Reaction Kinetics

Question Paper 3

Level	International A Level
Subject	Chemistry
Exam Board	CIE
Topic	Reaction Kinetics
Sub-Topic	
Paper Type	Theory
Booklet	Question Paper 3

Time Allowed: **62 minutes**

Score: **/51**

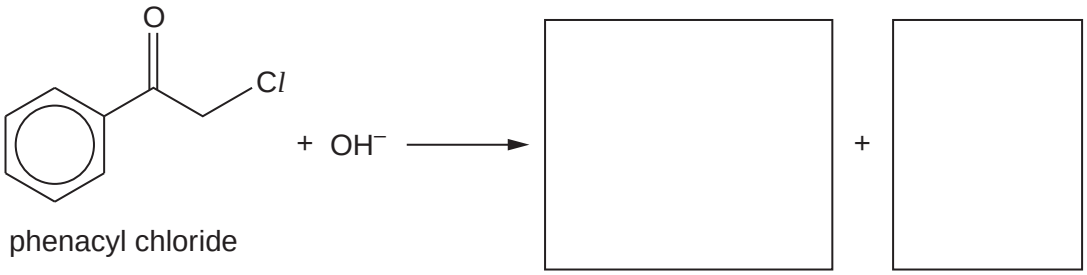
Percentage: **/100**

Grade Boundaries:

A*	A	B	C	D	E	U
>85%	777.5%	70%	62.5%	57.5%	45%	<45%

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 NaOH(aq).



phenacyl chloride

(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*?

.....

(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]

(c) (i) Describe an experiment that would show that CH_3COCl reacts with water at a much faster rate than phenacyl chloride. Include the reagents you would use, and the observations you would make with each chloride.

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(ii) Suggest an explanation for this difference in reactivity.

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[4]

[Total: 13]

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.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$$

This reaction is considered to go by the following steps.

step **1** $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step **2** $IO^- + H^+ \rightarrow HOI$

step **3** $HOI + H^+ + I^- \rightarrow I_2 + H_2O$

The general form of the rate equation is as follows.

$$\text{rate} = k[H_2O_2]^a[I^-]^b[H^+]^c$$

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

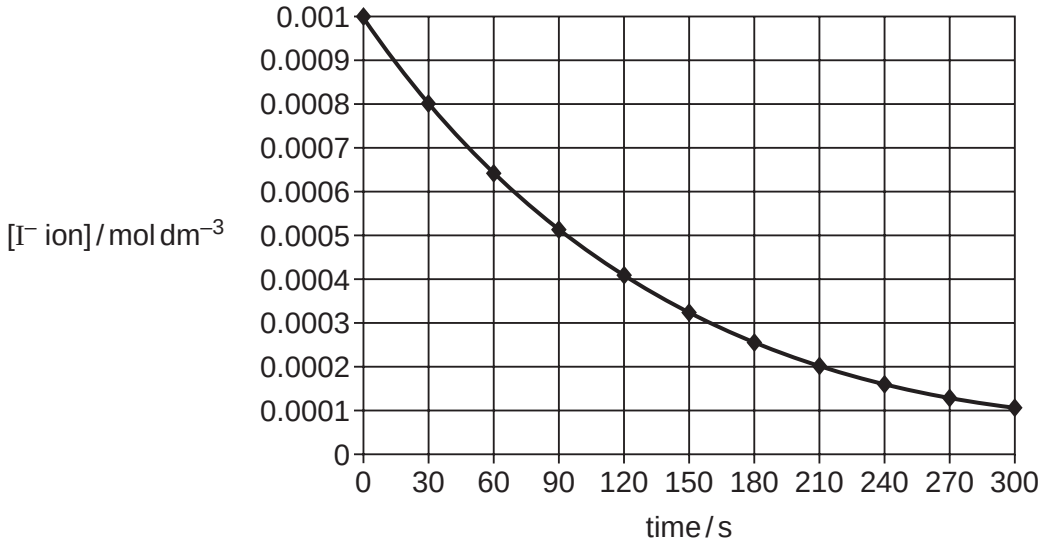
..... [1]

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

case	numerical value		
	a	*b*	*c*
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 $[H_2O_2]$ and $[H^+]$ were kept constant at 0.05 mol dm^{-3}, and $[I^-]$ 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.

$[H_2O_2]$ / mol dm^{-3}	$[H^+]$ / 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]

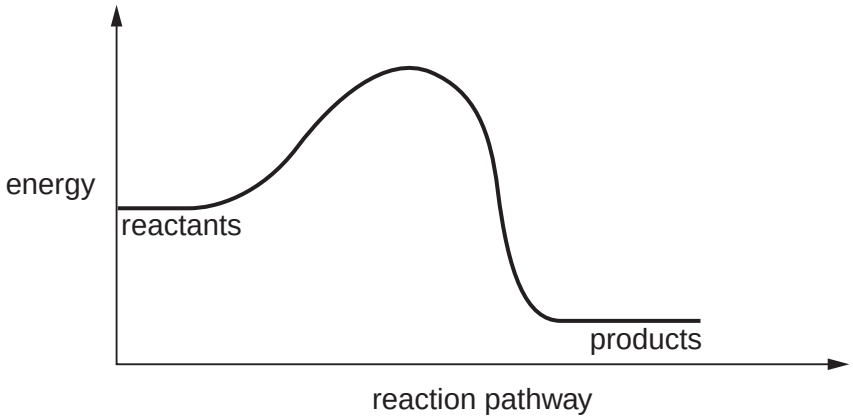
(f) From your results, deduce which of the three steps is the slowest (rate determining) step.

..... [1]

[Total: 11]

3 **(a)** Enzymes play a vital role in all living organisms, helping chemical reactions to take place at body temperature.

(i) The diagram below shows the reaction pathway of an enzyme-catalysed reaction without an enzyme present. On the diagram sketch the pathway if the enzyme was present.



(ii) What type of molecule are most enzymes?

.....

(iii) Why do many enzymes lose their catalytic effectiveness above 40 °C?

.....

[3]

(b) **(i)** Explain the difference between competitive and non-competitive inhibition of an enzyme.

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.....

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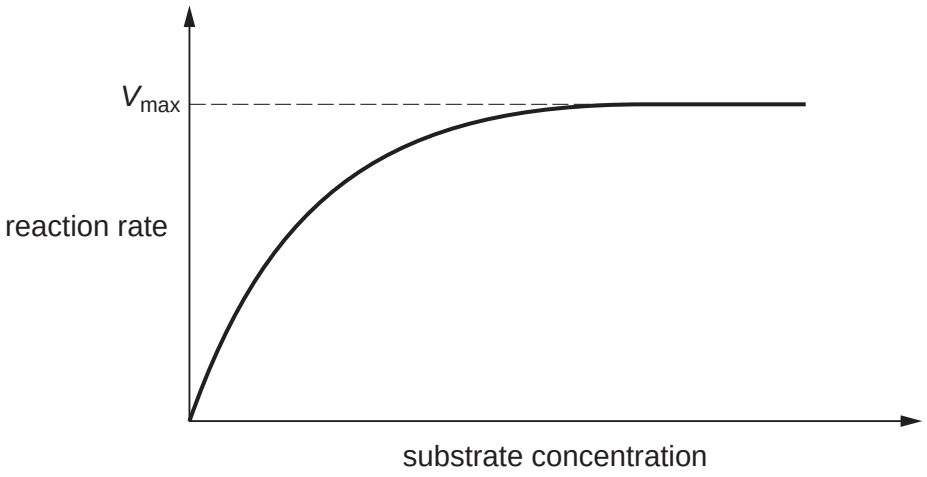
(ii) The graph below shows how the rate of an enzyme-catalysed reaction varies with substrate concentration in the absence of an inhibitor.

For a given amount of enzyme, V_{max} represents the rate when all of the active sites on the enzyme are being used.



Sketch on the diagram curves to show the effect on the rate of reaction of:

I a competitive inhibitor;

II a non-competitive inhibitor.

Clearly label your curves.

[4]

(c) Heavy metal ions like Hg^{2+} can bind irreversibly to enzymes and this can result in poisoning.

(i) Suggest to what atom or group Hg^{2+} ions bind.

.....

(ii) Explain how this affects enzyme activity.

.....

.....

.....

[3]

[Total: 10]

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

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g)$$

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

[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
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_2 ……

(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_2] = 0.0025 mol dm^{-3}.

rate of reaction =……

[6]

(b) Nitrogen monoxide plays an important catalytic role in the oxidation of atmospheric 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]

5 **(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.

$$(CH_3)_2C{=}O + H^+ + CN^- \longrightarrow (CH_3)_2C(OH)CN$$

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	$[(CH_3)_2CO]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	$[CN^-]$ / mol dm^{-3}	relative initial rate / mol dm^{-3} sec^{-1}
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

Mechanism A:
$(CH_3)_2C{=}O + H^+ \longrightarrow (CH_3)_2COH^+$
$(CH_3)_2COH^+ + CN^- \longrightarrow (CH_3)_2C(OH)CN$

Mechanism B:
$(CH_3)_2C{=}O + CN^- \longrightarrow (CH_3)_2C(O^-)CN$
$(CH_3)_2C(O^-)CN + H^+ \longrightarrow (CH_3)_2C(OH)CN$

(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]