvone exists as two optical isomers.



(i) Label the chiral carbon atom with an asterisk (*).

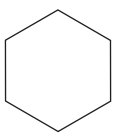
(1)

(ii) Give the molecular formula of carvone.

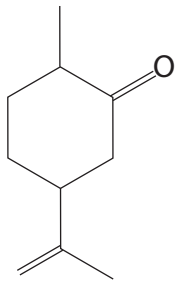
(1)

(iii) Complete the **skeletal** formula of the organic product formed when carvone reacts with excess bromine.

(2)



(b) Dihydrocarvone has the structure shown.



(i) State why dihydrocarvone does not exhibit geometric isomerism.

(1)

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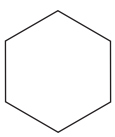
(ii) Complete the **skeletal** formula of the organic product formed when dihydrocarvone reacts with hydrogen cyanide in the presence of potassium cyanide.

(1)



(iii) State the number of different proton environments in a molecule of dihydrocarvone.

(1)

.....

(iv) Suggest one of the main absorbance ranges in the infrared spectrum of dihydrocarvone in the region 2500 to 1500 cm^{-1} and identify the bond responsible.

(1)

Bond .....

Range ..... cm^{-1}

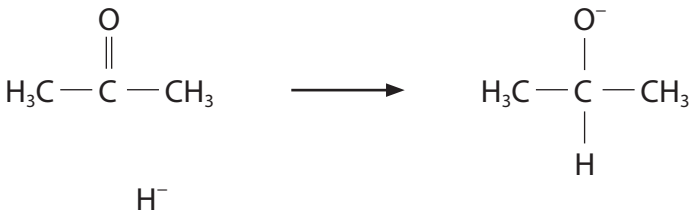
(c) Sodium tetrahydridoborate, $NaBH_4$, acts as a source of H^- ions and is a reducing agent.

Complete the mechanism for the reduction of propanone to propan-2-ol.

(i) In **Step 1**, add the relevant dipole, a lone pair of electrons and curly arrows.

(2)

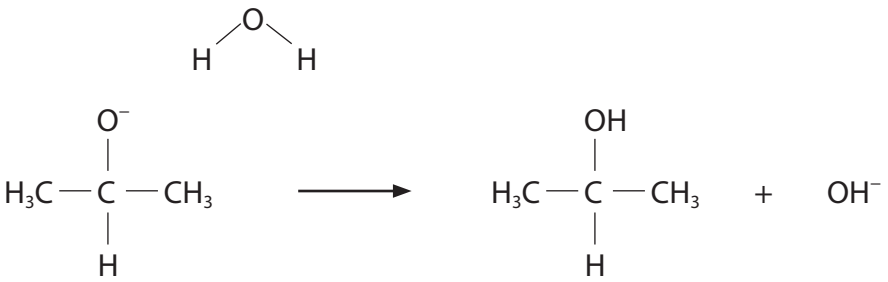
Step 1



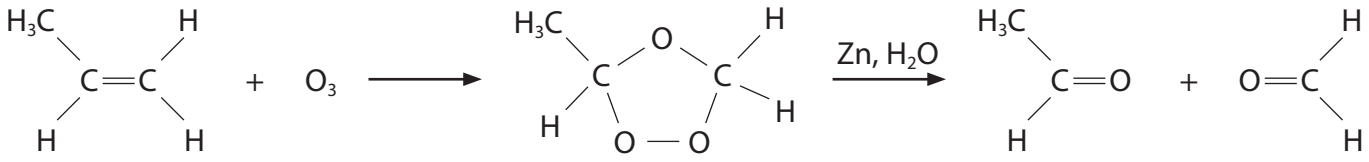
(ii) In **Step 2**, add a relevant lone pair of electrons and curly arrows.

(1)

Step 2



(d) When propene, C_3H_6, reacts with ozone, O_3, an ozonide is formed. The ozonide is then hydrolysed with water and zinc to form two carbonyl compounds.

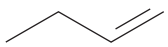


ozonide

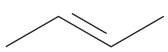
(i) Show how the reaction with ozone and subsequent hydrolysis can be used to distinguish between but-1-ene and but-2-ene, by giving the **structures** of the carbonyl products formed in each case.

(2)

But-1-ene



But-2-ene



(ii) Give the **structure** of an alkene that produces ethanal and butanone when it reacts with ozone, and the product is hydrolysed with water and zinc.

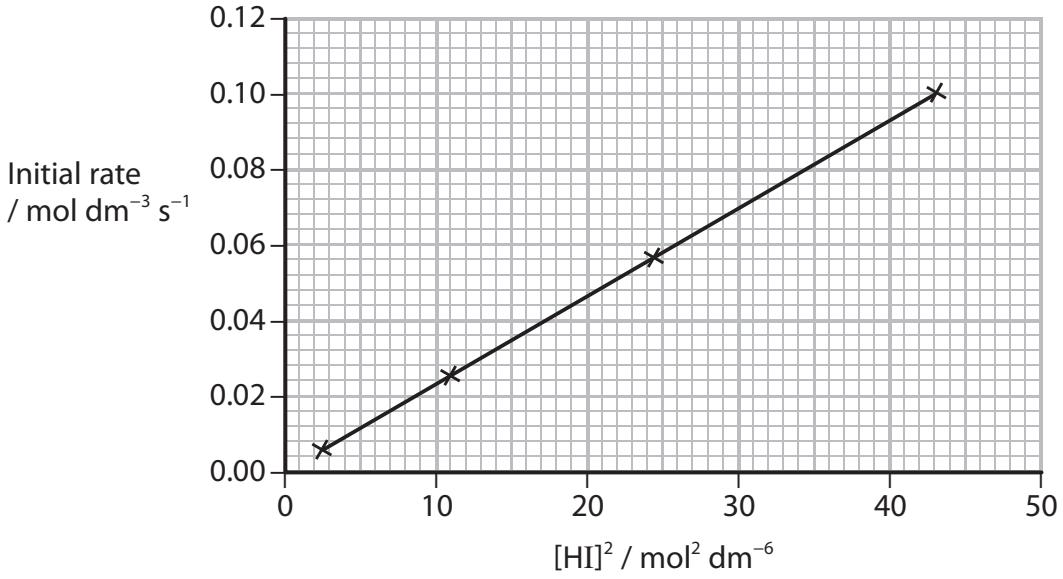
(1)

(Total for Question 15 = 14 marks)

16 Hydrogen iodide partially decomposes into hydrogen and iodine.

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

(a) A graph of the initial rate of reaction against the square of the initial concentration of hydrogen iodide is shown.



(i) Deduce the order of reaction with respect to hydrogen iodide.
Explain your reasoning.

(2)

.....

.....

.....

.....

(ii) Write the rate equation for the reaction.

(1)

(iii) In one of the experiments, the initial concentration of hydrogen iodide was 1.00 mol dm^{-3} and the initial rate of reaction was 0.00620 mol dm^{-3} s^{-1}.

Use the data to calculate the number of molecules decomposing in the first minute in 1.00 dm^3 of hydrogen iodide.
Assume that the rate of reaction remains constant for the first minute.

[Avogadro constant = 6.02×10^{23} mol^{-1}]

(2)

*(b) The activation energy for the forward reaction is 184 kJ mol^{-1}.

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

At 700 K, the rate constant is 2.32×10^{-3} dm^3 mol^{-1} s^{-1}.

Calculate the rate constant at 800 K and give your answer to **three** significant figures.

You should **not** attempt to use any graphical method to answer this question.

The Arrhenius equation is

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + A$$

[Gas constant, $R = 8.31$ J mol^{-1} K^{-1} and A is a constant]

(5)

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

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

(1)

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

(1)

.....

.....

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

DO NOT WRITE IN THIS AREA

(iii) In an experiment to determine K_c, 0.192 g of hydrogen iodide, in a 1 dm^3 vessel, was heated at 700 K until equilibrium was established.

0.00019 mol of iodine was present in the equilibrium mixture.

Calculate the value of K_c at 700 K.

(4)

*(iv) The enthalpy change for the forward reaction is +9.5 kJ mol^{-1}.

State and explain the effect of an increase in temperature on the entropy change of surroundings, $\Delta S_{surroundings}$, and hence on the value of K_c.

(3)

.....

.....

.....

.....

.....

.....

(Total for Question 16 = 19 marks)

17 Ethanol reacts with a carboxylic acid, **P**, to produce an ester, **Q**.

(a) Carboxylic acid **P** contains 58.8% carbon and 9.8% hydrogen by mass.
The mass spectrum of compound **P** has the molecular ion peak at $m/e = 102$.

Use **all** these data to confirm that the molecular formula of **P** is $C_5H_{10}O_2$.

(3)

(b) Draw the **displayed formulae** of the four possible structures of carboxylic acid **P**.

(2)

Carboxylic acid 1	Carboxylic acid 2
Carboxylic acid 3	Carboxylic acid 4

(c) The mass spectrum of carboxylic acid **P** has a major peak at $m/e = 43$.

Draw the structures of two species that could give this peak.

(2)

(d) Use your answers to (b) and (c) to identify which two of the carboxylic acids you have drawn in (b) could be carboxylic acid **P**.

(1)

(e) Draw the displayed formulae of the two possible ethyl esters that could be **Q**.

(2)

(f) Information from the high resolution proton nmr spectrum of ester **Q** is given.

Peak	Chemical shift, δ / ppm for TMS	Splitting pattern	Relative area below peak
A	0.96	doublet	6
B	1.26	triplet	3
C	2.10	split into 9	1
D	2.20	doublet	2
E	4.13	quartet	2

Use the data from the table to determine the **displayed** formula of ester **Q**.

Draw the formula below and on it label the protons responsible for the peaks A to E.

Explain the splitting pattern in peak B.

(5)

Displayed formula of **Q**

Explanation of splitting pattern in peak B

.....

.....

.....

.....

(Total for Question 17 = 15 marks)

TOTAL FOR SECTION B = 48 MARKS

SECTION C

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

18 This question is about solutions, enthalpy changes and entropy changes.

(a) (i) Draw a labelled Hess cycle and use it to calculate the enthalpy change of solution of barium chloride.

Show all of your working.

Hydration enthalpy of Ba^{2+}	–1360 kJ mol^{-1}
Hydration enthalpy of Cl^-	–364 kJ mol^{-1}
Lattice energy of $BaCl_2$	–2056 kJ mol^{-1}

(4)

(ii) Explain how you would expect the value of the enthalpy change of hydration of calcium ions to compare with that of barium ions.

(2)

(b) Barium sulfate, $BaSO_4$, dissolves to a very small extent in water and reaches equilibrium as shown in the equation.

$$BaSO_4(s) + aq \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The equilibrium constant for this reaction is

$$K_c = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$$

(i) Suggest why the concentration of solid barium sulfate, $[BaSO_4(s)]$, is not included in the expression for K_c.

(1)

(ii) The value for K_c is 1.00×10^{-10} mol^2 dm^{-6} at 298 K.

Calculate the maximum mass, in g, of barium sulfate that will dissolve in 50.0 cm^3 of water at 298 K.

(3)

(c) Hydrated barium hydroxide reacts with ammonium chloride as shown.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2(s) + 10H_2O(l)$$

(i) Use the Data Booklet to complete the table below.

(2)

	$Ba(OH)_2.8H_2O(s)$	$NH_4Cl(s)$	$NH_3(g)$	$BaCl_2(s)$	$H_2O(l)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−3345	−314.4	−46.1		
$S^{\ominus}$ / J mol^{-1} K^{-1}	427	94.6	192.3		

(ii) Use data from the table to calculate the standard enthalpy change, in kJ mol^{-1}, for this reaction.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2(s) + 10H_2O(l)$$

(2)

(iii) Use data from the table to calculate the standard entropy change of the system, in J mol^{-1} K^{-1}, for the same reaction.

$$Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow 2NH_3(g) + BaCl_2(s) + 10H_2O(l)$$

(2)

(iv) Use your answers to (c)(ii) and (c)(iii) to calculate ΔS_{total} for the reaction at 298 K.

(3)

*(v) It is possible that hydrated barium chloride, $BaCl_2.2H_2O$, forms instead of anhydrous barium chloride, $BaCl_2$, in this reaction.

Predict any effect on ΔS_{system} if hydrated barium chloride forms instead of anhydrous barium chloride.

Hence explain whether it is possible to predict the effect on the total entropy change of the reaction if hydrated barium chloride forms instead of anhydrous barium chloride.

(3)

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