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Surname	Other names
<b>Pearson</b> <b>Edexcel GCE</b>	Centre Number
	Candidate Number
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<h1 style="margin: 0;">Chemistry</h1> <p style="margin: 0;"><b>Advanced</b></p> <p style="margin: 0;"><b>Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)</b></p>	
Monday 9 June 2014 – Afternoon	Paper Reference
<b>Time: 1 hour 40 minutes</b>	<b>6CH04/01R</b>
<b>You must have: Data Booklet</b>	Total Marks
<b>Candidates may use a calculator.</b>	

## 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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## 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 .

If you change your mind, put a line through the box  and then mark your new answer with a cross .

1 Four organic compounds are:

- A  $\text{CH}_3\text{OH}$
- B  $\text{HCHO}$
- C  $\text{HCOOH}$
- D  $\text{HCOOCH}_3$

(a) Which of these compounds has a fruity smell?

(1)

- A
- B
- C
- D

(b) 0.01 mol of each compound is added separately to identical volumes of water. Which solution would have the lowest pH?

(1)

- A
- B
- C
- D

(c) 0.01 mol of each compound is heated separately with excess acidified sodium dichromate(VI) solution. Which compound reduces the largest amount of sodium dichromate(VI)?

(1)

- A
- B
- C
- D



(d) Which compound has the highest boiling temperature?

(1)

A

B

C

D

(e) Which of these compounds can be oxidized by ammoniacal silver nitrate?

(1)

A

B

C

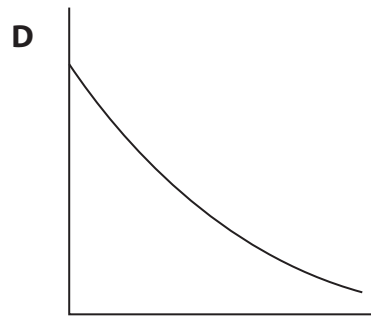
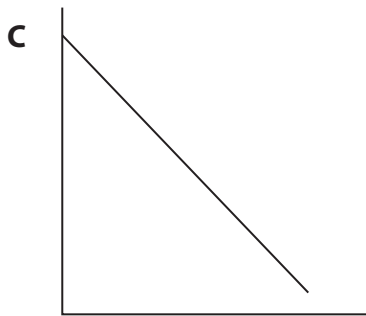
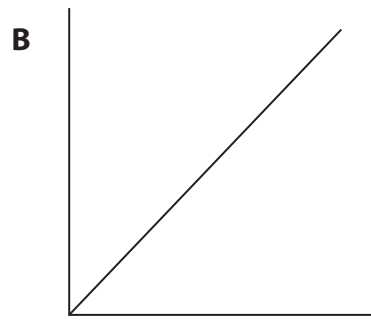
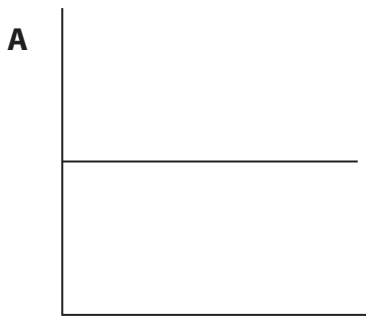
D

**(Total for Question 1 = 5 marks)**

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



2 Four sketch graphs are shown below.



(a) Which could be a graph of rate of reaction, on the vertical axis, against the concentration of a reactant for a zero order reaction?

(1)

- A
- B
- C
- D

(b) Which could be a graph of rate of reaction, on the vertical axis, against the square of the concentration of a reactant for a second order reaction?

(1)

- A
- B
- C
- D



(c) Which could be a graph of the concentration of a reactant, on the vertical axis, against time for a first order reaction?

(1)

- A
- B
- C
- D

(d) Which could be a graph of  $\ln(\text{rate})$ , on the vertical axis, against reciprocal of temperature,  $1/T$ , for a reaction?

You may use the equation  $\ln(\text{rate}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant}$

(1)

- A
- B
- C
- D

**(Total for Question 2 = 4 marks)**

**3** Which of the following mixtures would form the best buffer solution with pH 5 for use in a school laboratory?

- A Ethanoic acid and sodium ethanoate
- B Hydrochloric acid and sodium chloride
- C Sodium hydroxide and sodium methanoate
- D Ammonium chloride and ammonia

**(Total for Question 3 = 1 mark)**

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



4 Suggest the most likely pH for each of the following solutions.

(a) 5.0 mol dm<sup>-3</sup> hydrochloric acid.

(1)

- A +5
- B +0.7
- C -0.7
- D -5

(b) 0.20 mol dm<sup>-3</sup> strontium hydroxide, Sr(OH)<sub>2</sub>

$$K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

(1)

- A 13.3
- B 13.6
- C 14.0
- D 14.3

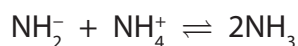
(c) A mixture of 20 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> nitric acid and 10 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> sodium hydroxide.

(1)

- A 0
- B 0.30
- C 0.48
- D 7

(Total for Question 4 = 3 marks)

5 In liquid ammonia the following equilibrium is present.



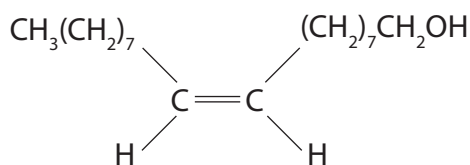
Identify the Brønsted-Lowry base(s).

- A NH<sub>2</sub><sup>-</sup> only
- B NH<sub>4</sub><sup>+</sup> only
- C NH<sub>2</sub><sup>-</sup> and NH<sub>3</sub>
- D NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub>

(Total for Question 5 = 1 mark)



- 6 The formula for oleyl alcohol, which is present in sperm whale oil and was used as a lubricant, is shown below.



- (a) The systematic name for oleyl alcohol is (1)

- A *E*-octadec-9-en-1-ol.  
 B *Z*-octadec-9-en-1-ol.  
 C *E*-octadec-8-en-1-ol.  
 D *Z*-octadec-8-en-1-ol.

- (b) Which intermolecular forces are present between oleyl alcohol molecules? (1)

- A London forces only  
 B Hydrogen bonds and London forces only  
 C Hydrogen bonds and permanent dipole–dipole forces only  
 D Hydrogen bonds, permanent dipole–dipole and London forces

- (c) Which of the following is the most likely structure of the species to cause a peak at  $m/e$  31 in the mass spectrum of oleyl alcohol? (1)

- A  $\text{CH}_3\text{O}$   
 B  $\text{CH}_2\text{OH}$   
 C  $\text{CH}_3\text{O}^+$   
 D  $\text{CH}_2\text{OH}^+$

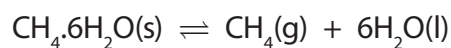
- (d) What would you expect to see if oleyl alcohol is tested separately with bromine water and heated with acidified sodium dichromate(VI) solution? (1)

	Bromine water	Acidified sodium dichromate(VI) solution
<input type="checkbox"/> A	Decolorises	Turns green
<input type="checkbox"/> B	No colour change	No colour change
<input type="checkbox"/> C	Decolorises	No colour change
<input type="checkbox"/> D	No colour change	Turns green

(Total for Question 6 = 4 marks)



- 7 Methane hydrate is found on continental shelves deep in oceans. It forms methane in an endothermic equilibrium reaction, which may be represented as



- (a) Which of the following changes would **decrease** the equilibrium yield of methane?

(1)

- A Decreasing the temperature and decreasing the pressure.
- B Increasing the temperature and decreasing the pressure.
- C Decreasing the temperature and increasing the pressure.
- D Increasing the temperature and increasing the pressure.

- (b) Which of the following would **increase** the value of the equilibrium constant,  $K_p$ , for the above equilibrium?

(1)

- A Decreasing the pressure
- B Increasing the pressure
- C Decreasing the temperature
- D Increasing the temperature

(Total for Question 7 = 2 marks)

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**TOTAL FOR SECTION A = 20 MARKS**





## SECTION B

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

8 This question is about calcium chloride,  $\text{CaCl}_2$ .

It can be formed by burning calcium in chlorine.



You must include a sign and units in your answers to the calculations in this question.

(a) (i) The standard molar entropy at 298 K for 1 mole of chlorine molecules,  $\text{Cl}_2$ , is  $+165 \text{ J mol}^{-1} \text{ K}^{-1}$ . Use this, and appropriate values from your Data Booklet, to calculate the standard entropy change,  $\Delta S_{\text{system}}^{\ominus}$ , for this reaction.

(2)

\*(ii) Explain fully why the sign for the standard entropy change of the system,  $\Delta S_{\text{system}}^{\ominus}$ , is as you would expect.

(2)

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.....

(b) Calculate the total entropy change,  $\Delta S_{\text{total}}^{\ominus}$ , in  $\text{J mol}^{-1} \text{ K}^{-1}$ , for this reaction, giving your answer to three significant figures.

(2)



(c) Use the standard entropy change of the surroundings,  $\Delta S_{\text{surroundings}}^{\ominus}$ , to calculate the standard enthalpy change,  $\Delta H^{\ominus}$ , in  $\text{kJ mol}^{-1}$ , for the reaction at 298 K.

(2)

(d) 0.0500 mol of calcium chloride, prepared by burning calcium in chlorine, is added to  $51.8 \text{ cm}^3$  of water.

$50.0 \text{ cm}^3$  of a  $1.00 \text{ mol dm}^{-3}$  solution is formed, and the temperature rise,  $\Delta T$ , is  $15.0^{\circ}\text{C}$ .

(i) Calculate the energy transferred, in joules, for this process using:

Energy transferred in joules = volume of **solution formed**  $\times 4.2 \times \Delta T$

(1)

(ii) Calculate the enthalpy change of solution,  $\Delta H_{\text{solution}}^{\ominus}$ , of calcium chloride in  $\text{kJ mol}^{-1}$ .

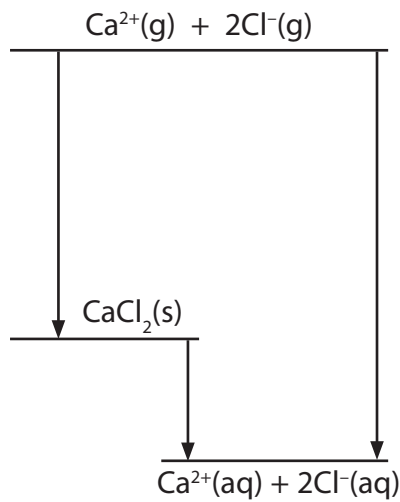
(2)



\*(iii) The enthalpy change of hydration of  $\text{Ca}^{2+}(\text{g})$  is  $-1560 \text{ kJ mol}^{-1}$ .

Use this, your value from (d)(ii) and the experimental lattice energy from your Data Booklet, to calculate the standard enthalpy change of hydration of  $\text{Cl}^{-}(\text{g})$ .

(3)



Answer .....  $\text{kJ mol}^{-1}$

(iv) Draw diagrams to represent hydrated calcium ions and hydrated chloride ions.

(2)

(v) Suggest why the addition of anhydrous calcium chloride to water results in an increase in temperature and a decrease in volume.

(2)

Temperature increases .....

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Volume decreases .....

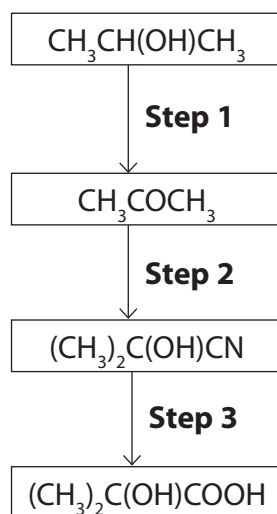
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**(Total for Question 8 = 18 marks)**



- 9 A flow chart for making 2-hydroxy-2-methylpropanoic acid from propan-2-ol is shown below.



- (a) (i) Give the reagents and conditions for **Step 1**.

(2)

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- (ii) Propanone is formed in **Step 1**.

Give a chemical test to identify the carbonyl group and a further test to show

the presence of the  $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$  group.

For both tests, give the observations that you would make.

(4)

Carbonyl group.....

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.....

$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-$  group.....

.....

.....

.....



- (b) (i) In **Step 2**, propanone undergoes an addition reaction with HCN in the presence of  $\text{CN}^-$  ions.

Give the mechanism for this reaction.

(3)

- (ii) Explain why this reaction would not take place at either a very low or very high pH.

(2)

Low pH.....

.....

High pH.....

.....

- (c) (i) The reaction in **Step 3** forms 2-hydroxy-2-methylpropanoic acid,  $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$ . Suggest the type of reaction occurring in **Step 3**.

(1)

.....



(ii) Explain why the presence of the alcoholic hydroxyl group cannot be confirmed in the infrared spectrum of 2-hydroxy-2-methylpropanoic acid. (1)

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.....

(iii) The hydrogen of the alcohol group in 2-hydroxy-2-methylpropanoic acid can be identified by a single peak in the nmr spectrum.  
Give the chemical shift you would expect for this peak. (1)

.....

(iv) How many peaks would you expect in a high resolution nmr spectrum for 2-hydroxy-2-methylpropanoic acid,  $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$ ? (1)

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(v) Explain why, in high resolution nmr, the peak due to the hydrogens of the 2-methyl group in 2-hydroxy-2-methylpropanoic acid is a singlet. (1)

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(vi) Would you expect 2-hydroxy-2-methylpropanoic acid to have optical isomers? Justify your answer. (1)

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- (d) (i) Molecules of 2-hydroxy-2-methylpropanoic acid react together to form a condensation polymer.

Draw a **displayed** formula for this polymer, showing two repeating units.

(2)

- (ii) Give the name of the functional group that links the two molecules in the polymer.

(1)

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(Total for Question 9 = 20 marks)

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**10** Persulfate ions,  $S_2O_8^{2-}$ , oxidize iodide ions in aqueous solution to form iodine and sulfate ions,  $SO_4^{2-}$ .

(a) Write the ionic equation for this reaction. State symbols are not required.

(1)

(b) The effect of iodide ion concentration on the rate of this reaction was measured.

A few drops of starch solution and a small measured volume of sodium thiosulfate solution were added to a known volume of potassium persulfate solution.

Potassium iodide solution was then added and the time taken for the mixture to change colour was measured.

The reaction was repeated using different concentrations of potassium iodide, but the same volumes and concentrations of sodium thiosulfate solution and potassium persulfate solution.

The rates of the reaction were compared using the reciprocal of the time (1/time) for the mixture to change colour as a measure of the initial rate.

(i) What is the final colour of the reaction mixture?

(1)

(ii) What would be observed if the reaction was carried out without the addition of sodium thiosulfate?

(1)

(iii) Explain why the concentration of iodide ions remains constant until the mixture changes colour.

(1)



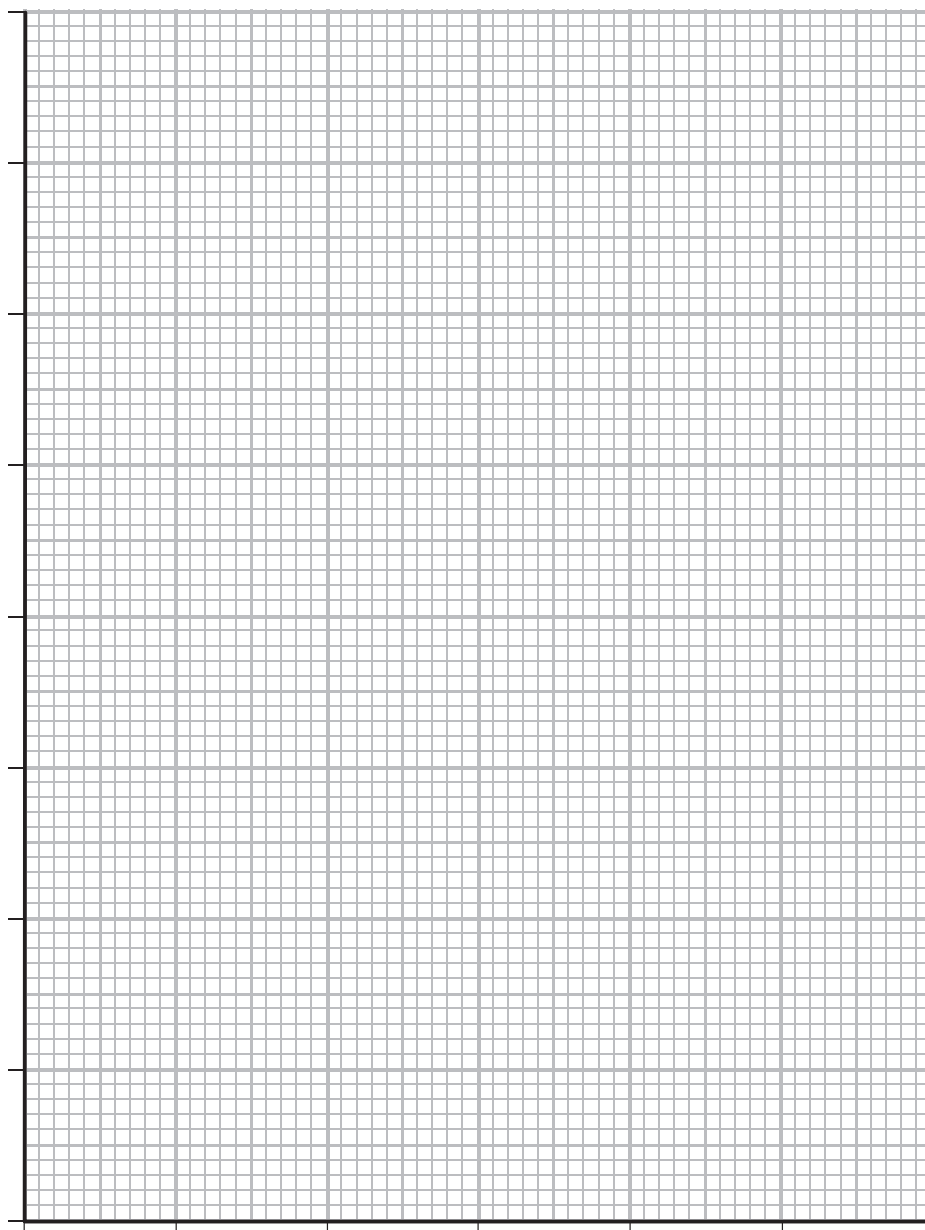


(c) The results obtained were tabulated as follows.

$[I^-]$ /mol dm <sup>-3</sup>	Time /s	1/time /s <sup>-1</sup>
0.0100	40.0	0.0250
0.0075	53.3	0.0188
0.0050	80.0	0.0125
0.0040	100.0	0.0100

(i) Plot a graph of 1/time on the vertical axis against concentration of iodide ions.

(2)



(ii)  $1/\text{time}$  is a measure of the initial rate of the reaction.

Deduce the order of reaction with respect to iodide ions.

Justify your answer.

(2)

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(iii) The reaction is first order with respect to persulfate ions. Write the overall rate equation for the reaction and deduce the units for the rate constant.

(2)

Rate =

Units for the rate constant.....



(d) The reaction in part (b) is repeated at two different temperatures, keeping the initial volumes and concentrations of the solutions constant.

T (Temperature) /K	1/time /s <sup>-1</sup>	1/T /K <sup>-1</sup>	ln(1/time)
293	0.0215	3.31 × 10 <sup>-3</sup>	-3.84
303	0.0430	3.20 × 10 <sup>-3</sup>	-3.15

(i) Calculate, without drawing a graph, the activation energy of the reaction. Remember to give a sign and units with your answer.

$$\ln(1/\text{time}) = -\frac{E_a}{R} \times \frac{1}{T} + \text{constant} \quad [R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}] \quad (3)$$

(ii) Suggest how the reliability of the activation energy determination could be improved, without changing the apparatus, solutions or method. (1)

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**(Total for Question 10 = 14 marks)**

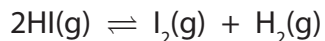
**TOTAL FOR SECTION B = 52 MARKS**



### SECTION C

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

- 11** The decomposition of hydrogen iodide to form iodine and hydrogen is an equilibrium reaction.



The equilibrium was investigated by taking sealed tubes containing the same mass of hydrogen iodide and heating them at 700 K for some time. At this temperature, the equilibrium takes about two days to be established.

The tubes were rapidly cooled to room temperature, which maintained the equilibrium concentrations, because at this temperature the reaction is extremely slow.

Each tube was opened under an aqueous solution of potassium iodide, which dissolved the hydrogen iodide and the iodine. The amount of iodine was found by titration and the composition of the equilibrium mixture calculated. From the number of moles of each substance at equilibrium, and the volume of the tubes, the equilibrium concentrations were calculated.

- (a) (i) How would the appearance of the contents of a tube change as it was cooled to room temperature?

(2)

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- (ii) How could you show that equilibrium had been established?

(2)

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(b) The equilibrium concentrations of one experiment are shown in the table below.

[HI] /mol dm <sup>-3</sup>	[H <sub>2</sub> ] /mol dm <sup>-3</sup>	[I <sub>2</sub> ] /mol dm <sup>-3</sup>
0.00353	0.00048	0.00048

\*(i) The volume of the tube in this experiment was 30 cm<sup>3</sup>. Calculate the initial mass of hydrogen iodide. Show your working.

(5)

(ii) Write an expression for the equilibrium constant,  $K_c$ , at 700 K.

(1)

(iii) Calculate the value for this equilibrium constant.

(1)



(iv) Does this equilibrium constant have units? Explain your answer.

(1)

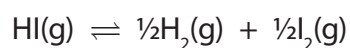
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(c) The equation for the reaction at 700 K can also be written



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

(1)

(ii) Using the same equilibrium concentrations as below, calculate the equilibrium constant,  $K_c'$ .

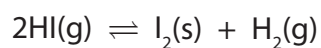
Deduce the relationship between this value and the value calculated in part (b)(iii).

(2)

[HI] /mol dm <sup>-3</sup>	[H <sub>2</sub> ] /mol dm <sup>-3</sup>	[I <sub>2</sub> ] /mol dm <sup>-3</sup>
0.00353	0.00048	0.00048



(d) Consider the following equilibrium reaction.



For this reaction  $K_p = \frac{P_{\text{H}_2}}{P_{\text{HI}}^2}$

Use the expression for  $K_p$  to explain the effect of an increase in total pressure on the position of the equilibrium.

(3)

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**(Total for Question 11 = 18 marks)**

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



