AH Exercise 1.6

Kinetics

2002 AH MC14 (74%) and 2006 AH MC25 (81%)

14. 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].

2004 AH MC27 (68%)

27. A suggested mechanism for the reaction

$$2A + B \rightarrow A_2B$$

is a two-step process

$$A + B \rightarrow AB \text{ (slow)}$$

$$AB + A \rightarrow A_2B \text{ (fast)}$$

This mechanism is consistent with the rate equation

A rate = k[A]^2 [B]

B rate = k[A] [B]

C rate = k[A] [A_2B]

D rate = k[AB].

2006 AH MC24 (71%)

24. For the reaction

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

the suggested mechanism is

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

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

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].

2009 AH MC21 (85%)

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

$$X + Y + Z \rightarrow \text{products}$$

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]

2014 AH MC23 (67%) and 2014 revAH MC14 (74%)

23. 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].

2015 AH MC24 (71%)

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

2001 AH MC7 (49%)

7. 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.

2009 AH MC20 (84%)

20. For the reaction

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

the rate equation is

rate = $k[NO]\,[Cl_2]$.

The overall order of this reaction is

A 1

B 2

C 3

D 5.

2016 AH MC11 (70%)

11. For the reaction

$2A + 2B \rightarrow C$

the rate equation is

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)

2003 AH MC21 (65%)

21. 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 correct?

A The reaction occurs by a simple one step mechanism.

B The reaction is second order overall.

C If the initial concentration of Q is doubled, the rate of the reaction will be doubled.

D As the reaction proceeds its rate will decrease.

2007 AH MC24 (71%)

24. 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.

2005 AH MC25 (57%)

25. 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.

2014 AH MC24 (52%) and 2014 revAH MC13 (71%)

24. The order of a reaction

A can only be obtained by experiment

B determines the speed of the overall reaction

C is determined by the stoichiometry involved

D is the sequence of steps in the reaction mechanism.

2015 AH MC25 (60%)

25. $2P + Q \rightleftharpoons R + S \quad \Delta G^\circ = +40\,kJ\,mol^{-1}$

Which of the following **cannot** be deduced from the above information?

A The feasibility of the reaction

B The order of the reaction

C The stoichiometry of the reaction

D The position of equilibrium

2015 AH MC26 (73%)

26. 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.

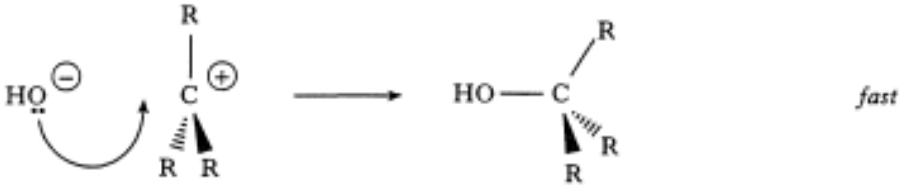
8. Bromoalkanes undergo nucleophilic substitution when heated with aqueous sodium hydroxide solution.

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

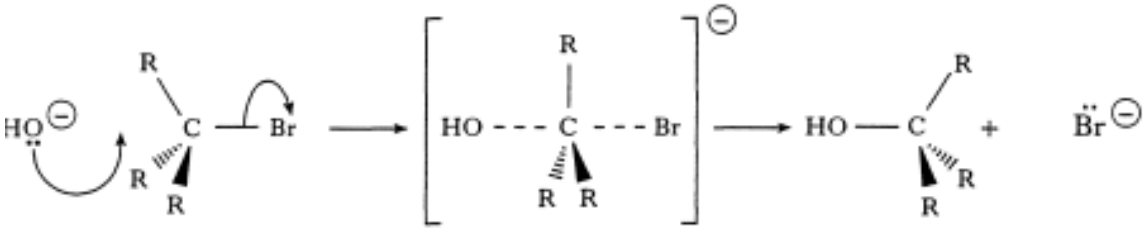
(where R = H and/or an alkyl group)

Two possible mechanisms for the reaction are outlined below.

Mechanism 1 (two-step process):



Mechanism 2 (single-step process):



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

(*c*) 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**

2003 AH L9a+b

9. 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	$2{\cdot}07 \times 10^{-3}$
2	0·6	0·3	0·002	$4{\cdot}14 \times 10^{-3}$
3	0·3	0·6	0·002	$4{\cdot}14 \times 10^{-3}$
4	0·3	0·3	0·004	$2{\cdot}07 \times 10^{-3}$

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

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

2004 AH L7c

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

(*c*) 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 $l^{-1}s^{-1}$
$9{\cdot}20 \times 10^{-15}$	$1{\cdot}11 \times 10^{-12}$	$6{\cdot}10 \times 10^{-17}$
$1{\cdot}81 \times 10^{-14}$	$1{\cdot}11 \times 10^{-12}$	$1{\cdot}20 \times 10^{-16}$
$1{\cdot}81 \times 10^{-14}$	$2{\cdot}23 \times 10^{-12}$	$2{\cdot}41 \times 10^{-16}$

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

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

2005 AH L7b

7. 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	$5{\cdot}0 \times 10^{-5}$
2	0·10	0·05	0·05	$1{\cdot}0 \times 10^{-4}$
3	0·10	0·10	0·05	$2{\cdot}0 \times 10^{-4}$
4	0·05	0·05	0·10	$2{\cdot}0 \times 10^{-4}$

(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**

2007 AH L5

4. 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**

2008 AH L10d

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

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

(*d*) 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	$3{\cdot}3 \times 10^{-6}$
2	0·50	0·10	$6{\cdot}6 \times 10^{-6}$
3	0·50	0·20	$1{\cdot}3 \times 10^{-5}$

(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**

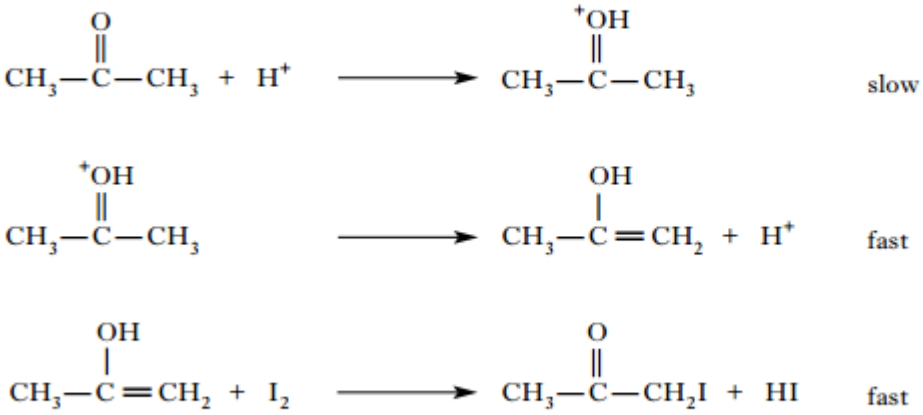
(iii) Outline the mechanism for this nucleophilic substitution reaction using structural formulae. **2**

2009 AH L7a

7. Iodine reacts with propanone as follows.

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

A possible mechanism for this reaction is



(*a*) Write a rate equation for this reaction based on the above mechanism. **1**

2010 AH L9

9. 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**

2013 AH L8a+b+c

8. 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**

2014 AH L10 and 2014 revAH L11

10. 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**

2015 AH L5b and 2015 revAH L6b

5. Nitrogen forms a variety of oxides.

(*b*) 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**

2016 AH L6b

6. Chlorine is a versatile element which forms a wide range of compounds.

(b) Chloride 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

2006 AH L7b+c+d

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

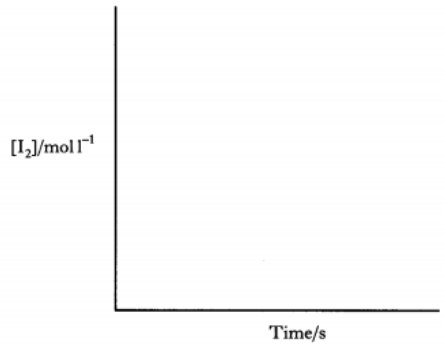
$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I(aq) + HI(aq)$$

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

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

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

(*b*) 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.



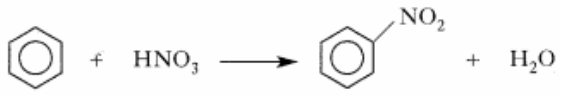
1

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

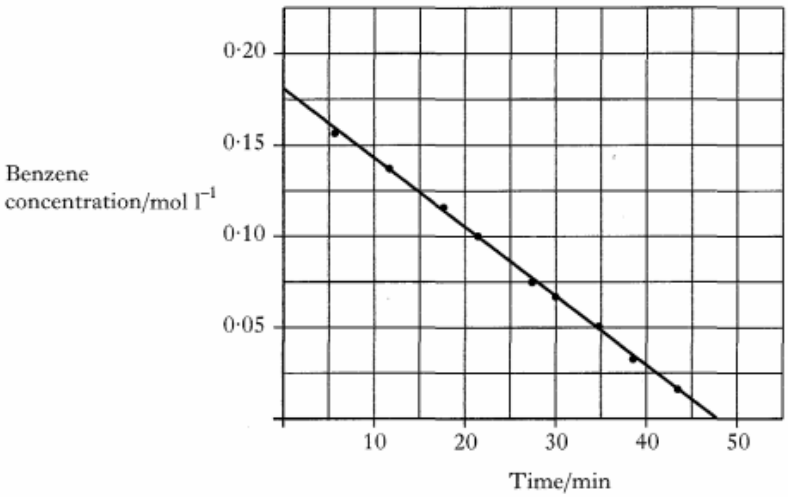
(*d*) What are the units for the rate constant, k? 1

2002 AH L5a

5. 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**

2014 AH L11d

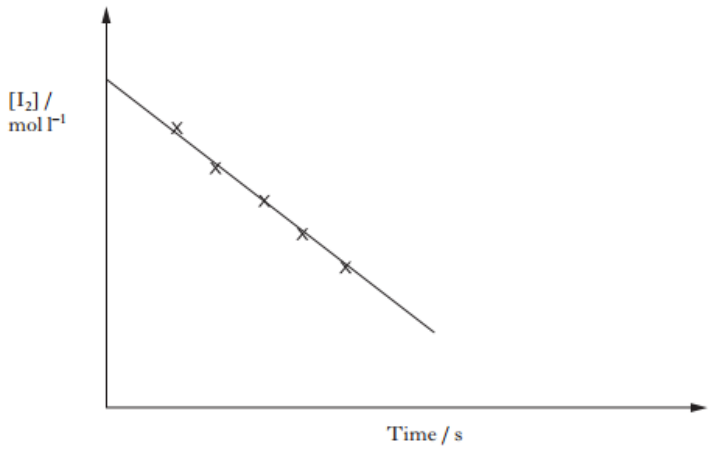
11.

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

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.

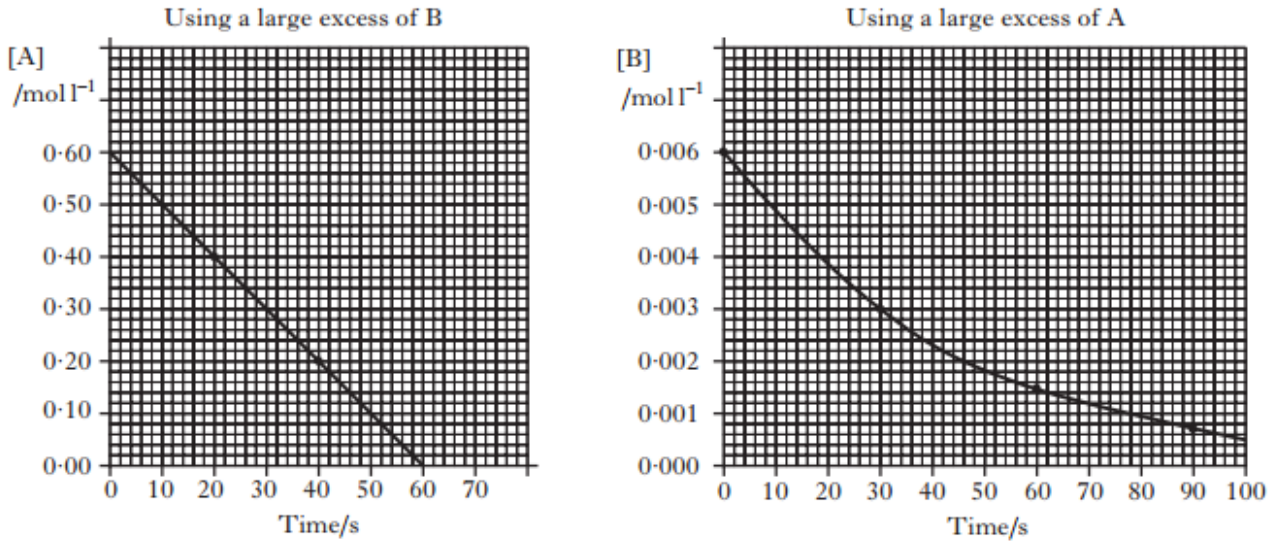


From the graph above determine the order of the reaction with respect to iodine. **1**

2012 AH L10

10. 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**

2011 AH L7

7. Consider the three reactions and their rate equations

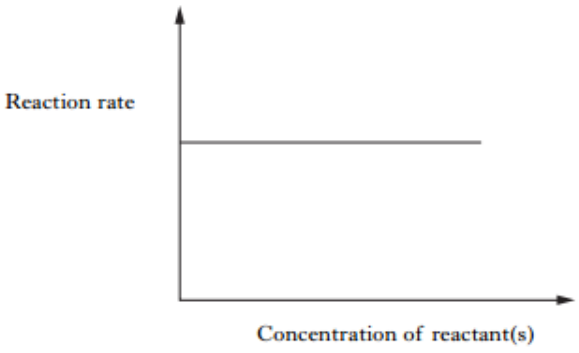
Reaction (1) $2N_2O_5 \longrightarrow 4NO_2 + O_2$ Rate = $k[N_2O_5]$

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

Reaction (3) $2NH_3 \longrightarrow N_2 + 3H_2$ 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**