Kinetics

1. The rate equation for a reaction is

$$\text{rate} = k[A]^2[B]$$

Which of the following statements is correct for this reaction?

A Doubling the concentration of A will double the reaction rate.
B Doubling the concentration of B will double the reaction rate.
C Doubling the concentration of B will have no effect on the reaction rate.
D Doubling the concentration of A and B will have no effect on the reaction rate.

2. The order of a reaction:

A depends on the stoichiometry of the overall reaction
B is the sequence of steps in the mechanism
C controls the speed of the overall reaction
D can only be obtained by experiment.

3. The results in the table were obtained for the reaction

$$X + 2Y \rightarrow Z$$

Experiment	[X] (mol l^{-1})	[Y] (mol l^{-1})	Initial rate (mol l^{-1} s^{-1})
1	0·030	0·030	0·0064
2	0·060	0·030	0·0128
3	0·030	0·015	0·0064

From these results, the rate equation is

A rate = k[X]
B rate = k[Y]
C rate = k[X][Y]
D rate = k[X][Y]^2.

4. Kinetic data for the reaction between bromate ions and bromide ions in the presence of hydrogen ions is shown below.

Experiment	[BrO_3^-] (mol l^{-1})	[Br^-] (mol l^{-1})	[H^+] (mol l^{-1})	*Initial rate* (mol l^{-1} s^{-1})
1	0·1	0·1	0·1	$8{\cdot}0 \times 10^{-4}$
2	0·2	0·1	0·1	$1{\cdot}6 \times 10^{-3}$
3	0·2	0·2	0·1	$3{\cdot}2 \times 10^{-3}$
4	0·1	0·1	0·2	$3{\cdot}2 \times 10^{-3}$

Which line in the table shows the order of reaction for each reactant?

	BrO_3^-	Br^-	H^+
A	1	1	0
B	1	1	2
C	1	2	2
D	2	2	0

5. The reaction between nitrogen monoxide and hydrogen occurs by the following mechanism.

$$2NO + H_2 \xrightarrow{\text{slow}} N_2 + H_2O_2$$
$$H_2O_2 + H_2 \xrightarrow{\text{fast}} 2H_2O$$

The overall order of this reaction is

A 2
B 3
C 4
D 5

Kinetics

6. The reaction $X + 2Y \rightarrow Z$ has the rate equation shown below.

$$\text{rate} = k[X][Y]$$

Which of the following could represent the rate determining step?

A $X + Y \rightarrow$ intermediate

B $Y + Y \rightarrow$ intermediate

C $X + Y \rightarrow Z$

D $XY + Y \rightarrow Z$

7. The following reaction is first order with respect to P and second order with respect to Q.

$$P + Q \rightarrow R + S$$

Which of the following statements is **not** correct?

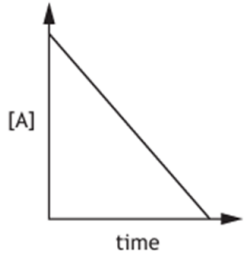
A The reaction is third order overall.

B The reaction occurs by a simple one step mechanism.

C The rate of the reaction decreases as the reaction proceeds.

D The rate of the reaction will double if the initial concentration of P is doubled.

8. The graph shows the change in concentration of reactant A as a reaction proceeds.



The order of reaction with respect to A is

A zero

B first

C second

D third.

9. For the reaction

$2A + 2B \rightarrow C$

the rate equation is

$\text{rate} = k[A][B]^2$.

Which of the following could be a possible mechanism for this reaction?

A $A + B \rightarrow X$ (fast)
$X + A + B \rightarrow C$ (slow)

B $A + 2B \rightarrow X$ (slow)
$X + A \rightarrow C$ (fast)

C $2A + B \rightarrow X$ (slow)
$X + B \rightarrow C$ (fast)

D $2A + B \rightarrow X$ (fast)
$X + B \rightarrow C$ (slow)

10. For the reaction

$2P + 2Q \rightarrow R$

the rate equation is

$rate = k[P]^2[Q]$.

Which of the following shows a possible mechanism for this reaction?

A $P + 2Q \rightarrow X$ slow
$X + P \rightarrow R$ fast

B $2P + Q \rightarrow X$ slow
$X + Q \rightarrow R$ fast

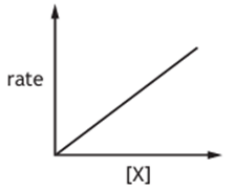
C $P + 2Q \rightarrow X$ fast
$X + P \rightarrow R$ slow

D $2P + Q \rightarrow X$ fast
$X + Q \rightarrow R$ slow

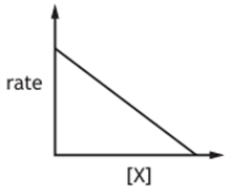
Kinetics

11. Which of the following graphs would be obtained for a reaction that is zero order with respect to reactant X?

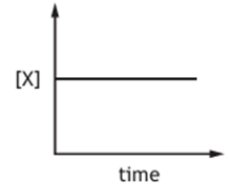
A



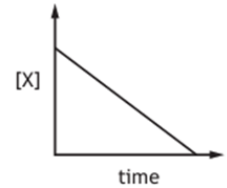
B



C



D



12. The rate of a chemical reaction is second order overall.

The units for the rate constant, k, are

A $\text{mol l}^{-1}\text{ s}^{-1}$

B $\text{l mol}^{-1}\text{ s}^{-1}$

C $\text{l}^2\text{ mol}^{-2}\text{ s}^{-1}$

D $\text{l}^{-2}\text{ mol}^2\text{ s}^{-1}$.

13. For the reaction

$A + B \rightarrow C$

the following data were obtained.

Experiment	*Initial concentration of A* (mol l^{-1})	*Initial concentration of B* (mol l^{-1})	*Initial rate of formation of C* ($\text{mol l}^{-1}\text{ s}^{-1}$)
1	0·1	0·1	0·05
2	0·2	0·1	0·05
3	0·1	0·2	X

Given that the rate equation is

$\text{Rate} = k[B]^2$

the value of X will be

A 0·05

B 0·10

C 0·15

D 0·20.

14. The rate equation for the reaction between nitrogen monoxide and chlorine is

$\text{rate} = k[NO]^2[Cl_2]$

The units for the rate constant, k, in this reaction are

A s^{-1}

B $\text{mol l}^{-1}\text{ s}^{-1}$

C $\text{l mol}^{-1}\text{ s}^{-1}$

D $\text{l}^2\text{ mol}^{-2}\text{ s}^{-1}$.

Kinetics

15 In a series of experiments P and Q reacted to form R. The time taken to produce a fixed concentration of R was recorded.

Experiment	Initial conc^{n} of P/mol l^{-1}	Initial conc^{n} of Q/mol l^{-1}	Time/s
1	0·05	0·05	46
2	0·05	0·10	23
3	0·10	0·05	46

The rate equation for this reaction is

A Rate = k[P]

B Rate = k[Q]

C Rate = k[Q]^2

D Rate = k[P][Q].

16. A suggested mechanism for the reaction

$2X + Y \rightarrow X_2Y$

is a two-step process

$X + Y \rightarrow XY$ (slow)

$XY + X \rightarrow X_2Y$ (fast)

This mechanism is consistent with the rate equation,

A rate = k[XY]

B rate = k[X][Y]

C rate = k[X]^2[Y]

D rate = k[X][XY].

17. The following data refer to initial reaction rates obtained for the reaction

$X + Y + Z \rightarrow$ products

Run	Relative concentrations			Relative initial rate
	[X]	[Y]	[Z]	
1	1·0	1·0	1·0	0·3
2	1·0	2·0	1·0	0·6
3	2·0	2·0	1·0	1·2
4	2·0	1·0	2·0	0·6

These data fit the rate equation

A Rate = k[X]

B Rate = k[X][Y]

C Rate = k[X][Y]^2

D Rate = k[X][Y][Z]

18. For the reaction

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

the suggested mechanism is

$NO(g) + Cl_2(g) \xrightarrow{slow} NOCl_2(g)$

$NOCl_2(g) + NO(g) \xrightarrow{fast} 2NOCl(g)$

The rate equation is

A rate = k[NO][Cl_2]

B rate = k[NO]^2[Cl_2]

C rate = k[$NOCl_2$][NO]

D rate = k[NO_2]^2[$NOCl_2$][Cl_2].

19. Which of the following is a correct statement about a catalyst?

For a chemical reaction it

A does not alter the value of the rate constant

B alters the value of the equilibrium constant

C alters the reaction mechanism

D has no effect on the value of the activation energy.

20. The following reaction is first order with respect to each of the reactants.

$A + B \rightarrow C + D$

Which of the following is correct?

A The rate of the reaction is independent of the concentration of either A or B.

B The overall reaction is first order.

C If the initial concentrations of A and B are both doubled, the rate of the reaction will be doubled.

D As the reaction proceeds, its rate will decrease.

21. In a chemical reaction the rate is doubled for every 10 °C rise in temperature. When the temperature is increased from 20 °C to 60 °C, the rate of the reaction will become faster by a factor of

A 3

B 4

C 8

D 16.

Kinetics

22. Two mechanisms have been proposed for the hydrolysis of 2-bromo-2-methylpropane.

One of these has only one step

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The other has two steps

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ (Slow)

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ (Fast)

The reaction is observed to follow first order kinetics. The rate equation for the overall reaction is

A rate = $k[(CH_3)_3CBr]$

B rate = $k[(CH_3)_3CBr][OH^-]$

C rate = $k[(CH_3)_3C^+]$

D rate = $k[(CH_3)_3C^+][OH^-]$.

23. The reaction between nitrogen monoxide (NO) and hydrogen occurs by the following mechanistic steps:

$$2NO + H_2 \xrightarrow{\text{slow}} N_2 + H_2O_2$$

$$H_2O_2 + H_2 \xrightarrow{\text{fast}} 2H_2O$$

The order of this reaction will be

A 1

B 2

C 3

D 4.

Kinetics

MARKS

1. Sulfur is formed in the reaction between sodium thiosulfate and hydrochloric acid.

(a) In an experiment to determine the rate equation for this reaction, a student obtained the following data.

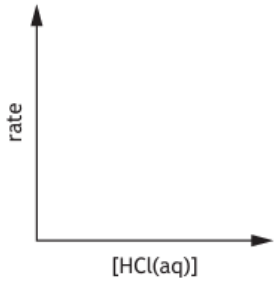
Experiment	$[Na_2S_2O_3(aq)]$ (mol l^{-1})	[HCl(aq)] (mol l^{-1})	Initial rate (mol l^{-1} s^{-1})
1	5.00×10^{-2}	2.00×10^{-1}	6.55×10^{-3}
2	1.00×10^{-1}	2.00×10^{-1}	1.31×10^{-2}
3	1.00×10^{-1}	4.00×10^{-1}	1.31×10^{-2}

(i) Determine the order of reaction with respect to $Na_2S_2O_3$. 1

(ii) The reaction is zero order with respect to HCl.

Complete the diagram below to show the effect of changing the concentration of HCl on the reaction rate. 1

(An additional diagram, if required, can be found on *page 33*.)



(iii) Write the overall rate equation for the reaction. 1

(iv) Calculate the value for the rate constant, k, including the appropriate units. 2

2. Ethanal reacts with hydroxide ions to form 3-hydroxybutanal.

(a) An experiment was carried out to determine the kinetics for the reaction.

The rate equation was found to be

$$\text{rate} = k\,[CH_3CHO(aq)]\,[OH^-(aq)]$$

(i) State the overall order of the reaction. 1

(ii) One set of reaction conditions gave the following data.

$[CH_3CHO(aq)]$ (mol l^{-1})	$[OH^-(aq)]$ (mol l^{-1})	Initial rate (mol l^{-1} s^{-1})
0.100	0.0150	1.72×10^{-3}

Calculate the value for the rate constant, k, including the appropriate units. 2

(iii) The reaction mechanism is shown.

Step 1 $CH_3CHO + OH^- \rightleftharpoons {}^-CH_2CHO + H_2O$

Step 2 $CH_3CHO + {}^-CH_2CHO \rightarrow CH_3CH(O^-)CH_2CHO$

Step 3 $CH_3CH(O^-)CH_2CHO + H_2O \rightarrow CH_3CH(OH)CH_2CHO + OH^-$

Explain which step is the rate-determining step. 1

Kinetics

3. The equation for the reaction between mercuric chloride and oxalate ions is shown.

$$2HgCl_2(aq) + C_2O_4^{2-}(aq) \rightarrow 2Cl^-(aq) + 2CO_2(g) + Hg_2Cl_2(s)$$

In an experiment to determine the kinetics for this reaction the following results were obtained.

Experiment	$[HgCl_2]$ (mol l^{-1})	$[C_2O_4^{2-}]$ (mol l^{-1})	Initial rate of reaction (mol l^{-1} s^{-1})
1	0.0840	0.200	0.860×10^{-6}
2	0.0840	0.400	3.44×10^{-6}
3	0.0420	0.400	1.72×10^{-6}
4	0.0320		2.11×10^{-6}

(a) Determine the order of the reaction with respect to

(i) $HgCl_2$ **1**

(ii) $C_2O_4^{2-}$ **1**

(b) Write the overall rate equation for the reaction. **1**

(c) (i) Calculate a value for the rate constant, k, including the appropriate units. **2**

(ii) Calculate the initial oxalate concentration, in mol l^{-1}, for experiment 4. **1**

Kinetics

4. At high temperatures, nitrogen monoxide can also react with hydrogen.

A proposed reaction mechanism is

Step 1 $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$ (slow)

Step 2 $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$ (fast)

(i) (A) Write a rate equation for this reaction. **1**

(B) The experimental rate constant is $2.7 \times 10^3\ l^2\ mol^{-2}\ s^{-1}$.

The table shows experimental rate data for the reaction.

[NO] (mol l^{-1})	[H_2] (mol l^{-1})	Initial reaction rate (mol $l^{-1}\ s^{-1}$)
	0.015	0.0040

Complete the table to show the concentration of nitrogen monoxide. **1**

(ii) Write a balanced equation for the overall reaction. **1**

5. In an experiment to determine the rate equation for this reaction, some of the data obtained by a student is shown below.

[$[Ni(OH_2)_6]^{2+}$] (mol l^{-1})	[NH_3] (mol l^{-1})	*Initial rate* (mol $l^{-1}\ s^{-1}$)
0·10	0·25	$1{\cdot}3 \times 10^2$

The student proposed the following rate equation.

$$rate = k\ [[Ni(OH_2)_6]^{2+}]\ [NH_3]$$

(i) Determine the overall order for this reaction. **1**

(ii) Calculate the value for the rate constant, k, including the appropriate units. **2**

Kinetics

6. Reaction kinetics can be used to determine the order and mechanism of chemical reactions.

A proposed mechanism for the reaction between hydrogen peroxide, $H_2O_2(aq)$, and iodide ions, $I^-(aq)$, is shown below.

Step 1 $H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(\ell)$ slow

Step 2 $IO^-(aq) + H_3O^+(aq) \rightarrow HIO(aq) + H_2O(\ell)$ fast

Step 3 $HIO(aq) + H_3O^+(aq) + I^-(aq) \rightarrow I_2(aq) + 2H_2O(\ell)$ fast

(a) State what is meant by the order of a reaction. **1**

(b) (i) Determine the overall order of reaction for the mechanism above. **1**

(ii) Write the rate equation for this reaction. **1**

(c) Write a balanced equation for the overall reaction. **1**

7. Butan-1-ol can also be synthesised from 1-bromobutane by a different type of chemical reaction.

An experiment was carried out to determine the kinetics for the reaction. Under certain conditions, the following results were obtained.

$[C_4H_9Br]$ (mol l^{-1})	$[OH^-]$ (mol l^{-1})	*Initial rate* (mol l^{-1} s^{-1})
0·25	0·10	$3{\cdot}3 \times 10^{-6}$
0·50	0·10	$6{\cdot}6 \times 10^{-6}$

(i) The reaction is first order with respect to both reactants.
Write the overall rate equation for the reaction. **1**

(ii) Calculate the value for the rate constant, k, including the appropriate units. **2**

Kinetics

8. Vanadium(III) ions can react with iron(III) ions in solution.

$$V^{3+}(aq) + Fe^{3+}(aq) \rightarrow V^{4+}(aq) + Fe^{2+}(aq)$$

(i) The reaction is first order with respect to both $V^{3+}(aq)$ and $Fe^{3+}(aq)$.
Write the rate equation for this reaction. **1**

(ii) In the presence of a $Cu^{2+}(aq)$ catalyst, the reaction mechanism is:

$$Cu^{2+}(aq) + V^{3+}(aq) \xrightarrow{\text{slow}} Cu^{+}(aq) + V^{4+}(aq)$$

$$Cu^{+}(aq) + Fe^{3+}(aq) \xrightarrow{\text{fast}} Cu^{2+}(aq) + Fe^{2+}(aq)$$

(A) State the order of the reaction with respect to $Fe^{3+}(aq)$ when a $Cu^{2+}(aq)$ catalyst is present.
Explain your answer. **2**

9. Chlorine dioxide, ClO_2, is used in water sterilisation.

An experiment was carried out to determine the kinetics for the reaction between chlorine dioxide and hydroxide ions.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_2^-(aq) + ClO_3^-(aq) + H_2O(\ell)$$

Under certain conditions the following results were obtained.

$[ClO_2]$ (mol l^{-1})	$[OH^-]$ (mol l^{-1})	*Initial rate* (mol $l^{-1}s^{-1}$)
$6{\cdot}00 \times 10^{-2}$	$3{\cdot}00 \times 10^{-2}$	$2{\cdot}48 \times 10^{-2}$
$1{\cdot}20 \times 10^{-1}$	$3{\cdot}00 \times 10^{-2}$	$9{\cdot}92 \times 10^{-2}$
$1{\cdot}20 \times 10^{-1}$	$9{\cdot}00 \times 10^{-2}$	$2{\cdot}98 \times 10^{-1}$

(i) Determine the order of reaction with respect to:

(A) ClO_2 **1**

(B) OH^- **1**

(ii) Write the overall rate equation for the reaction. **1**

(iii) Calculate the value for the rate constant, k, including the appropriate units. **2**

Kinetics

10. Nitrogen monoxide reacts with hydrogen as shown.

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

In a series of experiments, at a fixed temperature, the initial rates of this reaction were measured.

Experiment	Initial [NO]/ mol l^{-1}	Initial [H_2]/ mol l^{-1}	Initial rate/ mol $l^{-1}s^{-1}$
1	$2{\cdot}00 \times 10^{-3}$	$1{\cdot}20 \times 10^{-3}$	$7{\cdot}40 \times 10^{-4}$
2	$2{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**x**
3	$4{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**y**

The following rate equation was deduced.

$$\text{Rate} = k[NO]^2$$

(i) Using the information above, determine the numerical values for **x** and **y**. **2**

(ii) For experiment 1, calculate the value of the rate constant, k, including the appropriate units. **2**

11. The results of experiments on the alkaline hydrolysis of 2-iodobutane, $CH_3CHIC_2H_5$, are shown in the table below.

The equation for the hydrolysis is

$$CH_3CHIC_2H_5(\ell) + OH^-(aq) \rightarrow CH_3CH(OH)C_2H_5(\ell) + I^-(aq)$$

Experiment	$[CH_3CHIC_2H_5]$/mol l^{-1}	$[OH^-]$/mol l^{-1}	Initial Rate/mol $l^{-1}s^{-1}$
1	0·10	0·10	$1{\cdot}4 \times 10^{-4}$
2	0·20	0·20	$2{\cdot}9 \times 10^{-4}$
3	0·30	0·10	$4{\cdot}1 \times 10^{-4}$

(*a*) Determine the order of reaction with respect to

(i) $CH_3CHIC_2H_5$ **1**

(ii) OH^-. **1**

(*b*) Using your answers to part (*a*):

(i) write the rate equation for the reaction; **1**

(ii) calculate a value for the rate constant, k, including the appropriate units. **2**

Kinetics

12. A kinetics study was carried out on the reaction between a halogenoalkane, C_4H_9Br, and aqueous sodium hydroxide.

$$C_4H_9Br + NaOH \rightarrow C_4H_9OH + NaBr$$

The following results were obtained.

$[C_4H_9Br]$/mol l^{-1}	[NaOH]/mol l^{-1}	Initial Rate/mol $l^{-1}s^{-1}$
$8{\cdot}0 \times 10^{-4}$	0·10	0·15
$1{\cdot}6 \times 10^{-3}$	0·10	0·30
$1{\cdot}6 \times 10^{-3}$	0·20	0·30
$3{\cdot}2 \times 10^{-3}$	0·40	0·60

(*a*) What is the order of reaction with respect to

(i) the halogenoalkane

(ii) the sodium hydroxide? **1**

(*b*) Write the rate equation for the reaction. **1**

(*c*) Calculate a value for the rate constant, k, including the appropriate units. **2**

13. The rate equation for the reaction between nitrogen dioxide and fluorine is

$$\text{Rate} = k[NO_2][F_2]$$

A proposed reaction mechanism is

Step one $NO_2 + F_2 \rightarrow NO_2F + F$

Step two $NO_2 + F \rightarrow NO_2F$.

(*a*) Which step in the proposed reaction mechanism would be **faster**? **1**

(*b*) Write a balanced equation for the overall reaction. **1**

(*c*) What is the overall order of the reaction? **1**

(*d*)

Experiment	$[NO_2]$/mol l^{-1}	$[F_2]$/mol l^{-1}	Initial rate/ mol l^{-1} s^{-1}
1	0·001	0·003	$1{\cdot}2 \times 10^{-4}$
2	0·006	0·001	$2{\cdot}4 \times 10^{-4}$
3	0·002	0·004	$3{\cdot}2 \times 10^{-4}$

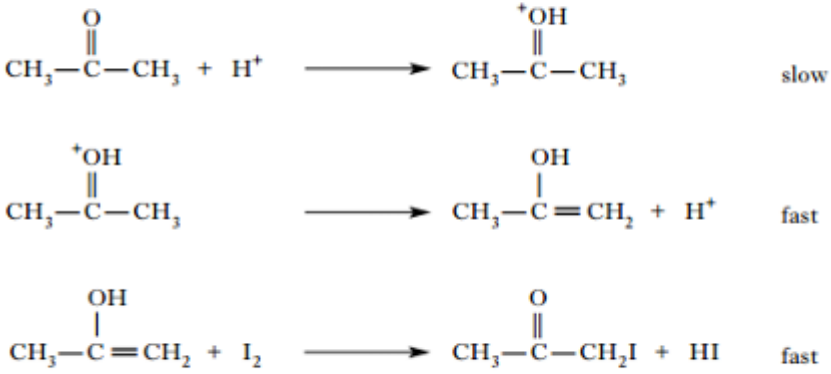
Use the data in the table to calculate a value for the rate constant, k, including the appropriate units. **2**

Kinetics

14. Iodine reacts with propanone as follows.

$$I_2 + CH_3COCH_3 \longrightarrow CH_3COCH_2I + HI$$

A possible mechanism for this reaction is



Write a rate equation for this reaction based on the above mechanism.

15. A mixture of butan-1-ol and butan-2-ol can be synthesised from 1-bromobutane in a two stage process.

$$CH_3CH_2CH_2CH_2Br \xrightarrow[\textbf{Stage 1}]{KOH/C_2H_5OH} CH_3CH_2CH{=}CH_2 \xrightarrow[\textbf{Stage 2}]{H_2O/H^+} \text{butan-1-ol} + \text{butan-2-ol}$$

1-Bromobutane reacts with hydroxide ions in a nucleophilic substitution reaction to produce butan-1-ol. The following results were obtained for this reaction.

Experiment	[1-Bromobutane]/mol l^{-1}	$[OH^-]$/mol l^{-1}	Initial rate/mol l^{-1} s^{-1}
1	0·25	0·10	$3·3 \times 10^{-6}$
2	0·50	0·10	$6·6 \times 10^{-6}$
3	0·50	0·20	$1·3 \times 10^{-5}$

(i) What is the overall order of this reaction? **1**

(ii) Calculate a value for the rate constant of this reaction, giving the appropriate units. **2**

Kinetics

16. A kinetics study was carried out on the reaction between a haloalkane, C_4H_9Br, and aqueous sodium hydroxide.

$$C_4H_9Br + NaOH \rightarrow C_4H_9OH + NaBr$$

The following results were obtained.

$[C_4H_9Br]$/mol l^{-1}	[NaOH]/mol l^{-1}	Initial Rate/mol $l^{-1}s^{-1}$
$8{\cdot}0 \times 10^{-4}$	0·10	0·15
$1{\cdot}6 \times 10^{-3}$	0·10	0·30
$1{\cdot}6 \times 10^{-3}$	0·20	0·30
$3{\cdot}2 \times 10^{-3}$	0·40	0·60

(*a*) What is the order of reaction with respect to

(i) the haloalkane

(ii) the sodium hydroxide? **1**

(*b*) Write the rate equation for the reaction. **1**

(*c*) Calculate a value for the rate constant, k, including the appropriate units. **2**

17 The following table of results was obtained for the reaction below.

$$H_2O_2(aq) + 2HI(aq) \longrightarrow 2H_2O(\ell) + I_2(aq)$$

Experiment	$[H_2O_2]$/mol l^{-1}	[HI]/mol l^{-1}	Initial rate/mol l^{-1} s^{-1}
1	$3{\cdot}2 \times 10^{-4}$	$4{\cdot}1 \times 10^{-4}$	$4{\cdot}3 \times 10^{-9}$
2	$6{\cdot}4 \times 10^{-4}$	$4{\cdot}1 \times 10^{-4}$	$8{\cdot}6 \times 10^{-9}$
3	$3{\cdot}2 \times 10^{-4}$	$8{\cdot}2 \times 10^{-4}$	$8{\cdot}6 \times 10^{-9}$
4	$6{\cdot}4 \times 10^{-4}$	$8{\cdot}2 \times 10^{-4}$	$1{\cdot}72 \times 10^{-8}$

(*a*) Determine the order of this reaction with respect to

(i) H_2O_2

(ii) HI. **1**

(*b*) Write the rate equation for the reaction. **1**

(*c*) Calculate a value for the rate constant, k, including the appropriate units. **2**

Kinetics

18. The bromate ion, BrO_3^-, is a useful oxidising agent.

(*b*) The following table of results was obtained for the reaction between bromate ions and bromide ions under acidic conditions.

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

Experiment	$[BrO_3^-]$/ mol l^{-1}	$[Br^-]$/ mol l^{-1}	$[H^+]$/ mol l^{-1}	Initial rate/ mol l^{-1} s^{-1}
1	0·05	0·05	0·05	$5·0 \times 10^{-5}$
2	0·10	0·05	0·05	$1·0 \times 10^{-4}$
3	0·10	0·10	0·05	$2·0 \times 10^{-4}$
4	0·05	0·05	0·10	$2·0 \times 10^{-4}$

(i) Deduce the order of reaction with respect to each of the three reactants. **1**

(ii) Write the rate equation for the reaction. **1**

(iii) Calculate the rate constant for this reaction giving the appropriate units. **2**

19. Ozone, O_3, is one of the earth's key defences against damaging ultra-violet radiation.

The following table shows how the initial rate of **reaction 2** varies with changing concentrations of $NO_2(g)$ and $O(g)$ at a fixed temperature.

$[O]$/mol l^{-1}	$[NO_2]$/mol l^{-1}	Initial rate/mol l^{-1} s^{-1}
$9·20 \times 10^{-15}$	$1·11 \times 10^{-12}$	$6·10 \times 10^{-17}$
$1·81 \times 10^{-14}$	$1·11 \times 10^{-12}$	$1·20 \times 10^{-16}$
$1·81 \times 10^{-14}$	$2·23 \times 10^{-12}$	$2·41 \times 10^{-16}$

(i) Determine the overall order of this reaction. **1**

(ii) Calculate a value for the rate constant, k, including appropriate units. **3**

Kinetics 2003 & 2001

20 The following table of results was obtained for the reaction below.

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + 2H_2O(\ell)$$

Experiment	$[H_2O_2]$/ mol l^{-1}	$[I^-]$/ mol l^{-1}	$[H^+]$/ mol l^{-1}	Initial rate/ mol $l^{-1}s^{-1}$
1	0·3	0·3	0·002	$2·07 \times 10^{-3}$
2	0·6	0·3	0·002	$4·14 \times 10^{-3}$
3	0·3	0·6	0·002	$4·14 \times 10^{-3}$
4	0·3	0·3	0·004	$2·07 \times 10^{-3}$

(*a*) Write the rate equation for the reaction. 1

(*b*) Calculate the rate constant for this reaction giving the appropriate units. 3

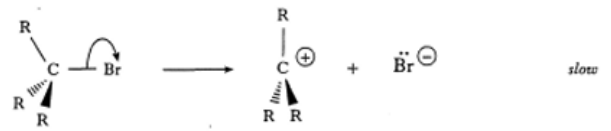
21 Bromoalkanes undergo nucleophilic substitution when heated with aqueous sodium hydroxide solution.

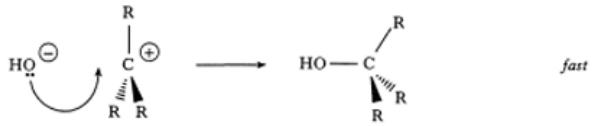
$$R_3CBr + OH^- \rightarrow R_3COH + Br^-$$

(where R = H and/or an alkyl group)

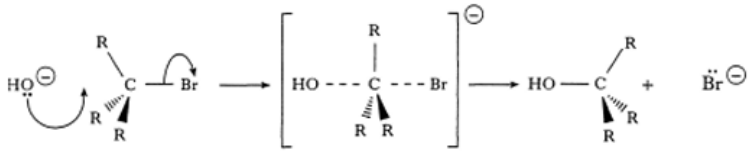
Two possible mechanisms for the reaction are outlined below.

Mechanism 1 (two-step process):





Mechanism 2 (single-step process):



a) A bromoalkane reacts as in **mechanism 1**.
Write the rate equation that would be obtained in a kinetic study of the reaction.

b) Another bromoalkane reacted as in **mechanism 2** and the following kinetic data were obtained:

Experiment	Concentration of R_3CBr/mol l^{-1}	Concentration of NaOH(aq)/mol l^{-1}	Relative rate
1	0·05	0·10	1
2	0·05	0·20	*x*
3	0·10	*y*	10

Determine values for *x* and *y*. 2

Kinetics

22 In a **PPA**, the kinetics of the acid-catalysed propanone/iodine reaction were studied.

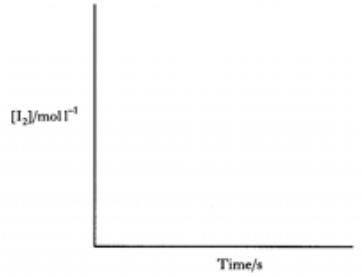
$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + HI(aq)$$

The reaction is first order with respect to propanone and first order with respect to the hydrogen ions which catalyse the reaction. The order with respect to iodine is unknown. The rate equation is

$$\text{Rate} = k[I_2]^x[CH_3COCH_3][H^+]$$

The aim of the experiment was to determine **x**.

a) The experiment proved that the order of the reaction with respect to iodine was zero. Copy the axes shown and sketch the graph which would be obtained.

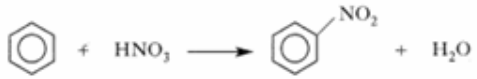


1

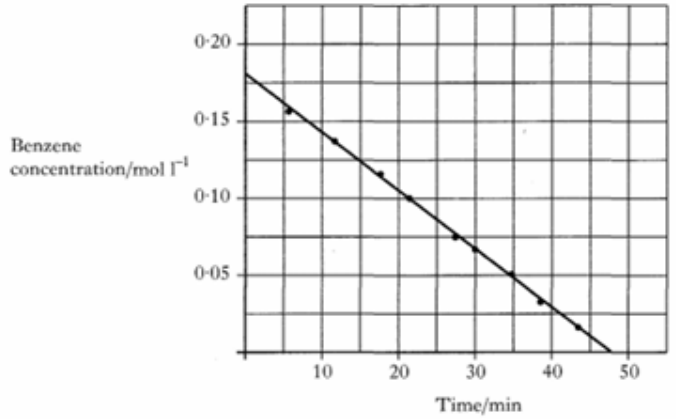
b) What is the overall order of the reaction? 1

c) What are the units for the rate constant, k? 1

23. Benzene can be nitrated by reaction with concentrated nitric acid.



The graph below shows the results obtained on nitrating benzene in an excess of concentrated nitric acid.



Results from a separate experiment showed the reaction to be first order with respect to nitric acid.

(*a*) (i) From the graph, deduce the order of the reaction with respect to benzene. 1

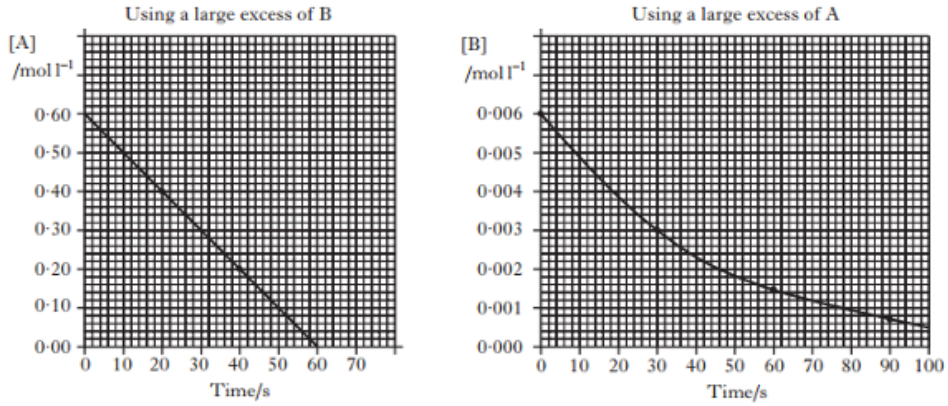
(ii) Write the rate equation for the reaction. 1

(iii) What must be the **minimum** number of steps in the reaction mechanism for it to be consistent with this rate equation? 1

Kinetics 2012

24 The graphs show how the concentrations of reactants A and B change with time for the reaction

$$A + B \rightarrow C$$



(a) What is the order of reaction with respect to A? **1**

(b) What is the order of reaction with respect to B? **1**

(c) What are the units of the rate constant in this reaction? **1**

25 Consider the three reactions and their rate equations

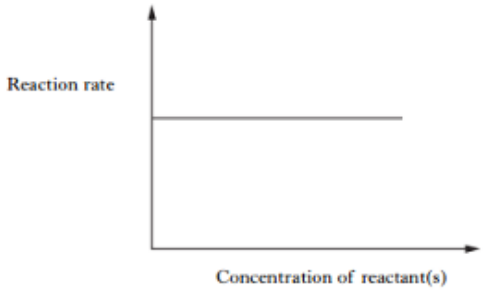
Reaction (1) $2N_2O_5 \rightarrow 4NO_2 + O_2$ Rate = $k[N_2O_5]$

Reaction (2) $2NO + Cl_2 \rightarrow 2NOCl$ Rate = $k[NO]^2[Cl_2]$

Reaction (3) $2NH_3 \rightarrow N_2 + 3H_2$ Rate = $k[NH_3]^0$

(a) What is the overall order of Reaction (2)? **1**

(b) The graph below was plotted using experimental results from one of the reactions.



Explain which of the reactions would give this graph. **1**

(c) For Reaction (2), when the concentrations of NO and Cl_2 are both 0·250 mol l^{-1}, the initial reaction rate is $1{\cdot}43 \times 10^{-6}$ mol l^{-1} s^{-1}.

Use this information to calculate the rate constant, k, including the appropriate units. **2**

Kinetics 2014

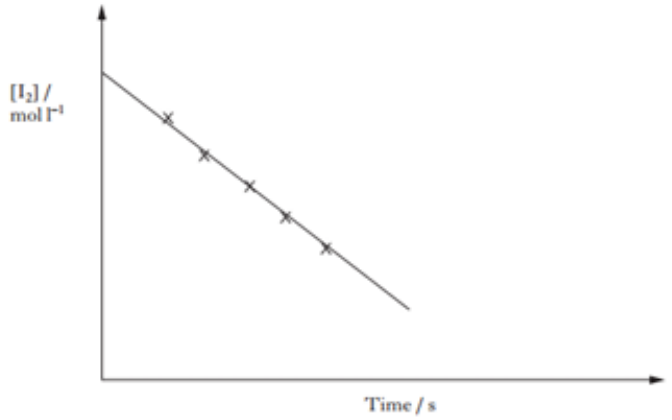
26

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + HI(aq)$$

The reaction between propanone and iodine is first order with respect to both propanone and hydrogen ions.

In a PPA the order with respect to iodine was determined by using very high initial concentrations of propanone and hydrogen ions compared with that of iodine. Samples of the reaction mixture were removed at regular intervals and added to a solution that essentially stopped the reaction. The iodine concentration was then determined by titration using starch solution as an indicator.

(*d*) The graph shows how the iodine concentration varies as the reaction proceeds.



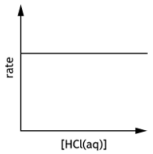
From the graph above determine the order of the reaction with respect to iodine. **1**

Kinetics Answers

1. B
2. D
3. A
4. B
5. B
6. A
7. B
8. A
9. B
10. B
11. D
12. B
13. D
14. D
15. B
16. B
17. B
18. A
19. C
20. D
21. D
22. A
23. C

1a (i) 1st order

(ii)



(iii) Rate = $k[Na_2S_2O_3(aq)]$

(iv) 0.131 s^{-1}

$$k = \frac{\text{rate}}{[Na_2S_2O_3]} = \frac{6.55\times10^{-3}\ \text{mol l}^{-1}\ \text{s}^{-1}}{5.00\times10^{-2}\ \text{mol l}^{-1}} = 0.131\ \text{s}^{-1}$$

2 a (i) Second.

(ii) 1.15 l $mol^{-1}s^{-1}$

$$k = \frac{\text{rate}}{[CH_3CHO][OH^-]} = \frac{1.72\times10^{-3}\ \text{mol l}^{-1}\ \text{s}^{-1}}{0.100\ \text{mol l}^{-1} \times 0.0150\ \text{mol l}^{-1}} = 1.15\ \text{l mol}^{-1}\ \text{s}^{-1}$$

(iii) Step 1

AND

CH_3CHO and OH^- are involved

3. a (i) 1st/first

(ii) 2nd/second

b Rate = $k\ [HgCl_2]\ [C_2O_4^{2-}]^2$

c (i) $2{\cdot}56 \times 10^{-4}$ $l^2\ mol^{-2}\ s^{-1}$

$$k = \frac{\text{rate}}{[HgCl_2][C_2O_4^{2-}]^2} = \frac{0.860\times10^{-6}\ \text{mol l}^{-1}\ \text{s}^{-1}}{0.0840\ \text{mol l}^{-1} \times (0.200)^2\ \text{mol}^2\ \text{l}^{-2}} = 2.56\times10^{-4}\ \text{l}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

(ii) 0·508 (mol l^{-1})

$$\text{Rate} = k \times [HgCl_2] \times [C_2O_4^{2-}]^2$$
$$2.11\times10^{-6} = 2.56\times10^{-4} \times 0.0320 \times [C_2O_4^{2-}]^2$$

$$[C_2O_4^{2-}]^2 = \frac{2.11\times10^{-6}}{2.56\times10^{-4} \times 0.0320} = 0.258\ \text{mol}^2\ \text{l}^{-2}$$

$$[C_2O_4^{2-}] = \sqrt{0.258}\ \text{mol l}^{-1} = 0.508\ \text{mol l}^{-1}$$

Kinetics Answers

4. a Rate = $k[NO(g)]^2[H_2(g)]$

b (i) $[NO]^2 = \frac{Rate}{K[H_2]} = \frac{0.0040}{2.7\times10^3 \times 0.015} = 9.87\times10^{-5}$

$[NO] = 9.94\times10^{-3}$ mol l^{-1}

(ii) $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ State symbols are not required but any that are given must be correct.

5 (i) second

(ii) 5200 l mol^{-1} s^{-1} $k = \frac{rate}{[[Ni(OH_2)_6]^{2+}][NH_3]} = \frac{1.3\times10^2 \text{ mol } l^{-1} s^{-1}}{0.10 \text{ mol } l^{-1} \times 0.25 \text{ mol } l^{-1}} = 5200 \text{ l mol}^{-1} s^{-1}$

6. a) The number of particles of reactant(s) involved in the rate determining step/slowest step.

b (i) second

(ii) Rate = $k[H_2O_2][I^-]$

c) $H_2O_2(aq) + 2I^-(aq) + 2H_3O^+(aq) \rightarrow I_2(aq) + 4H_2O(l)$ State symbols are not required but any that are given must be correct.

7 (i) rate = $k[C_4H_9Br][OH^-]$

(ii) $1\cdot3 \times 10^{-4}$ l mol^{-1} s^{-1}

$rate = k[C_4H_9Br][OH^-]$

$k = \frac{rate}{[C_4H_9Br] \times [OH^-]}$

$= \frac{3.3\times10^{-6} \text{ mol } l^{-1} s^{-1}}{0.25 \text{ mol } l^{-1} \times 0.10 \text{ mol } l^{-1}}$

$= 1.32\times10^{-4}$ l mol^{-1} s^{-1}

8 (i) Rate = $k [V^{3+}(aq)] [Fe^{3+}(aq)]$

(ii) Zero order / 0

Fe^{3+} is not a reactant in slow step /RDS

9. (i) 2nd order/2 (A) 1st order/1. (B)

(ii) Rate = $k [ClO_2]^2 [OH^-]$

(iii) 230 l^2 mol^{-2} s^{-1}

10 (i) $x = 7\cdot40 \times 10^{-4} / 7.4 \times 10^{-4}$

$y = 2\cdot96 \times 10^{-3} / 3\cdot0 \times 10^{-3}$

(ii) 185 l mol^{-1} s^{-1} $k = \frac{7\cdot40\times10^{-4}}{(2\cdot00\times10^{-3})^2}$

11a (i) 1 or first

(ii) 0 or zero

b (i) Rate = $k[CH_3CHIC_2H_5]$

(ii) Accept $(1\cdot37 - 1\cdot45) \times 10^{-3}$ s^{-1}

$k = \frac{rate}{[CH_3CHIC_2H_5]}$

$= \frac{1\cdot4 \times 10^{-4} \text{ mol } l^{-1} s^{-1}}{0\cdot10 \text{ mol } l^{-1}}$

$= 1.4 \times 10^{-3} s^{-1}$

12 (i) First order

(ii) Zero order

b) Rate = $k[C_4H_9Br]$

c) $187\cdot5$ s^{-1} $k = Rate/[C_4H_9Br] = 0\cdot15/8\cdot0 \times 10^{-4} =$

13 a) Step two

b) $2NO_2 + F_2 \rightarrow 2NO_2F$ OR $NO_2 + \frac{1}{2}F_2 \rightarrow NO_2F$

c) 2nd order **or** 2

d) k = Initial rate/$[NO_2][F_2]$ = **40 l mol $^{-1}$s^{-1}**

Kinetics Answers

14. Rate = $k[CH_3COCH_3]\,[H_3O^+]$

15. (i) 2nd order

(ii) 1.32×10^{-4} or 1.3×10^{-4} $l\,mol^{-1}\,s^{-1}$ Rate = $k[OH^-][1\text{-bromobutane}]$

$$k = \frac{3 \cdot 3 \times 10^{-6}}{0 \cdot 1 \times 0 \cdot 25} = 1.32 \times 10^{-4} \text{ or } 1.3 \times 10^{-4}$$

16. a (i) First or 1 (ii) Zero or 0

b Rate = $k[C_4H_9Br]$

c $187 \cdot 5\ s^{-1}$ $k = \text{Rate}/[C_4H_9Br]$

$0 \cdot 15/8 \cdot 0 \times 10^{-4}$

17. a (i) 1/1st order

(ii) 1/1st order

b Rate = $k[H_2O_2][HI]$

C 0.0328/0.033 $mol^{-1}\,l\,s^{-1}$ $k = \dfrac{\text{Rate}}{[H_2O_2][HI]}$

$$= \frac{4.3 \times 10^{-9}}{3.2 \times 10^{-4} \times 4.1 \times 10^{-4}}$$

18. (i) 1st order wrt $[BrO_3^-]$
1st order wrt $[Br^-]$
2nd order wrt $[H^+]$

(ii) Rate = $k\,[BrO_3^-]\,[Br^-]\,[H^+]^2$

(iii) 8 $l^3mol^{-3}\,s^{-1}$ $k = \dfrac{\text{rate}}{[BrO_3^-][Br^-][H^+]^2} = \dfrac{5 \times 10^{-5}\ mol\ l^{-1}\ s^{-1}}{(0.05\ mol\ l^{-1}) \times (0.05\ mol\ l^{-1}) \times (0.05 mol\ l^{-1})^2} =$

19. (i) Second order or 2

(ii) 5.97×10^9 l $mol^{-1}s^{-1}$ Rate = $k\,[O][NO_2]$

$$k = \frac{\text{rate}}{[O][NO_2]} = \frac{6.10 \times 10^{-17}\ mol\ l^{-1}s^{-1}}{(9.20 \times 10^{-15} mol\ l^{-1}) \times (1.11 \times 10^{-12} mol\ l^{-1})} =$$

20. (i) Rate = $k[H_2O_2]\,[I^-]$

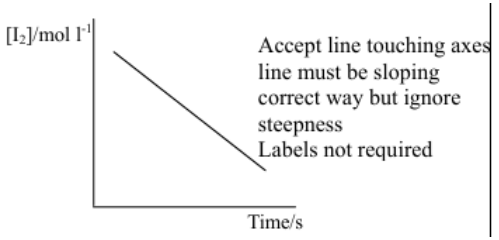
(ii) 2.3×10^{-2} $mol^{-1}\,l\,s^{-1}$ $k = \dfrac{\text{Rate}}{[H_2O_2] \times [I^-]}$

$$= \frac{2.07 \times 10^{-3}}{0.3 \times 0.3}$$

21 a) Rate = $k[CR_3Br]$

b) x = 2
y = 0.5

22. a)



b) 2 or 2nd order

c) $mol^{-1}\,l\,s^{-1}$

23 (i) Zero order

(ii) Rate = $k\,[HNO_3]$

(iii) 2

Benzene is not involved in the slow rate determining step
Mechanism must have a 2nd faster step which benzene takes part in.

Kinetics Answers

24. a) Zero or 0

b) First or 1

c) s^{-1}

25 a) Third order/3rd/3

b) Reaction 3

Concentration of reactant has no effect on rate

c) $\mathbf{9{\cdot}15 \times 10^{-5}\ \ l^2\ mol^{-2}\ s^{-1}}$ $\quad k = \dfrac{\text{Rate}}{[NO]^2[Cl_2]}$

$$\frac{1{\cdot}43 \times 10^{-6}}{(0{\cdot}250)^2(0{\cdot}250)}$$

26. 0 or zero order