

Kinetics

Rate determining step

1. For each of the everyday processes described below, identify the step that slows the process down.

(a) Making a cup of tea

Step 1: Get a mug out of the cupboard

Step 2: Add a tea bag

Step 3: Boil the water

Step 4: Leave the tea bag to stew

(b) Playing with a model helicopter received as a Christmas present

Step 1: Spot the present under the tree

Step 2: Unwrap the present

Step 3: Charge the batteries for 24 h

Step 4: Play with the helicopter

(c) Getting out of the house in the morning on time

Step 1: Alarm goes off

Step 2: Get out of bed

Step 3: Have a shower

Step 4: Eat breakfast

(3 marks)

The overall rate of these processes is controlled by the *rate of the slowest step*. For a chemical reaction we call this step the **rate determining** or **rate limiting step**.

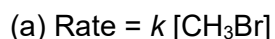
For each of the multi-step reactions below, write the overall equation for the reaction and identify the rate limiting step.

2. **Step 1:** $\text{CH}_3\text{Br} \xrightarrow{\text{slow}} \text{CH}_3^+ + \text{Br}^-$
Step 2: $\text{CH}_3^+ + \text{OH}^- \xrightarrow{\text{fast}} \text{CH}_3\text{OH}$
Overall equation
Rate limiting step
3. **Step 1:** $\text{NO} + \text{NO} \xrightarrow{\text{slow}} \text{N}_2\text{O}_2$
Step 2: $\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{\text{fast}} 2 \text{NO}_2$
Overall equation
Rate limiting step
4. **Step 1:** $\text{NO} + \text{NO} \xrightarrow{\text{fast}} \text{N}_2\text{O}_2$
Step 2: $\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{\text{slow}} \text{N}_2\text{O} + \text{H}_2\text{O}$
Step 3: $\text{N}_2\text{O} + \text{H}_2 \xrightarrow{\text{fast}} \text{N}_2 + \text{H}_2\text{O}$
Overall equation
Rate limiting step
(6 marks)

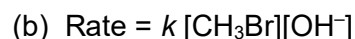
BONUS MARK

In a chemical reaction, any step that occurs after the rate determining step will not affect the rate. Therefore any species that are involved in the mechanism after the rate determining

step do not appear in the rate expression. Use this information to predict which of the options below is the correct rate expression for the reaction shown in question 2.



or



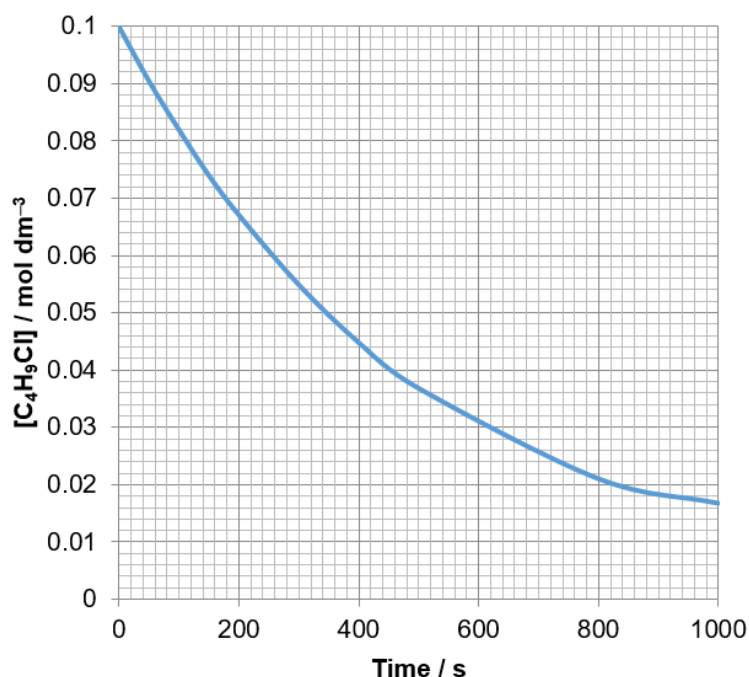
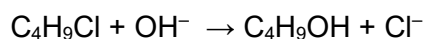
(1 mark)

Calculating reaction rate

1. What is the definition for *the rate of a reaction*?

(2 marks)

2. A simple way to determine the rate of a reaction is to measure the change in concentration of one reagent with time. The graph below shows the change in concentration of $[\text{C}_4\text{H}_9\text{Cl}]$ during the reaction;



- (a) Use the graph to calculate the rate of reaction at;

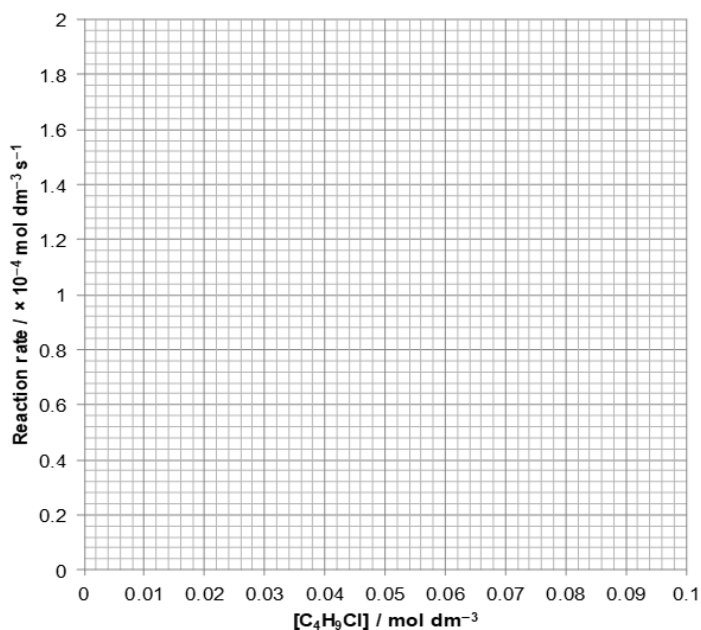
i. $t = 0 \text{ s}$

ii. $t = 200 \text{ s}$
.....
.....

iii. $t = 600 \text{ s}$

(4 marks)

- (b) Use the values for the reaction rate you have calculated to sketch a graph of reaction rate (y-axis) against $[C_4H_9Cl]$ (x-axis). (3 marks)



- (c) From your graph, is the reaction zero order, first order or second order with respect to $[C_4H_9Cl]$?

.....

(1 mark)

Measuring reaction rate in the lab

The rate of a reaction is defined as *the change in concentration of reactants or products per unit time*. The units of rate are $\text{mol dm}^{-3} \text{s}^{-1}$.

The method chosen to measure the rate of a reaction depends on the individual reaction. For each of the reactions below, use the observations made to **calculate the initial rate of the reaction**.

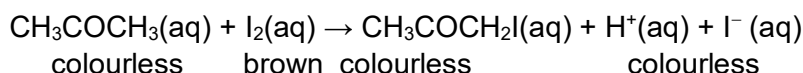
1. Measuring the rate of a reaction when a precipitate is formed;



A student wished to investigate how temperature affected the rate of the reaction between sodium thiosulfate and acid. He reacted 10 cm^3 of a 0.02 mol dm^{-3} solution of sodium thiosulfate with 40 cm^3 of hydrochloric acid (excess) at $22 \text{ }^\circ\text{C}$. The time taken to produce a precipitate of $1 \times 10^{-4} \text{ mol}$ of sulfur was found to be 56 s.

Initial rate of production of sulfur = _____ $\text{mol dm}^{-3} \text{s}^{-1}$ (2 marks)

2. Measuring the rate of a reaction in which there is a change in colour;

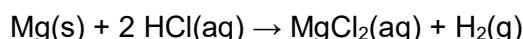


A student followed the reaction between iodine and propanone to produce iodopropanone. She set up the first experiment as described in the table below and found it took 279 s for the brown colour of the iodine to disappear.

| 2.0 mol dm^{-3} propanone / cm^3 | $1.0 \text{ mol dm}^{-3} \text{HCl}$ / cm^3 | $0.005 \text{ mol dm}^{-3} \text{I}_2$ / cm^3 | H_2O / cm^3 | Time / s |
|--|---|---|--------------------------------------|----------|
| 5 | 5 | 2 | 13 | 279 |

Initial rate of loss of iodine = $\text{mol dm}^{-3} \text{s}^{-1}$ (3 marks)

3. Measuring the rate of a reaction in which a gas is produced;



The student reacted a 3 cm strip of magnesium ribbon with 25 cm^3 of $2.0 \text{ mol dm}^{-3} \text{HCl}$ (an excess). He found that 14 cm^3 of gas was produced in the first 10 seconds of the reaction.

(You may assume the reaction was carried out at RTP where 1 mole of gas has a volume of 24 dm^3 .)

Initial rate of loss of hydrochloric acid = _____ $\text{mol dm}^{-3} \text{s}^{-1}$ (4 marks)

Determining the rate equation

For each of the following sets of experimental data determine;

- The rate equation for the reaction,
- The value of the rate constant, k including its units.

1.

| Experiment | [A] / mol dm ⁻³ | [B] / mol dm ⁻³ | Initial rate of loss of [A] / mol dm ⁻³ s ⁻¹ |
|------------|----------------------------|----------------------------|--|
| 1 | 1.20×10^{-3} | 3.30×10^{-3} | 4.02×10^{-4} |
| 2 | 1.20×10^{-3} | 6.60×10^{-3} | 4.02×10^{-4} |
| 3 | 2.40×10^{-3} | 6.60×10^{-3} | 1.61×10^{-3} |

Rate =

k = (3 marks)

2.

| | Run 1 | Run 2 | Run 3 |
|---|----------------------|----------------------|----------------------|
| [A] / mol dm ⁻³ | 0.15 | 0.30 | 0.45 |
| [B] / mol dm ⁻³ | 0.10 | 0.10 | 0.20 |
| $\frac{-d[B]}{dt}$ / mol dm ⁻³ s ⁻¹ | 2.5×10^{-4} | 2.5×10^{-4} | 5.0×10^{-4} |

Rate =

k = (3 marks)

3.

| Experiment | [X] / mol dm ⁻³ | [Y] / mol dm ⁻³ | [Z] / mol dm ⁻³ | Initial rate / mol dm ⁻³ s ⁻¹ |
|------------|----------------------------|----------------------------|----------------------------|---|
| 1 | 0.05 | 0.10 | 0.15 | 5.20×10^{-4} |
| 2 | 0.10 | 0.10 | 0.15 | 2.08×10^{-3} |
| 3 | 0.05 | 0.10 | 0.30 | 5.20×10^{-4} |
| 4 | 0.15 | 0.05 | 0.15 | 2.34×10^{-3} |

Rate =

k = (4 marks)

Arrhenius and rate

1. A reaction between A and B was found to be first order with respect to both.

(a) Write the rate equation for the reaction

(1 mark)

(b) The rate constant k varies with temperature. Use the data together with the rate equation you have written in part (a) to complete the table below;

(4 marks)

| Temperature / K | [A] / mol dm ⁻³ | [B] / mol dm ⁻³ | Rate / mol dm ⁻³ s ⁻¹ | k / mol ⁻¹ dm ³ s ⁻¹ |
|-----------------|----------------------------|----------------------------|---|---|
| 288 | 0.015 | 0.030 | 2.70×10^{-8} | |
| 313 | 0.015 | 0.015 | 2.16×10^{-7} | |
| 338 | 0.030 | 0.030 | 9.18×10^{-6} | |
| 363 | 0.030 | 0.015 | 3.52×10^{-5} | |

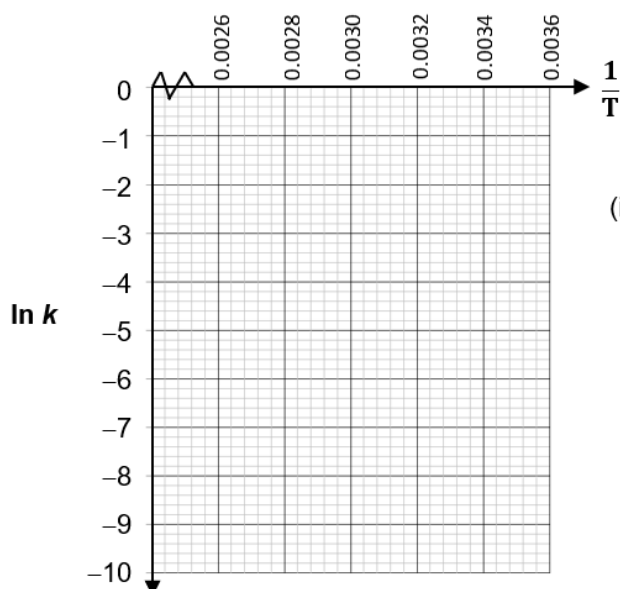
(c) A scientist wishes to use this data to determine the activation energy for the reaction. He can do this using the Arrhenius equation;

$$k = A e^{-E_A/RT} \quad \text{where}$$

k is the rate constant
 E_A is the activation energy
 T is the temperature in Kelvin
 R is the gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$)
 A is a constant

A more useful form of the same equation is, $\ln k = \ln A - \frac{E_A}{R} \left(\frac{1}{T}\right)$. A graph of $\ln k$ vs $\frac{1}{T}$ is therefore a straight line with a gradient equal to $-\frac{E_A}{R}$.

(i) Use the axes below to plot a graph of $\ln k$ vs $\frac{1}{T}$ for the data calculated in part (b). (4 marks)



(ii) Therefore calculate the value of the activation energy, E_A , for this reaction.

.....
(1 mark)

Kinetics – Answers

Rate determining step

- (a) Step 3 Boil the water
(b) Step 3 Charge the batteries for 24 h
(c) Step 2 Get out of bed (although this may depend on the individual!)

(3 marks)
 - Overall equation: $\text{CH}_3\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Br}^-$
Rate limiting step: $\text{CH}_3\text{Br} \rightarrow \text{CH}_3^+ + \text{Br}^-$ (Step 1)

(2 marks)
 - Overall equation: $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$
Rate limiting step: $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$ (Step 1)

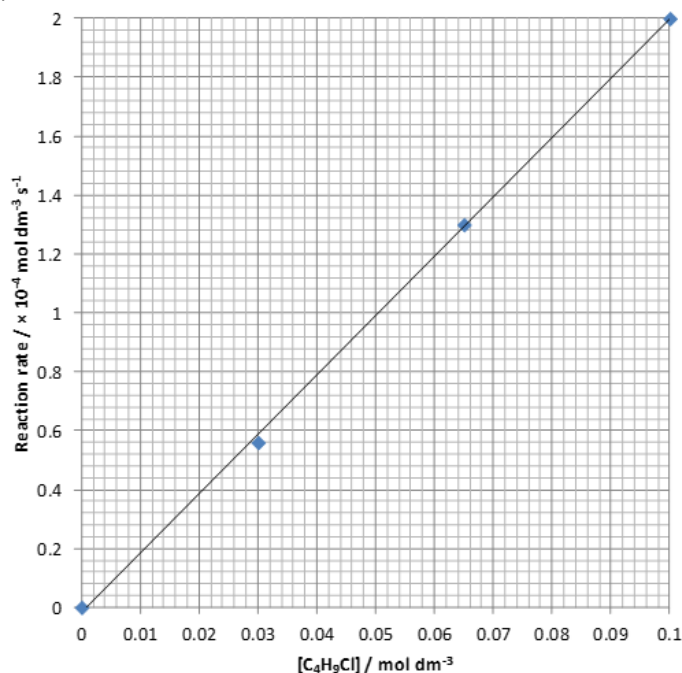
(2 marks)
 - Overall equation: $2 \text{NO} + 2 \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$
Rate limiting step: $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (Step 2)

(2 marks)
- BONUS MARK** Answer = (a) Rate = $k [\text{CH}_3\text{Br}]$
- (1 mark)

Calculating reaction rate

- The rate of a reaction is the change in concentration of reactants or products per unit time
(2 marks)
- (a) i. $2.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
ii. $1.3 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
iii. $5.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$
(1 mark for each correct value, 1 mark for the correct units for rate)

(b)



(3 marks)

(c) The reaction is first order with respect to $\text{C}_4\text{H}_9\text{Cl}$.

(1 mark)

Measuring reaction rate in the lab

1. Change in concentration of sulfur = $(1 \times 10^{-4} \text{ mol} - 0 \text{ mol}) / 0.05 \text{ dm}^3 = 2 \times 10^{-3} \text{ mol dm}^{-3}$
(1 mark)

Initial rate of production of sulfur = $2 \times 10^{-3} \text{ mol dm}^{-3} / 56 \text{ s} = \underline{3.6 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}}$
(1 mark)

2. Moles of iodine in reaction mixture at start = $0.002 \text{ dm}^3 \times 0.005 \text{ mol dm}^{-3} = 1 \times 10^{-5} \text{ mol}$
(1 mark)

Change in concentration of iodine = $(1 \times 10^{-5} \text{ mol} - 0 \text{ mol}) / 0.025 \text{ dm}^3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$
(1 mark)

Initial rate of loss of iodine = $4 \times 10^{-4} \text{ mol dm}^{-3} / 279 \text{ s} = \underline{1.4 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}}$
(1 mark)

3. Moles in 14 cm^3 of hydrogen at RTP = $0.014 \text{ dm}^3 / 24 \text{ dm}^3 = 5.8 \times 10^{-4} \text{ mol}$
(1 mark)

Moles of acid used up to produce this many moles of hydrogen = $5.8 \times 10^{-4} \text{ mol} \times 2 = 1.17 \times 10^{-3} \text{ mol}$
(1 mark)

Change in concentration of acid = $1.17 \times 10^{-3} \text{ mol} / 0.025 \text{ dm}^3 = 0.047 \text{ mol dm}^{-3}$
(1 mark)

Initial rate of loss of hydrochloric acid = $0.047 \text{ mol dm}^{-3} / 10 \text{ s} = \underline{0.0047 \text{ mol dm}^{-3} \text{ s}^{-1}}$
(1 mark)

Determining the rate equation

1. Rate = $k[A]^2$; $k = 280 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
(2 marks for the identification of the correct order wrt A and B, 1 mark for k with correct units)

2. Rate = $k[B]$; $k = 2.5 \times 10^{-3} \text{ s}^{-1}$
(2 marks for the identification of the correct order wrt A and B, 1 mark for k with correct units)

3. Rate = $k[X]^2[Y]$; $k = 2.08 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$
(3 marks for the identification of the correct order wrt X, Y and Z, 1 mark for k with correct units)

Arrhenius and rate

1. (a) Rate = $k[A][B]$

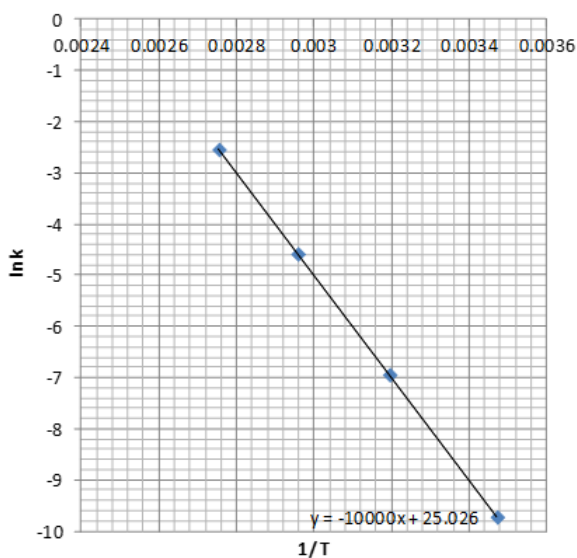
(1 mark)

(b)

| Temperature / K | [A] / mol dm ⁻³ | [B] / mol dm ⁻³ | Rate / mol dm ⁻³ s ⁻¹ | k / mol ⁻¹ dm ³ s ⁻¹ |
|-----------------|----------------------------|----------------------------|---|---|
| 288 | 0.015 | 0.030 | 2.70×10^{-8} | <u>6.0×10^{-5}</u> |
| 313 | 0.015 | 0.015 | 2.16×10^{-7} | <u>9.6×10^{-4}</u> |
| 338 | 0.030 | 0.030 | 9.18×10^{-6} | <u>0.010</u> |
| 363 | 0.030 | 0.015 | 3.52×10^{-5} | <u>0.078</u> |

(c)

(i)



| $1/T$ | $\ln k$ |
|---------|---------|
| 0.00347 | -9.72 |
| 0.00319 | -6.95 |
| 0.00296 | -4.59 |
| 0.00275 | -2.55 |

(4 marks)

(ii) Gradient = - 10000, $\therefore \frac{E_A}{R} = 10000$. Therefore $E_A = \underline{83100 \text{ J or } 83.1 \text{ kJ}}$

(1 mark)