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

1	Which of the following methods would not be suitable for measuring the rate of the
	reaction between methanoic acid and bromine?

$$HCOOH(aq) + Br_2(aq) \rightarrow 2H^+(aq) + 2Br^-(aq) + CO_2(g)$$

- A Colorimetry
- **B** Measuring change in electrical conductivity
- C Quenching samples and titrating with acid
- **D** Measuring change in pressure

(Total for Question 1 = 1 mark)

2 The equation below shows the hydrolysis of a bromoalkane.

$$RBr + OH^{-} \rightarrow ROH + Br^{-}$$

For a particular bromoalkane, the rate equation is

rate =
$$k[RBr]$$

The bromoalkane, RBr, is most likely to be

- \triangle A CH₃Br
- B CH₃CH₂Br
- \square C (CH₃)₃CCH₂Br
- \square **D** (CH₃)₃CBr

(Total for Question 2 = 1 mark)

- 3 A decrease in the entropy of the system, ΔS_{system} , occurs when
 - **A** water freezes.
 - **B** water boils.
 - C water reacts with sodium.
 - **D** water reacts with ethanoyl chloride.

(Total for Question 3 = 1 mark)

4	Methanol	is	produced	in	the o	equilibrium	reaction
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$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$
 $\Delta H = -18.3 \text{ kJ mol}^{-1}$

Addition of more hydrogen to the equilibrium mixture at constant temperature

- ☐ A increases the equilibrium yield of methanol.
- **B** decreases the equilibrium yield of methanol.
- \square **C** increases the value of K_p .
- \square **D** decreases the value of K_p .

(Total for Question 4 = 1 mark)

The equation for the equilibrium between $NO_2(g)$ and $N_2O_4(g)$ can be written in two ways.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
 Equilibrium constant = K_c

or

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2O_4(g)$$
 Equilibrium constant = K'_c

Which expression is correct?

$$\boxtimes$$
 A $K_c = K'_c$

B
$$K_c = (K'_c)^2$$

$$\square$$
 C $K_c = 2(K'_c)$

D
$$K_{\rm c} = \frac{1}{2}K'_{\rm c}$$

(Total for Question 5 = 1 mark)

6 4.0 mol of methanoic acid are reacted with 6.0 mol of ethanol.

$$HCOOH(l) + C_2H_5OH(l) \rightleftharpoons HCOOC_2H_5(l) + H_2O(l)$$

The equilibrium mixture contains 3.0 mol of HCOOC₂H₅.

The equilibrium constant, K_c , for the reaction is

■ A 0.33

■ B 1.0

◯ C 3.0

■ D 4.0

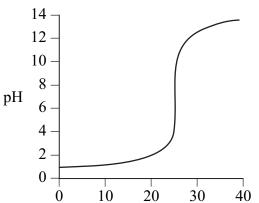
(Total for Question 6 = 1 mark)

- 7 A solution of hydrochloric acid has pH 3.0. When it is made 10 times more dilute, the pH is
 - \triangle A 0.3
 - **■ B** 2.0
 - **□ C** 4.0
 - **D** 13.0

(Total for Question 7 = 1 mark)

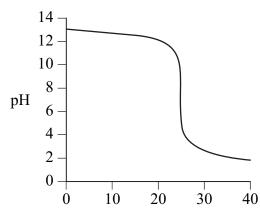
8 The titration curves below were obtained using different acids and bases, each with concentration 0.1 mol dm⁻³.

A



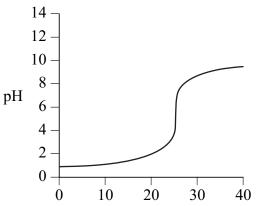
Volume 0.1 mol dm⁻³ solution added / cm³

В



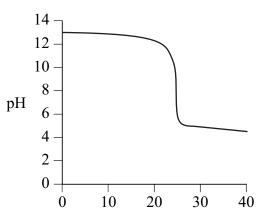
Volume 0.1 mol dm⁻³ solution added / cm³

 \mathbf{C}



Volume 0.1 mol dm⁻³ solution added / cm³

D



Volume $0.1 \text{ mol dm}^{-3} \text{ solution added } / \text{ cm}^3$

	(Total for Question 9 = 1 m	ark)
■ D	ethanol refluxed with potassium dichromate(VI) and sulfuric acid.	
区 C	ethyl ethanoate with dilute sulfuric acid.	
⋈ B	ethanoyl chloride with water.	
\mathbf{X} A	ethanal with lithium tetrahydridoaluminate.	
Ethano	ic acid is not a product in the reaction of	
	(Total for Question 8 = 3 ma	rks)
■ D	Titrations A, B, C and D.	
■ C	Titration C only.	
\square B	Titrations A , B and D only.	
$\boxtimes \mathbf{A}$	Titrations A and B only.	(1)
(c) An	indicator with p K_{In} 8.5 is suitable for the following titrations.	(4)
■ D		
■ B		
\mathbf{X} A		(1)
(b) Wh	ich curve is produced by adding ethanoic acid to 25 cm³ of sodium hydroxide?	(1)
⋈ D		
B		
\mathbf{X} A		(-)
		(1)
	 B C D D (b) Wh A B C D A B C D D Ethano A B C Ethano A B C C C C 	 B C D (b) Which curve is produced by adding ethanoic acid to 25 cm³ of sodium hydroxide? A B C D (c) An indicator with pK_{In} 8.5 is suitable for the following titrations. A Titrations A and B only. B Titrations A, B and D only. C Titration C only. D Titrations A, B, C and D. (Total for Question 8 = 3 ma Ethanoic acid is not a product in the reaction of A ethanal with lithium tetrahydridoaluminate. B ethanoyl chloride with water. C ethyl ethanoate with dilute sulfuric acid.

(1)
(1)
(1)
ks)

16 Nitrogen(IV) oxide, NO₂, is a brown gas which is a pollutant in air. It is produced in the reaction below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) The table below shows the results of a series of experiments to measure the rate of this reaction at 298 K.

Experiment	Initial concentra	Initial rate	
number	$[O_2(g)]$	[NO(g)]	$/ \text{ mol dm}^{-3} \text{ s}^{-1}$
1	0.0050	0.0125	5.10×10^{-4}
2	0.0100	0.0125	10.2×10^{-4}
3	0.0100	0.0250	40.8×10^{-4}

reaction with respect to nitrogen(II) oxide, NO.	(2)

(i) State, with reasons, the order of reaction with respect to oxygen and the order of

(ii) Write	the rate equation for the reaction.		(1)
(iii) Calcı	ulate the value of the rate constant. Include	e units in your answer.	(2)
	IV) oxide in air reacts with carbon monoxitwo-step reaction mechanism has been sug		
Step 1:	$2NO_2(g) \rightarrow NO(g) + NO_3(g)$	Slow	
Step 2:	$NO_3(g) + 2CO(g) \rightarrow NO(g) + 2CO_2(g)$	Fast	
(i) Write	the equation for the overall reaction whic	h takes place.	(1)
	overall reaction is second order. Suggest a sying your answer.	rate equation for this reaction,	(2)
		(Total for Question 16 = 8 ma	rks)

17	7 Ammonia is manufactured using the reaction				
		$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$			
	(a) (i)	Calculate $\Delta S_{\text{system}}^{\oplus}$ for this reaction at 298 K. Give your answer in J mol ⁻¹ K ⁻¹ and include a sign. You will need to refer to your data booklet.			
		[Note that the standard molar entropy values for gaseous diatomic elements are given for half a mole of molecules, and not per mole of molecules eg entropy for 1 mol of N_2 is $2\times 95.8~J~mol^{-1}~K^{-1}$.]	(2)		
	(ii)	Using ideas about disorder, explain whether the sign of your answer to (a)(i) is as expected.	(2)		
••••	(b) At 7	700 K, the enthalpy change for this reaction, $\Delta H = -110.2 \text{ kJ mol}^{-1}$.			
	(i)	Calculate the entropy change of the surroundings, $\Delta S_{\rm surroundings}$, at 700 K. Include a sign and units in your answer.	(2)		

	(ii)	Calculate ΔS_{system} for this reaction at 700 K. At this temperature the total entropy change, $\Delta S_{\text{total}} = -78.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Include a sign and units in your answer.	(1)
	(iii)	What does the value of ΔS_{total} , which is $-78.7 \text{ J K}^{-1} \text{ mol}^{-1}$ at 700 K, indicate about the relative proportions of nitrogen, hydrogen and ammonia at equilibrium?	(1)
(c)	A m	nixture of nitrogen, hydrogen and ammonia is at equilibrium at 150 atm. The	
(0)	part	ial pressures of nitrogen and ammonia in the mixture are 21 atm and atm respectively.	
	(i)	Write an expression for the equilibrium constant, K_p , for the formation of ammonia, in terms of partial pressures for this reaction, and calculate its value at 700 K. Include units in your answer.	t (4)

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) In the manufacture of ammonia, pressures of between 100 and 250 atm are used. State and explain one advantage, in terms of the yield of ammonia, of using a pressure above 100 atm.		
		(1)	
*(iii)	In the manufacture of ammonia, a temperature of about 700 K is used.		
	For this exothermic reaction how does $\Delta S_{\text{surroundings}}$ change as temperature increases?		
	Explain how this change affects the value of ΔS_{total} and the equilibrium constant as temperature increases.		
	Hence explain the disadvantage of using a temperature higher than 700 K.	(4)	
(iv)	Suggest one advantage of using a temperature higher than 700 K.		
		(1)	

18 Methanoic acid, ethanoic acid and iodic(I) acid, HIO, are all	ıll weak acids.
-------------------------------------------------------------------------	-----------------

(a) The values of the acid dissociation constant, K_a , for methanoic and ethanoic acid at 298 K are given below. Iodic(I) acid has a p K_a of 10.64. Complete the table by calculating the value of K_a for iodic(I) acid.

(1)

Acid	$K_{\rm a}$ / mol dm ⁻³
methanoic acid	1.6×10^{-4}
ethanoic acid	1.7×10^{-5}
iodic(I) acid	

(b) (i) Write the expression for K_a for methanoic acid, HCOOH.

(1)

(ii) Calculate the pH of a solution of methanoic acid with concentration 0.50 mol dm⁻³ at 298 K.

(3)

(iii) State one of the assumptions you have made when calculating the pH in (ii).

(1)

(c) The following equilibrium occurs in a mixture of pure methanoic and ethanoic acids	
$HCOOH + CH_3COOH \rightleftharpoons HCOO^- + CH_3COOH_2^+$	
(i) Give the formulae of the two Brønsted-Lowry acids in this equilibrium.	(1)
 (ii) Write an equation showing the products of the equilibrium which is set up when iodic(I) acid is mixed with ethanoic acid. HIO + CH₃COOH ⇒ +	(1)
(d) A shampoo is buffered by the addition of a mixture of methanoic acid and sodium methanoate.The pH of this shampoo is 4.9. Calculate the hydrogen ion concentration in the shampoo, and hence the ratio of methanoate ions to methanoic acid.	(2)
(Total for Question 18 = 10 ma	rks)
TOTAL FOR SECTION B = 50 MAR	RKS

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 ⋈.

- 19 Methods for investigating reaction rates include
 - A colorimetry.
 - **B** measurement of change in volume.
 - C measurement of change of mass.
 - **D** quenching followed by titrating with acid.

Which method would be most suitable to investigate the rate of the following reactions?

(a) $HCOOCH_3(aq) + NaOH(aq) \rightarrow HCOONa(aq) + CH_3OH(aq)$

(1)

- \mathbf{A}
- \square B
- \square C
- \triangleright D
- (b) $(CH_3)_2C = CH_2(g) + HI(g) \rightarrow (CH_3)_3CI(g)$

(1)

- \mathbf{X} A
- \mathbb{Z} B
- \boxtimes C
- \times **D**
- (c) $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

(1)

- \mathbf{X} A
- \mathbf{B}
- \mathbf{K} C
- \bowtie D

(Total for Question = 3 marks)

20

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

This reaction is first order with respect to hydrogen and second order with respect to nitrogen(II) oxide.

By what factor will the initial rate increase if the concentration of hydrogen and nitrogen(II) oxide are both tripled?

- \triangle A 3
- **⋈ B** 9
- **◯** C 12
- **D** 27

(Total for Question = 1 mark)

- 21 Which reaction has the most positive entropy change for the system, ΔS_{system} ?
 - \square **A** NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H₂O(l)
 - \square **B** AgNO₃(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO₃(aq)
 - \square C $C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(l)$
 - \square **D** $C_4H_{10}(g) \rightarrow C_2H_4(g) + C_2H_6(g)$

(Total for Question = 1 mark)

22 Barium carbonate decomposes in an endothermic reaction when heated to 1500 K.

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$$

What are the signs of the entropy changes at 1500 K?

		$\Delta S_{ m system}$	$\Delta S_{ m surroundings}$
×	A	+	+
×	В	+	_
×	C	_	+
×	D	_	_

(Total for Question = 1 mark)

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

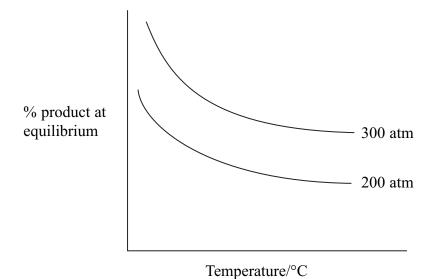
23 What are the units of K_c for the following equilibrium?

$$2SO_2(g) + O_2(g) \implies 2SO_3(g)$$

- \mathbf{X} A atm
- \blacksquare **B** atm⁻¹
- \square **C** dm³ mol⁻¹
- \square **D** mol dm⁻³

(Total for Question = 1 mark)

24 The graph below shows the yield of product in a gaseous equilibrium at different temperatures and pressures.



The forward reaction in the equilibrium is

- \square **A** exothermic, and the number of moles of gas is increasing.
- \square B endothermic, and the number of moles of gas is increasing.
- \square C exothermic, and the number of moles of gas is decreasing.
- **D** endothermic, and the number of moles of gas is decreasing.

(Total for Question = 1 mark)

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

- 25 Which of the following is **not** a reaction of a Brønsted-Lowry acid and base?
 - \square A CH₃Cl + OH⁻ \rightarrow CH₃OH + Cl⁻
 - \square **B** NH₃ + HCl \rightarrow NH₄⁺ + Cl⁻
 - \square C $H_2O + HSO_4^- \rightarrow H_2SO_4 + OH^-$
 - \square **D** $HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

(Total for Question = 1 mark)

- **26** A buffer solution is made from ammonia and ammonium chloride. When a small amount of acid is added to this buffer
 - ☑ A hydrogen ions in the acid combine with chloride ions to make HCl.
 - \square **B** hydrogen ions in the acid combine with NH₃ to make NH₄⁺.
 - C NH₄⁺ ions dissociate to make more NH₃.
 - \square **D** the hydrogen ions in the acid prevent dissociation of the NH₄Cl.

(Total for Question = 1 mark)

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

- 27 Information about four samples of acid is shown below.
 - Sample 1: 1.0 mol dm⁻³ HCl
 - Sample 2: $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$
 - Sample 3: 0.1 mol dm⁻³ HCl
 - Sample 4: 0.1 mol dm⁻³ CH₃COOH

Which of the following lists shows the samples in order of increasing pH?

- \triangle **A** 1, 2, 3, 4
- \square **B** 4, 3, 2, 1
- \square **C** 2, 1, 3, 4
- \square **D** 4, 3, 1, 2

(Total for Question = 1 mark)28

- 28 Which reaction has an enthalpy change equal to the enthalpy of hydration of the sodium ion?
 - \square A Na⁺(g) + excess H₂O(l) \rightarrow Na⁺(aq)
 - \square **B** Na⁺(g) + 1 mol of H₂O(l) \rightarrow Na⁺(aq)
 - \square C Na⁺(s) + excess H₂O(l) \rightarrow Na⁺(aq)
 - \square **D** Na⁺(s) + 1 mol of H₂O(l) \rightarrow Na⁺(aq)

(Total for Question = 1 mark)

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

29 Hydrogen can be manufactured by reacting methane with steam, as shown in the equation below.

$$CH_4(g) + H_2O(g) \implies CO(g) + 3H_2(g)$$
 $\Delta H_{298}^{\oplus} = +206.1 \text{ kJ mol}^{-1}$

Use these values:

the standard entropy of 1 mol of $H_2(g)$ is $(2 \times 65.3) = 130.6 \text{ J mol}^{-1} \text{ K}^{-1}$ the standard entropy of 1 mol of $H_2O(g)$ is 188.7 J mol⁻¹ K⁻¹

You will also need to refer to the data booklet in the calculations which follow.

(a) Calculate the standard entropy change of the system, $\Delta S_{\text{system}}^{\ominus}$, for this reaction at 298 K.

(2)

(b) Calculate the standard entropy change of the surroundings, $\Delta S_{\text{surroundings}}^{\ominus}$, for this reaction at 298 K. Include a sign and units in your answer.

(2)

(c) Calculate the total entropy change, $\Delta S_{\text{total}}^{\oplus}$, for this reaction at 298 K.

Explain why this value shows that the reaction is not spontaneous at this temperature.

(2)

(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

$$CH_4(g) + H_2O(g) \implies CO(g) + 3H_2(g)$$

Amount in equilibrium 0.80 0.80 1.20 3.60 mixture / mol

*(i) Write the expression for the equilibrium constant, K_p , of the reaction and calculate its value. Include units in your answer.

(6)

(ii) The total entropy change in $J \text{ mol}^{-1} \text{ } K^{-1}$ is related to the equilibrium constant by the equation

$$\Delta S_{\text{total}}^{\oplus} = R \ln K_{\text{p}}$$
 or $\Delta S_{\text{total}}^{\oplus} = 2.3R \log K_{\text{p}}$

Calculate the total entropy change at the temperature of the reaction.

$$[R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}]$$

(1)

(iii) Calculate the temperature at which this equilibrium is reached using your answer to (ii) for $\Delta S_{\text{total}}^{\ominus}$. Assume that ΔH is still +206.1 kJ mol ⁻¹ and that $\Delta S_{\text{system}}^{\ominus} = +225 \text{ J K}^{-1} \text{ mol}^{-1}$. (This is not the same as the value for $\Delta S_{\text{system}}^{\ominus}$ calculated in (a) which is at 298 K.)	
calculated in (a) winch is at 270 K.)	(2)
*(e) Use the magnitude and signs of the entropy changes to explain the effect of a	
temperature increase on the equilibrium constant of this endothermic reaction.	(2)
	(-)
(Total for Question = 17 mar	·ks)

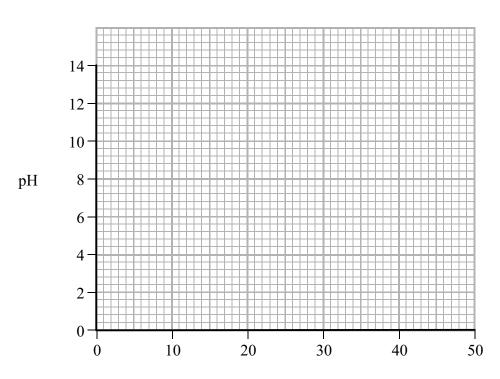
30 (a) Calculate the pH of 0.25 mol dm ⁻³ hydrochloric acid. (1)
(b) Propanoic acid, CH ₃ CH ₂ COOH, is a weak acid with $K_a = 1.3 \times 10^{-5}$ mol dm ⁻³ at 25 °C.	
(i) Write the expression for K_a for propanoic acid. (1))
(ii) Calculate the pH of 0.25 mol dm ⁻³ propanoic acid at 25°C. (2	
(c) During a titration, 10 cm ³ 0.10 mol dm ⁻³ sodium hydroxide was added to 10 cm ³ of 0.25 mol dm ⁻³ propanoic acid.	
(i) Write an equation for the reaction which occurs. State symbols are not required. (1)
(ii) At this point the titration mixture contains 1.5×10^{-3} moles of propanoic acid and 1.0×10^{-3} moles of propanoate ion.	
Use your expression for K_a for propanoic acid to calculate the pH of the mixture. (2)

*(iii) When a further small amount of 0.10 mol dm⁻³ sodium hydroxide is added in the titration, the pH changes very little. Explain why the pH change is small.

(3)

(iv) Draw the titration curve showing the change in pH when 0.10 mol dm⁻³ sodium hydroxide is added to 10 cm³ of 0.25 mol dm⁻³ propanoic acid until present in excess. The equivalence point is 25 cm³.

(3)



Volume of sodium hydroxide solution/cm³

(v) Explain, referring to your data booklet, whether bromocresol green would be a suitable indicator for this titration.	a (2)
(d) Propanoic acid is produced in the reactions shown below.	
CH ₃ CH ₂ CN Reaction 1	
CH ₃ CH ₂ COCl Reaction 2 CH ₃ CH ₂ COOH	
CH ₃ CH ₂ CHO Reaction 3	
(i) Suggest a reagent which could be used to carry out reaction 1 .	(1)
(ii) Write an equation for reaction 2 . State symbols are not required.	(1)
(iii) What would be observed if reaction 3 was carried out using potassium dichromate(VI) and sulfuric acid?	
	(1)

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Identify a suitable reagent for this re	eaction.		(2)
	T)	Sotal for Question	= 20 marks)

31	A student investigated the reaction between iodine and propanone in acidic conditions.	
	$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + HI(aq)$	
	 50 cm³ of 0.020 mol dm⁻³ iodine solution was measured into a flask. 25 cm³ of propanone and 25 cm³ of 1.0 mol dm⁻³ sulfuric acid were measured into a second flask. Several 10 cm³ samples of 0.5 mol dm⁻³ sodium hydrogencarbonate solution were placed in separate conical flasks. The mixture of propanone and sulfuric acid was added to the iodine, and a clock started. At two minute intervals, 10 cm³ of the reaction mixture was removed and added to one of the flasks containing sodium hydrogencarbonate solution. The contents of this flask were then titrated with 0.01 mol dm⁻³ sodium thiosulfate. 	
	(a) Explain the purpose of adding the reaction mixture to the sodium hydrogencarbonat	e. (2)
	(b) What indicator should be used in the titration?	(1)
k	*(c) In this experiment the concentration of the iodine was 0.020 mol dm ⁻³ and the concentrations of propanone and sulfuric acid were both 1.00 mol dm ⁻³ . Why was the iodine solution used much less concentrated than the propanone and sulfuric acid?	
		(2)

Volume of sodium thiosulfate used in titration/cm ³	I from the results of the experiment is shown below.	
Use the graph to deduce the ord	Time/s ler of reaction with respect to iodine, explaining you	r
reasoning.	or or reaction with respect to found, explaining you	(2)
(e) The solutions used in this exper cylinders or pipettes.	iment could be measured using either measuring	
Give one advantage of using a r pipette.	measuring cylinder and one advantage of using a	
		(2)

(f) In a further investigation, different volumes of sulfuric acid, propanone, iodine and water were mixed. The time taken for the mixture to go colourless was measured.

The experiments were repeated and the results below show average values for the rate of the reaction.

Expt	$\begin{array}{c} 2 \text{ mol dm}^{-3} \\ \text{H}_2\text{SO}_4 \\ /\text{cm}^3 \end{array}$	2 mol dm ⁻³ propanone /cm ³	Water /cm ³	0.01 mol dm ⁻³ iodine /cm ³	Rate /mol dm ⁻³ s ⁻¹
1	20.0	8.0	0	4.0	8×10^{-5}
2	10.0	8.0	10.0	4.0	4×10^{-5}
3	20.0	4.0	4.0	4.0	4×10^{-5}

 (i)	Explain why water is added in experiments 2 and 3.	(1)
 ······		
 (ii)	Show how you would use the data in the table to deduce the order of reaction with respect to propanone and hydrogen ions. Write the rate equation for the reaction.	
		(3)
	(Total for Question = 13 mark	as)