

# Reaction Kinetics

- 2 (a) Bromate(V) ions,  $\text{BrO}_3^-$ , react with bromide ions in the presence of acid to produce bromine. Write an **ionic** equation for this reaction.

.....  
 ..... [2]

- (b) The initial rate of this reaction was measured, starting with different concentrations of the three reactants.

The following results were obtained.

experiment number	$[\text{BrO}_3^-]$ / $\text{mol dm}^{-3}$	$[\text{Br}^-]$ / $\text{mol dm}^{-3}$	$[\text{H}^+]$ / $\text{mol dm}^{-3}$	initial rate / $\text{mol dm}^{-3} \text{ s}^{-1}$
1	0.040	0.020	0.50	$2.64 \times 10^{-4}$
2	0.040	0.020	1.00	$1.06 \times 10^{-3}$
3	0.040	0.080	0.50	$1.06 \times 10^{-3}$
4	0.080	0.020	0.50	$5.21 \times 10^{-4}$

- (i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

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- (ii) Write the rate equation for this reaction.

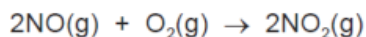
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- (iii) Use the results of experiment 1 to calculate the rate constant,  $k$ , for this reaction. Include the units of  $k$ .

rate constant,  $k =$  ..... units ..... [6]

[Total: 8]

- 1 (a) The oxidation of nitrogen(II) oxide is shown in the equation.



The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

experiment number	[NO] / mol dm <sup>-3</sup>	[O <sub>2</sub> ] / mol dm <sup>-3</sup>	initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
1	0.032	0.012	4.08 × 10 <sup>-3</sup>
2	0.032	0.024	8.15 × 10 <sup>-3</sup>
3	0.064	0.024	3.28 × 10 <sup>-2</sup>
4	0.096	0.036	

- (i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

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.....

- (ii) Calculate the initial rate in experiment 4. Give your answer to **two** significant figures.

initial rate = ..... mol dm<sup>-3</sup> s<sup>-1</sup>

- (iii) Write the rate equation for this reaction.

.....

- (iv) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

rate constant, *k* = ..... units .....

[6]

(b) (i) On the following axes

- draw two Boltzmann distribution curves, at two different temperatures,  $T_1$  and  $T_2$  ( $T_2 > T_1$ ),
- label the curves and the axes.



(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction.

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[5]

(c) The compound nitrosyl fluoride, NOF, can be formed by the following reaction.



The rate is first order with respect to NO and  $\text{F}_2$ .  
The reaction mechanism has **two** steps.

Suggest equations for the two steps of this mechanism, stating which is the rate determining slower step.

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..... [2]

[Total: 13]

w/14/qp41

1 A bromoalkane, R-Br, is hydrolysed by aqueous sodium hydroxide.

(a) (i) Write a balanced equation for this reaction.

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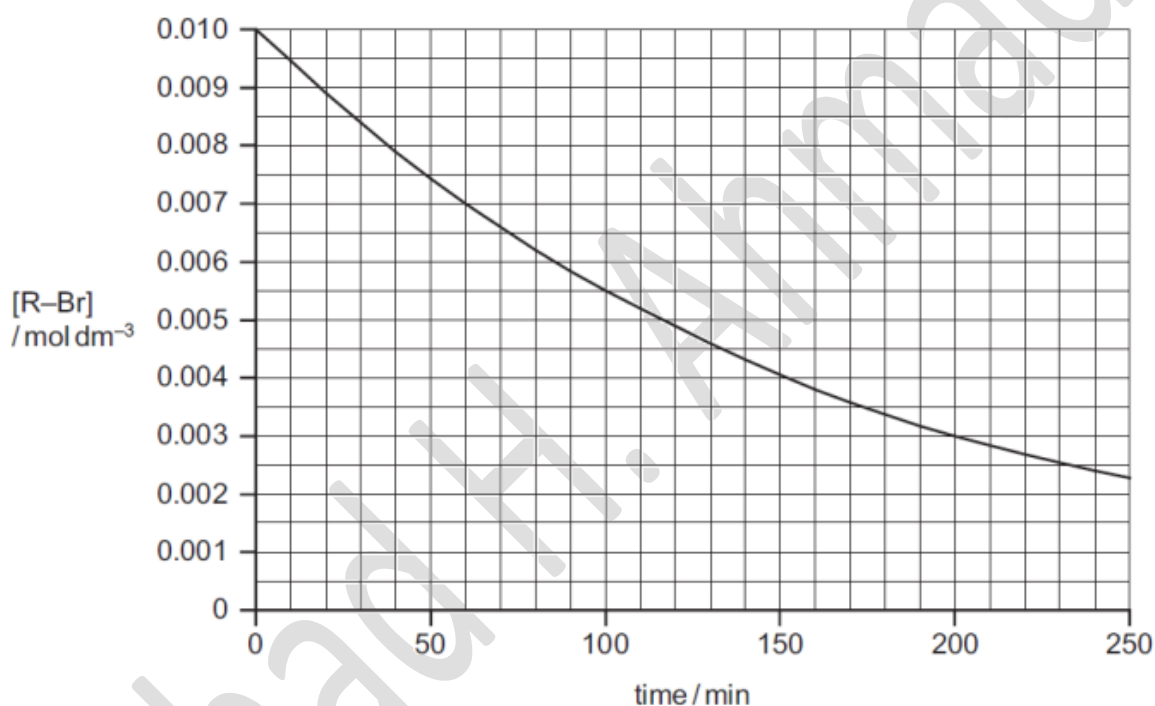
(ii) What *type of reaction* is this?

.....

[2]

(b) The concentration of bromoalkane was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different NaOH concentrations. The graph below shows the results of an experiment using  $[\text{NaOH}] = 0.10 \text{ mol dm}^{-3}$ .



When the experiment was repeated using  $[\text{NaOH}] = 0.15 \text{ mol dm}^{-3}$ , the following results were obtained.

time / min	[R-Br] / mol dm <sup>-3</sup>
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to confirm that the reaction is first order with respect to R–Br. Show all your working, and show clearly any construction lines you draw.

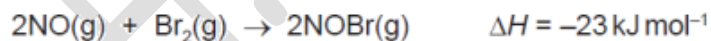
(iii) Use the graphs to calculate the order of reaction with respect to NaOH. Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

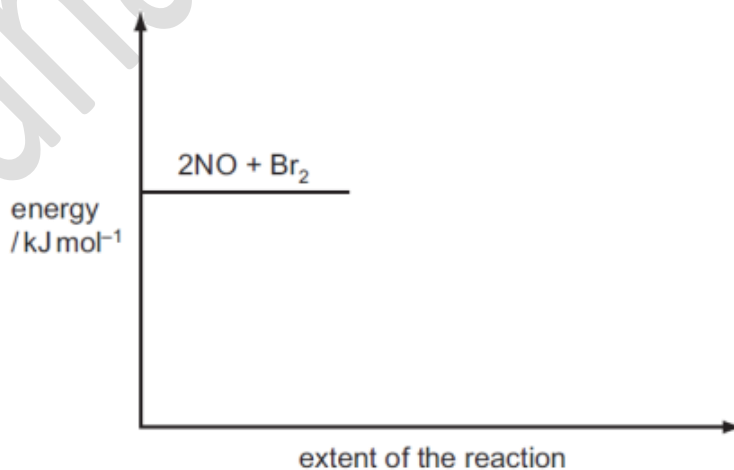
(c) Nitric oxide, NO, and bromine vapour react together according to the following equation.



The reaction has an activation energy of +5.4 kJ mol<sup>-1</sup>.

Use the following axes to sketch a fully-labelled reaction pathway diagram for this reaction.

Include all numerical data on your diagram.

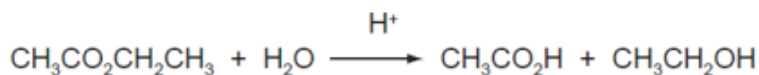


[2]

[Total: 11]

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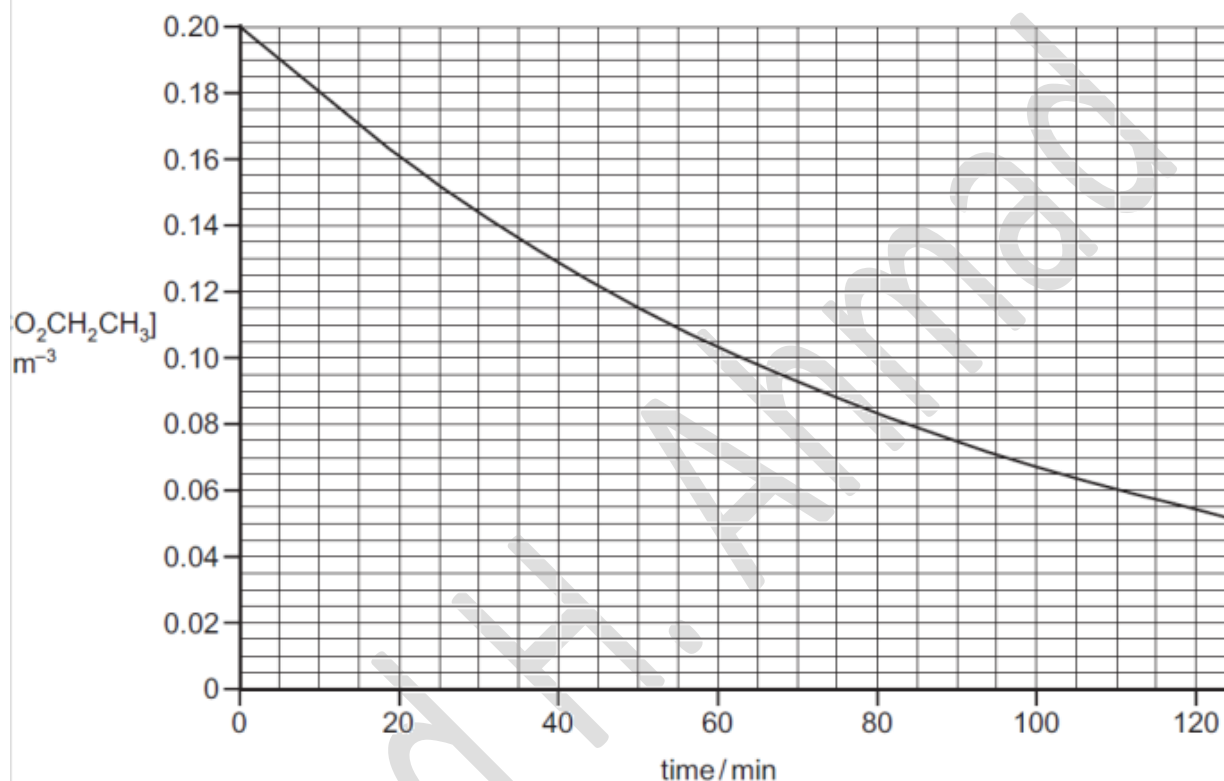
- 2 Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.



The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed.

Two separate experiments were carried out, with different  $\text{HCl}$  concentrations.

The following graph shows the results of an experiment using  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ .



- (a) When the experiment was carried out using  $[\text{HCl}] = 0.2 \text{ mol dm}^{-3}$ , the following results were obtained.

time / min	$[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3]$ / $\text{mol dm}^{-3}$
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

- (i) Plot these data on the axes above, and draw a line of best fit.

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- (ii) Use one of the graphs to show that the reaction is first order with respect to  $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$ .

Show all your working, and show clearly any construction lines you draw on the graphs.

- (iii) Use the graphs to calculate the order of reaction with respect to  $\text{HCl}$ .

Show all your working, and show clearly any construction lines you draw on the graphs.

- (iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

- (b) (i) Why is it **not** possible to determine the order of reaction with respect to water in this experiment?

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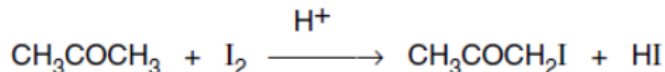
- (ii) Although  $[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3]$  decreases during each experiment,  $[\text{HCl}]$  remains the same as its initial value.

Why is this?

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[2]

1 The reaction between iodine and propanone is catalysed by hydrogen ions.



The reaction is found to be first order with respect to  $[\text{CH}_3\text{COCH}_3]$  and with respect to  $[\text{H}^+]$ , and zero order with respect to  $[\text{I}_2]$ .

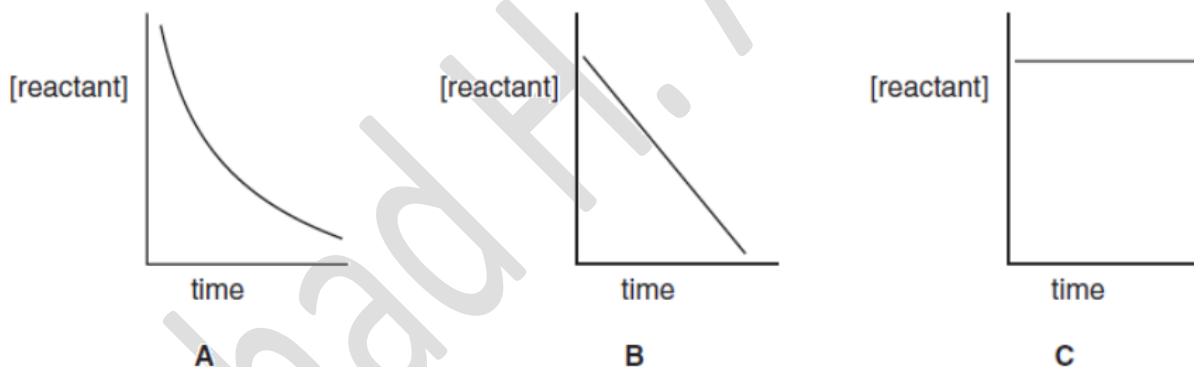
(a) What do you understand by the term *order of reaction*?

.....  
 .....[1]

(b) Construct a rate equation for the reaction.

.....[1]

The following sketches show three ways in which the concentration of reagents might vary during the reaction.

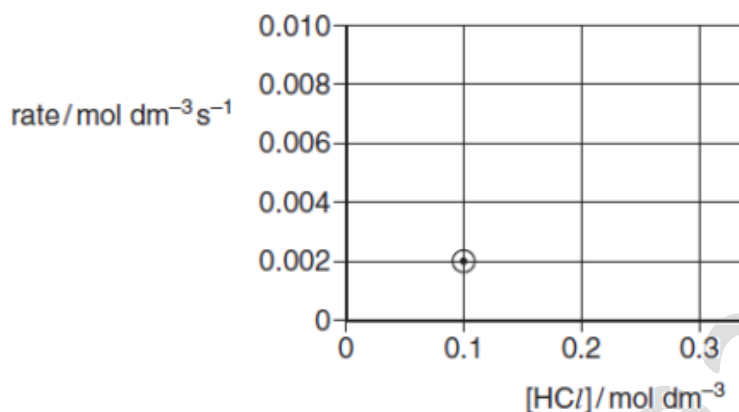


(c) Which of the above graphs correctly describes how the concentration of reactant changes with time for

- (i) the propanone concentration, \_\_\_\_\_
- (ii) the iodine concentration? \_\_\_\_\_

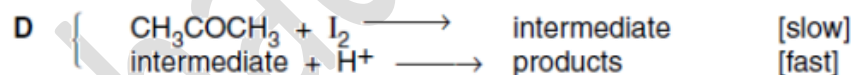
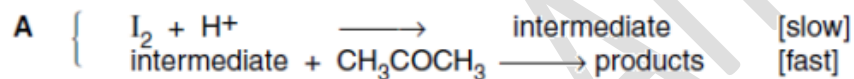
[2]

- (d) When carried out in  $0.1 \text{ mol dm}^{-3}$   $\text{HCl}$  solution, the rate was found to be  $0.002 \text{ mol dm}^{-3} \text{ s}^{-1}$ . Predict the rate of reaction in  $0.2 \text{ mol dm}^{-3}$   $\text{HCl}$  and in  $0.3 \text{ mol dm}^{-3}$   $\text{HCl}$  solution. Plot your figures on the following graph, and draw a line through the points.



[2]

- (e) Only one of the following outline reaction mechanisms is consistent with the observed kinetics.



Decide which mechanism is consistent, explaining the reasons for your choice.

Mechanism letter (A, B, C or D) \_\_\_\_\_

Reasons

.....  
 .....  
 .....  
 .....[3]

(f) When the starting concentrations of propanone, iodine and  $\text{H}^+$  were  $0.20 \text{ mol dm}^{-3}$ ,  $0.01 \text{ mol dm}^{-3}$  and  $0.5 \text{ mol dm}^{-3}$  respectively, the rate of decrease of  $[\text{I}_2]$  was found to be  $3.3 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

(i) Suggest a method you could use to measure  $[\text{I}_2]$ .

.....

(ii) Use these figures and your rate equation in part (b) to calculate a value for the rate constant  $k$ .

.....

(iii) What are the units of  $k$ ?

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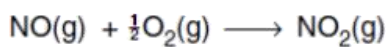
[3]

[Total : 12]

w/03/qp4

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- 1 The oxidation of nitrogen monoxide occurs readily according to the following equation.



The following table shows how the initial rate of this reaction depends on the concentrations of the two reactants.

[NO] / mol dm <sup>-3</sup>	[O <sub>2</sub> ] / mol dm <sup>-3</sup>	initial rate / mol dm <sup>-3</sup> s <sup>-1</sup>
0.0050	0.0050	0.02
0.0050	0.0075	0.03
0.010	0.0075	0.12

- (a) (i) Use the data to determine the order of reaction with respect to each of the reagents.

order with respect to NO .....

order with respect to O<sub>2</sub> .....

- (ii) Write the rate equation for the reaction, and use it to calculate a value for the rate constant, *k*, stating its units.

rate equation .....

numerical value of *k* = .....

units of *k* .....

- (iii) Use your rate equation in (ii) to calculate the rate of reaction when [NO] = [O<sub>2</sub>] = 0.0025 mol dm<sup>-3</sup>.

rate of reaction = .....

[6]

(b) Nitrogen monoxide plays an important catalytic role in the oxidation of atmospheric  $\text{SO}_2$  in the formation of acid rain.

(i) State the type of catalysis shown in this process.

.....

(ii) Explain the steps involved in this process by writing equations for the reactions that occur.

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[3]

[Total: 9]

s/06/qp4

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2 (a) What do you understand by the term *order of reaction*?

..... [1]

(b) Cyanohydrins can be made by reacting ketones with an acidified solution of sodium cyanide.



In a series of experiments, the reaction was carried out with different concentrations of the three reagents, and the following relative initial rates were obtained.

experiment number	$[(\text{CH}_3)_2\text{CO}]$ / mol dm <sup>-3</sup>	$[\text{H}^+]$ / mol dm <sup>-3</sup>	$[\text{CN}^-]$ / mol dm <sup>-3</sup>	relative initial rate / mol dm <sup>-3</sup> sec <sup>-1</sup>
1	0.020	0.060	0.060	1.00
2	0.020	0.050	0.050	0.833
3	0.020	0.050	0.060	1.00
4	0.025	0.050	0.050	1.042

(i) Use the data in the table to deduce the order of the reaction with respect to

propanone .....

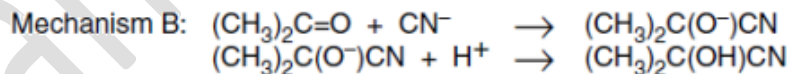
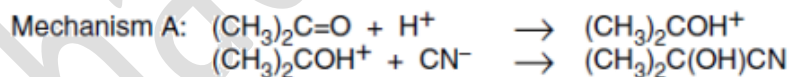
hydrogen ions .....

cyanide ions .....

(ii) Hence write a rate equation for this reaction.

.....

Two different mechanisms have been suggested for this reaction



(iii) Which mechanism is consistent with the rate equation you deduced in (ii), and which step in this mechanism is the slower (rate determining) step? Explain your answer.

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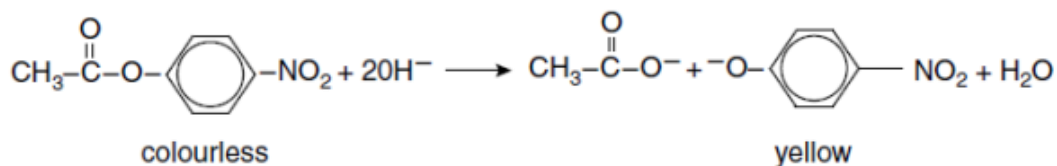
[7]

[Total: 8]





- 2 The ester 4-nitrophenyl ethanoate hydrolyses in alkaline solution according to the following equation.



- (a) Suggest, and briefly describe, a suitable experimental technique for studying the rate of this reaction.

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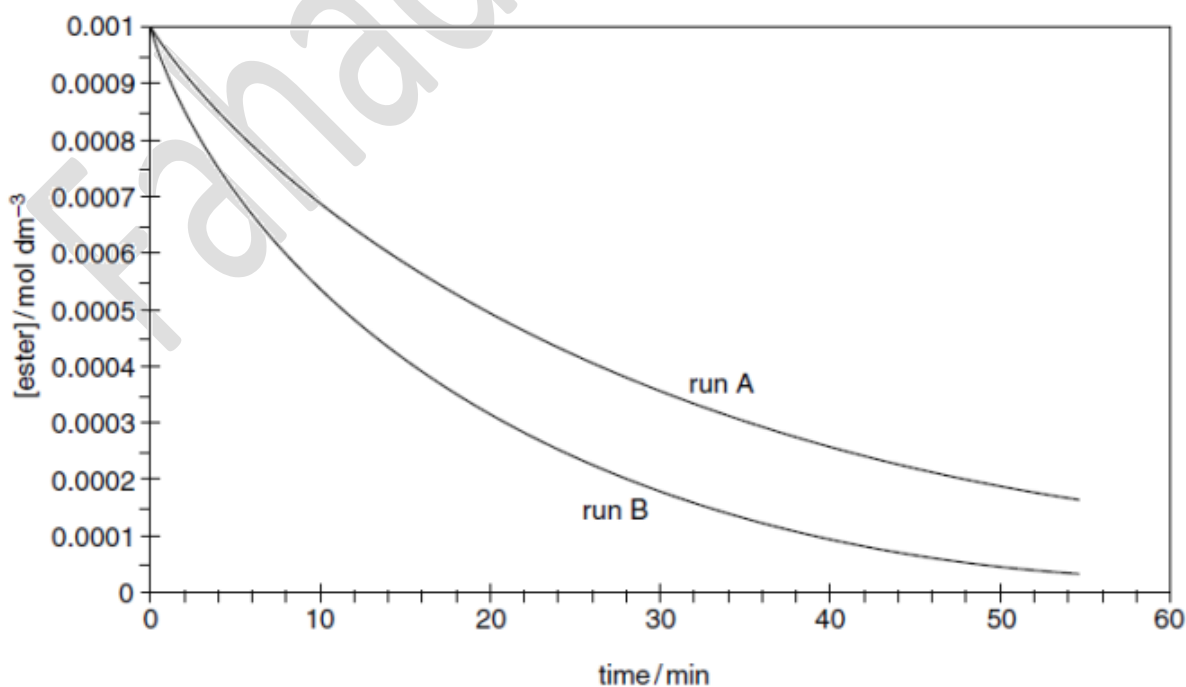
[4]

- (b) The reaction rate was studied using two solutions of different hydroxide ion concentrations.

run A:  $[\text{OH}^-] = 0.20 \text{ mol dm}^{-3}$

run B:  $[\text{OH}^-] = 0.40 \text{ mol dm}^{-3}$

The following graphs show how the concentration of the ester, 4-nitrophenyl ethanoate, varied over time in the two runs.



- (i) By drawing tangents on the graphs, measure and calculate the initial rates of reaction during the two runs. Give the units in each case.

initial rate of run A .....

initial rate of run B .....

[3]

- (ii) By using your results, calculate the overall order of reaction with respect to  $[\text{OH}^-]$ .

..... [1]

- (iii) From the curve of run B, determine the order of reaction with respect to [ester].

..... [1]

- (iv) Explain how you arrived at you answer in (iii).

.....

..... [1]

- (v) Write a rate equation for the reaction.

..... [1]

- (vi) Use your rate equation and the initial rates to calculate a value for the rate constant, including units.

.....

..... [2]

[Total: 13]

s/02/qp4

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3 (a) Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

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.....

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.

Choose **one** example of each type, and for **each** example you should

- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy.

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Fahad H. Ahmad

- 2 (a) (i) What is meant by the term *ligand* as applied to the chemistry of the transition elements?

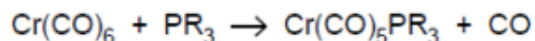
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- (ii) Describe the type of bonding that occurs between a ligand and a transition element.

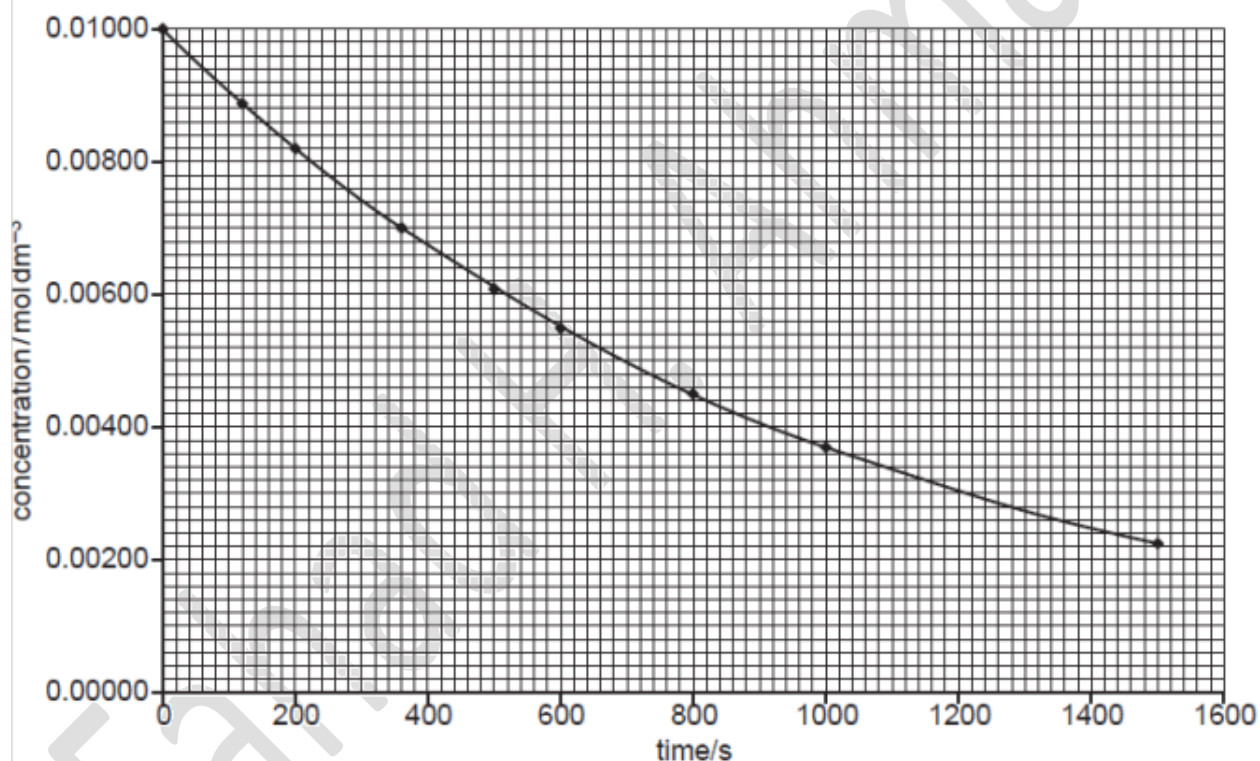
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[2]

- (b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.



Two separate experiments were carried out to study the rate of this reaction. In the first experiment, the ligand  $\text{PR}_3$  was in a large excess and  $[\text{Cr}(\text{CO})_6]$  was measured with time. The results are shown on the graph below.

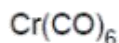


In the second experiment,  $\text{Cr}(\text{CO})_6$  was in a large excess, and  $[\text{PR}_3]$  was measured with time. The following results were obtained.

time / s	$[\text{PR}_3] / \text{mol dm}^{-3}$
0	0.0100
120	0.0076
200	0.0060
360	0.0028

- (i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

- (ii) Use the graphs to determine the order of reaction with respect to  $\text{Cr}(\text{CO})_6$  and  $\text{PR}_3$ . In each case explain how you arrived at your answer.



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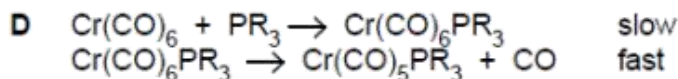
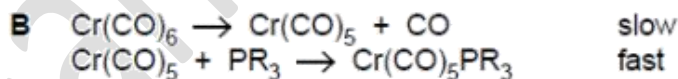
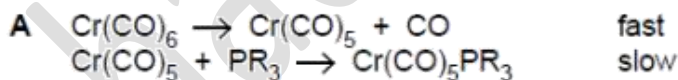
- (iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

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- (iv) State the units of the rate constant.

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- (v) Four possible mechanisms for this reaction are given below. Draw a circle around the letter next to the one mechanism which is consistent with the rate equation you have written in (iii).



Explain your answer.

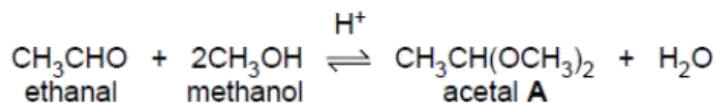
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[9]



w/11/qp43

- 2 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.



- (a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	[CH <sub>3</sub> CHO] / mol dm <sup>-3</sup>	[CH <sub>3</sub> OH] / mol dm <sup>-3</sup>	[H <sup>+</sup> ] / mol dm <sup>-3</sup>	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

- (i) Use the data in the table to determine the order with respect to each reactant.

order with respect to [CH<sub>3</sub>CHO] .....

order with respect to [CH<sub>3</sub>OH] .....

order with respect to [H<sup>+</sup>] .....

- (ii) Use your results from part (i) to write the rate equation for the reaction.

.....

- (iii) State the units of the rate constant in the rate equation .....

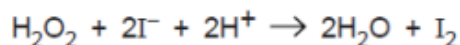
- (iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm<sup>-3</sup>.

relative rate = .....

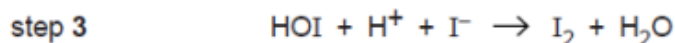
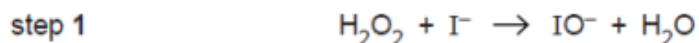
[6]

w/11/qp41

- 2 In the late 19th century the two pioneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.



This reaction is considered to go by the following steps.



The general form of the rate equation is as follows.

$$\text{rate} = k[\text{H}_2\text{O}_2]^a[\text{I}^-]^b[\text{H}^+]^c$$

- (a) Suggest how the appearance of the solution might change as the reaction takes place.

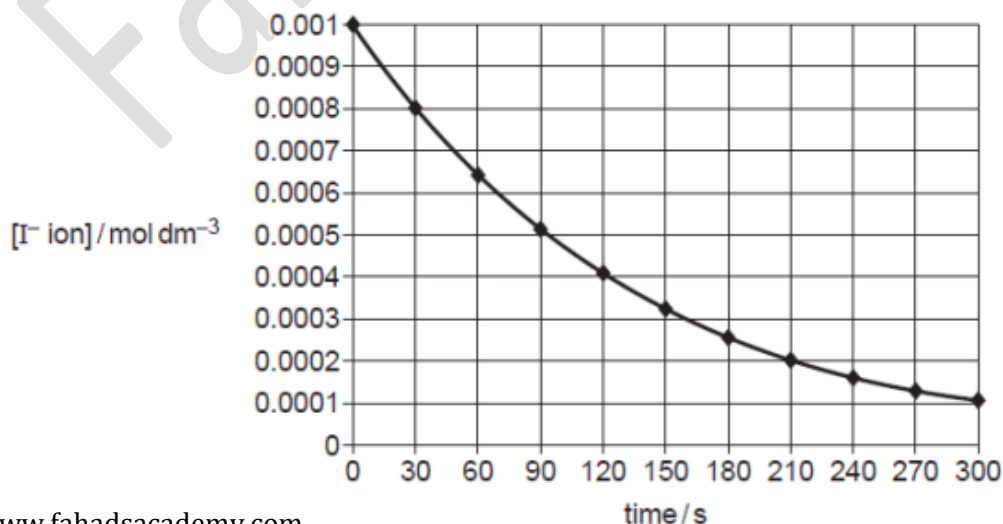
..... [1]

- (b) Suggest values for the orders *a*, *b* and *c* in the rate equation for each of the following cases.

case	numerical value		
	<i>a</i>	<i>b</i>	<i>c</i>
step 1 is the slowest overall			
step 2 is the slowest overall			
step 3 is the slowest overall			

[3]

A study was carried out in which both  $[\text{H}_2\text{O}_2]$  and  $[\text{H}^+]$  were kept constant at  $0.05 \text{ mol dm}^{-3}$ , and  $[\text{I}^-]$  was plotted against time. The following curve was obtained.





To gain full marks for the following answers you will need to draw relevant construction lines on the graph opposite to show your working. Draw them using a pencil and ruler.

(c) Calculate the initial rate of this reaction and state its units.

rate = ..... units ..... [2]

(d) Use half-life data calculated from the graph to show that the reaction is first order with respect to  $[I^-]$ .

..... [2]

(e) Use the following data to deduce the orders with respect to  $[H_2O_2]$  and  $[H^+]$ , explaining your reasoning.

$[H_2O_2]/\text{mol dm}^{-3}$	$[H^+]/\text{mol dm}^{-3}$	relative rate
0.05	0.05	1.0
0.07	0.05	1.4
0.09	0.07	1.8

.....  
 .....

order with respect to  $[H_2O_2]$  = .....

order with respect to  $[H^+]$  = .....

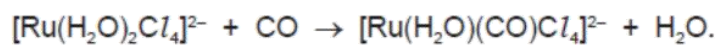
[2]

(f) From your results, deduce which of the three steps is the slowest (rate determining) step.

..... [1]

[Total: 11]

(c) Carbon monoxide reacts with a ruthenium(II) chloride complex according to the equation



(i) Describe the *type of reaction* that is occurring here.

.....

The following table shows how the initial rate of this reaction varies with different concentrations of reactants.

$[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-} / \text{mol dm}^{-3}$	$[\text{CO}] / \text{mol dm}^{-3}$	rate / $\text{mol dm}^{-3} \text{s}^{-1}$
$1.1 \times 10^{-2}$	$1.7 \times 10^{-3}$	$1.6 \times 10^{-7}$
$1.6 \times 10^{-2}$	$3.6 \times 10^{-3}$	$2.3 \times 10^{-7}$
$2.2 \times 10^{-2}$	$2.7 \times 10^{-3}$	$3.2 \times 10^{-7}$

(iii) Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

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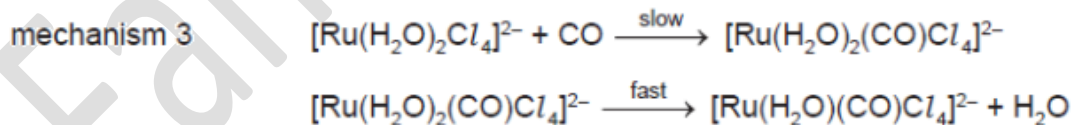
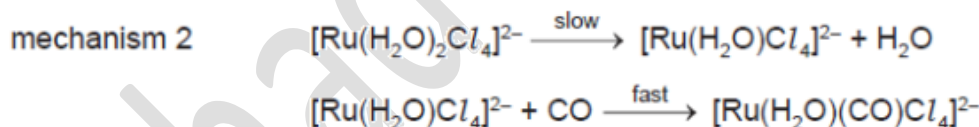
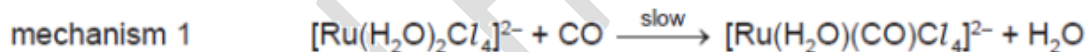
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There are three possible mechanisms for this reaction, which are described below.



(iv) Deduce which of these three mechanisms is consistent with the rate equation you suggested in part (iii). Explain your answer.

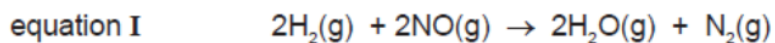
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[10]

(b) At 800 K, nitrogen monoxide reacts with hydrogen according to the following equation.



The following table shows how the initial rate of this reaction depends on the partial pressures of the reagents.

experiment	$p(\text{H}_2)/\text{atm}$	$p(\text{NO})/\text{atm}$	initial rate / $\text{atm s}^{-1}$
1	0.64	1.60	$1.50 \times 10^{-7}$
2	0.64	0.80	$3.75 \times 10^{-8}$
3	0.32	1.60	$7.50 \times 10^{-8}$

(i) Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

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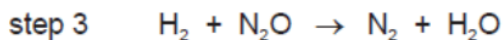
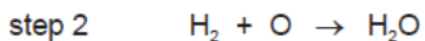
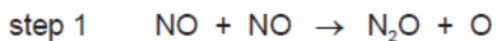
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(ii) Write down the rate equation and the units of the rate constant.

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The following mechanism has been put forward for this reaction.



(iii) Show how the overall stoichiometric equation I can be derived from the three equations for the individual steps given above.

(iv) Suggest which of the three reactions in the mechanism is the rate determining step. Explain your answer.

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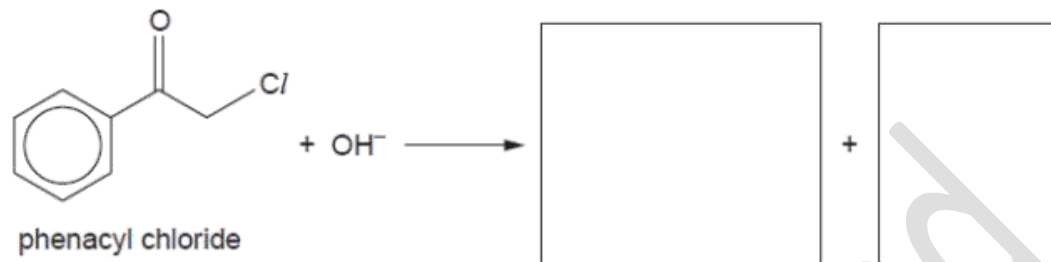
[8]

s/12/qp41

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- 1 Phenacyl chloride has been used as a component of some tear gases. Its lachrymatory and irritant properties are due to it reacting with water inside body tissues to produce hydrochloric acid.

It undergoes a nucleophilic substitution reaction with  $\text{NaOH(aq)}$ .



- (a) Write the formulae of the products of this reaction in the two boxes above. [2]

When the rate of this reaction was measured at various concentrations of the two reagents, the following results were obtained.

experiment number	[phenacyl chloride]	[NaOH]	relative rate
1	0.020	0.10	1.0
2	0.030	0.10	1.5
3	0.025	0.20	2.5

- (b) (i) What is meant by the term *order of reaction*?

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- (ii) Use the above data to deduce the order with respect to each reactant. Explain your reasoning.

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- (iii) Write the overall rate equation for the reaction.

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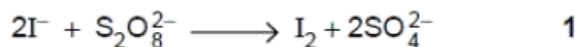
- (iv) Describe the mechanism for this reaction that is consistent with your overall rate equation.  
You should show all intermediates and/or transition states and partial charges, and you should represent the movements of electron pairs by curly arrows.

[7]

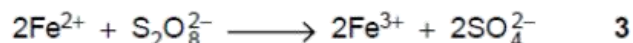
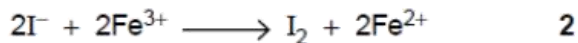
s/10/qp43

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- 4 (a) The reaction between iodide ions and persulfate ions,  $S_2O_8^{2-}$ , is slow.



The reaction can be speeded up by adding a small amount of  $Fe^{2+}$  or  $Fe^{3+}$  ions. The following two reactions then take place.



- (i) What type of catalysis is occurring here?

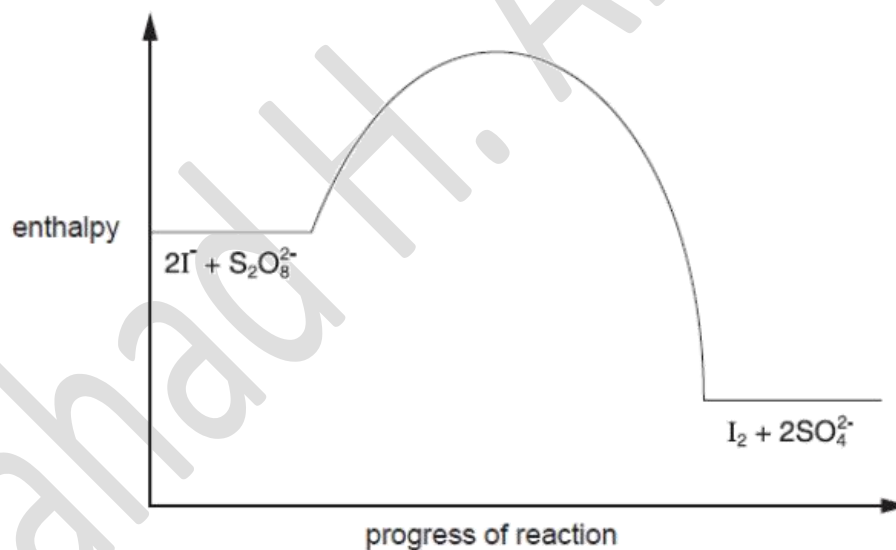
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- (ii) The rates of reactions 2 and 3 are both faster than that of reaction 1. By considering the species involved in these reactions, suggest a reason for this.

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- (iii) The following reaction pathway diagram shows the enthalpy profile of reaction 1.



Use the same axes to draw the enthalpy profiles of reaction 2 followed by reaction 3, starting reaction 2 at the same enthalpy level as reaction 1.

[4]



(b) The oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the atmosphere is speeded up by the presence of nitrogen oxides.

(i) Describe the environmental significance of this reaction.

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(ii) Describe a major source of  $\text{SO}_2$  in the atmosphere.

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(iii) By means of suitable equations, show how nitrogen oxides speed up this reaction.

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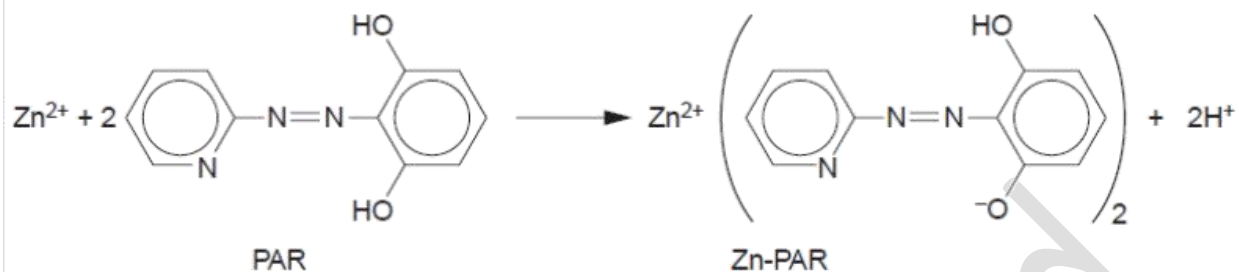
[4]

s/09/qp4

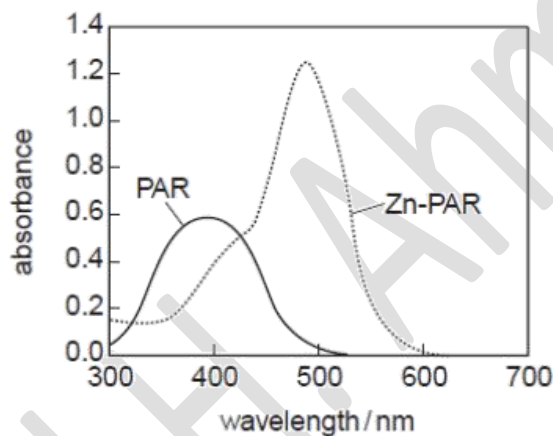
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(d) Zinc is an essential element for plant and animal life. It is often administered in the form of a chelate, which is a complex between a metal ion and a polydentate ligand.

The rate of the reaction between zinc ions and the ligand 4-(2-pyridylazo)resorcinol, PAR, has been studied.



Both PAR and its zinc complex absorb radiation in the UV-visible region. The figure below shows their absorption spectra.



(i) Devise a suitable experimental technique for studying how the rate of this reaction varies with  $[\text{Zn}^{2+}(\text{aq})]$ .

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