

KINETICS



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SECTION 1 – Recap of AS Kinetics

What is reaction rate?

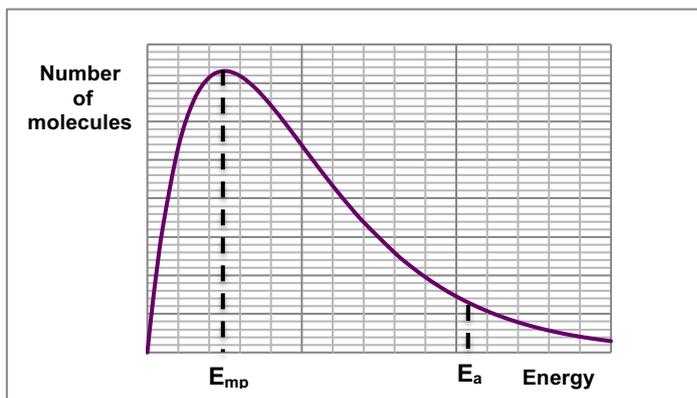
- The rate of a chemical reaction is a measure of how fast a reaction takes place.
- It is defined as the change in concentration of a reactant or product per unit time.
- For example, in a reaction between magnesium and hydrochloric acid, the rate could be measured in terms of the change in concentration of the hydrochloric acid per second.

Collision theory

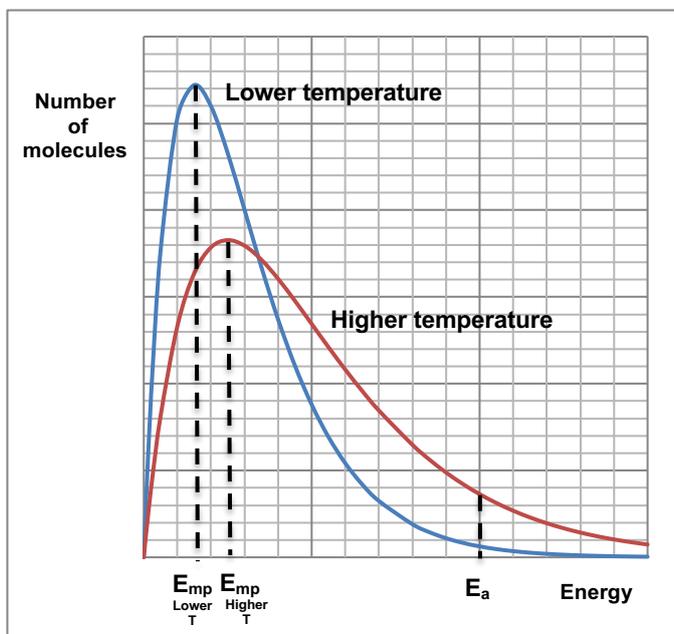
- For particles to react they must collide with sufficient energy to react and at the correct orientation.
- The minimum energy particles need to react is called the **activation energy**.

Maxwell-Boltzmann distribution

- The particles in substance do not all have the same amount of energy.
- The energy of the particles in a gas is shown by a Maxwell-Boltzmann distribution.
- There are no particles with no energy (i.e. they all have some energy).
- The area under the curve represents the total number of particles.
- The peak of the curve gives the energy that more particles have than any other energy (sometimes labelled E_{mp} , i.e. most probable energy).
- The activation energy (E_a) can be shown on the axis. Often only a small proportion of molecules have energy greater than or equal to the activation energy.
- When particles collide with each other they gain or lose energy, and so the energy of each individual particle is constantly changing. This means that a particle that does not have enough energy to react may gain enough in a collision so that it can react in a further collision.



- As the temperature changes, the average energy of the particles increases and so the distribution curve changes. The total area under the curve stays the same as there are the same number of particles, and so the peak will move to higher energy but less particles will have that energy.

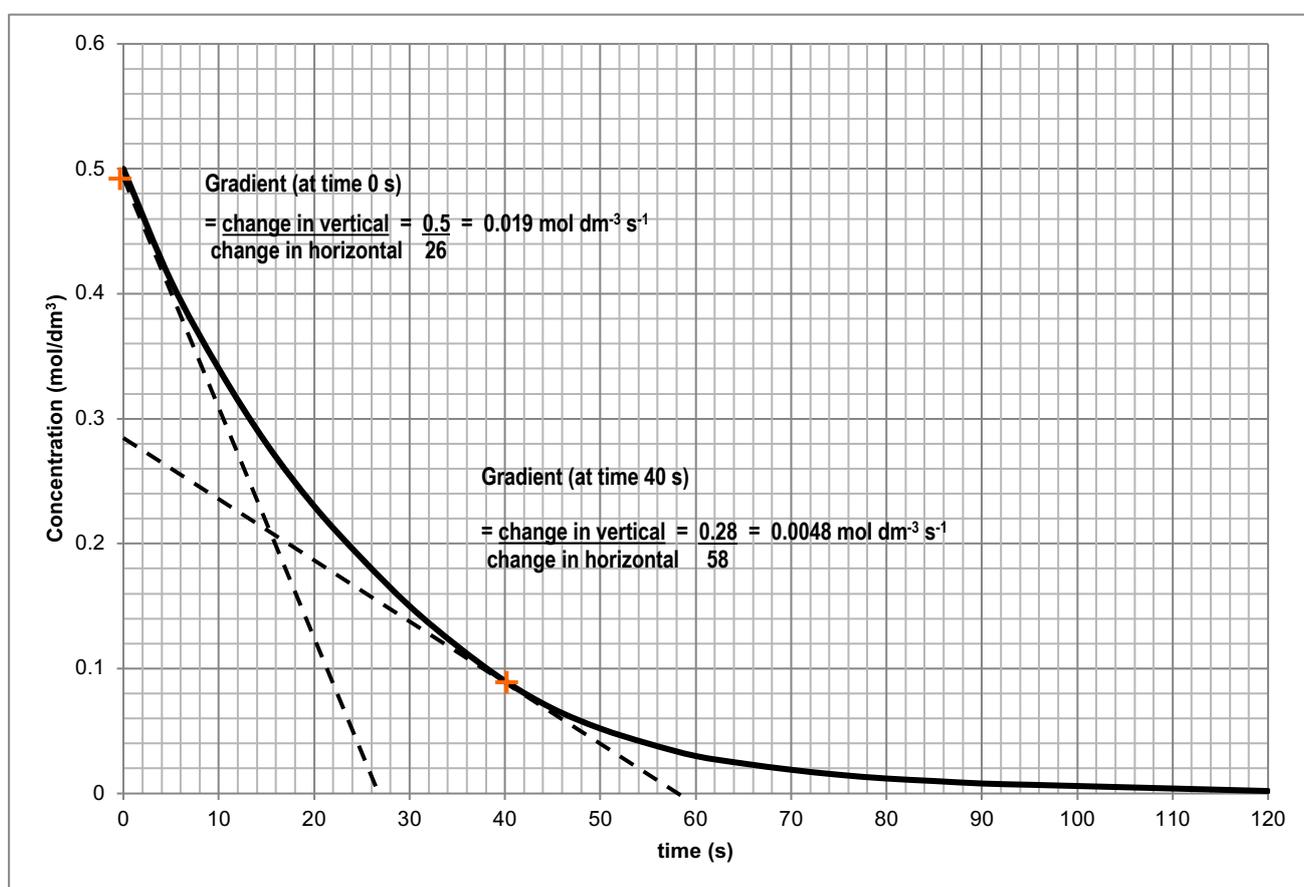


Factors affecting rates

Factor	Effect	Reason
Concentration of a solution	The higher the concentration, the faster the reaction (unless that reagent is zero order)	Particles are closer together and so there are more frequent successful collisions
Surface area of a solid	The more pieces a solid is broken up into, the greater the surface area (a powder has a massive surface area). The greater the surface area, the faster the reaction.	There are more particles exposed at the surface that can be collided with, and so there are more frequent successful collisions
Pressure of gases (gases that are reactants)	The higher the pressure, the faster the reaction (unless that reagent is zero order)	Particles are closer together and so there are more frequent successful collisions
Temperature	The higher the temperature, the faster the reaction.	Particles have more energy and so a greater proportion of the collisions are successful. The particles also move faster and so collisions are more frequent. Therefore there are more frequent successful collisions.
Catalyst	A catalyst is a substance that increases the rate of a reaction but is not used up.	It provides an alternative route / mechanism with a lower activation energy and therefore a greater proportion of the collisions are successful.

SECTION 2 – Finding rates using gradients

- Graphs can be plotted to show how the concentration of a reactant or product changes during the course of a reaction.
- The gradient of this graph at any time equals the rate of reaction at that time.
- The steeper the line, the faster the reaction.
- We can calculate the gradient by drawing a tangent to the line at any point (tip – make the gradient line quite long – if it is too short then there will be a larger degree of error in the gradient calculation stemming from reading the values)
- In the graph below, the rate at 0 seconds (the rate at the start – the **initial rate**) is $0.019 \text{ mol dm}^{-3} \text{ s}^{-1}$. The rate after 40 seconds is $0.0048 \text{ mol dm}^{-3} \text{ s}^{-1}$.
- Most reactions start faster and slow down due to there being less reactant particles as time goes on and so less frequent successful collisions between reactant particles.



TASK 1 – Finding rates using gradients

- 1** Magnesium reacts with hydrochloric acid to form hydrogen gas. The data below shows how the hydrochloric acid concentration varied with time.

Time (s)	0	10	20	30	40	50	60	70	80
[HCl] (mol dm ⁻³)	1.00	0.51	0.25	0.16	0.13	0.11	0.09	0.08	0.06

- a) Plot a graph of acid concentration against time.
b) By drawing gradients, calculate the rate at 0, 10, 20 and 30 seconds.
c) Explain why the rate changes during the reaction as it does.
- 2** Sodium reacts with water to form sodium hydroxide solution and hydrogen gas. The data below shows how the concentration of sodium hydroxide solution varies with time.

Time (s)	0	10	20	30	40	50	60	70	80
[NaOH] (mol dm ⁻³)	0.00	0.23	0.37	0.45	0.49	0.51	0.53	0.55	0.56

- a) Plot a graph of sodium hydroxide concentration against time.
b) By drawing gradients, calculate the rate at 0, 20 and 40 seconds.

SECTION 3 – Introduction to rate equations and orders

Consider any reaction where one of the reactants is A. By experiment the rate of the reaction can be related to the concentration of A:

$$\text{rate} \propto [\text{A}]^n \quad \text{where } [\] \text{ means concentration in mol dm}^{-3}$$

n is called the **order of reaction** with respect to that reactant, and is usually 2, 1 or 0

Order	Zero order	First order	Second order
n	0	1	2
The effect	the reaction rate is proportional to $[\text{A}]^0$ (= 1) and so the rate is not affected by changes in $[\text{A}]$	the reaction rate is proportional to $[\text{A}]$	the reaction rate is proportional to $[\text{A}]^2$
[A] x 2	rate unchanged	rate x 2	rate x 2^2 (i.e. x 4)
[A] x 3	rate unchanged	rate x 3	rate x 3^2 (i.e. x 9)
[A] x 10	rate unchanged	rate x 10	rate x 10^2 (i.e. x 100)
[A] is ÷ 2	rate unchanged	rate ÷ 2	rate ÷ 2^2 (i.e. ÷ 4)

Consider a reaction between A and B: $x \text{ A} + y \text{ B} \rightarrow \text{products}$

For any reaction the effects of the concentration of each individual reactant can be combined into a rate equation, which for the above reaction would be of the form:

$$\text{reaction rate} \propto [\text{A}]^m [\text{B}]^n$$

$$\text{reaction rate} = k [\text{A}]^m [\text{B}]^n \quad (k = \text{rate constant})$$

e.g. for the above rate equation: order of reaction with respect to: A is m , B is n , overall order is $(m+n)$

The **order of reaction** with respect to a given reactant is the power to which the concentration of the reactant is raised in the rate equation.

The **overall order of reaction** is the sum of the powers of the concentration terms in the rate equation.

- The values of m and n must be found experimentally and cannot be found from looking at the equation (i.e. m and n are nothing to do with x and y) - so the rate equation can only be found by experiment.
- Rate equations provide a lot of information about the mechanism for the reaction.
- In some reactions, a catalyst appears in the rate equation (or even one of the products if the product is a catalyst for that reaction – autocatalysis).
- k is the rate constant for a reaction (k is different for different reactions).
- The only thing that affects the value of k is temperature (k increases with temperature).
- The units of k depend on the order of the reaction (note rate is usually in $\text{mol dm}^{-3} \text{ s}^{-1}$, concentrations are in mol dm^{-3}).

TASK 2 – What orders mean

1 Consider this reaction: $A + B + C \rightarrow D$

The rate equation is: $\text{rate} = k [B] [C]^2$

Complete the table to show how changing the concentrations affects the rate.

Initial rate ($\text{mol dm}^{-3} \text{ s}^{-1}$)	Change in concentration of reagents	Effect on rate	New initial rate ($\text{mol dm}^{-3} \text{ s}^{-1}$)
2.5	[A] x 3	None	2.5
0.75	[B] x 4		
12	[C] x 10		
0.50	[D] x 5		
0.25	[A] ÷ 4		
2.8	[B] ÷ 10		
3.5	[C] ÷ 3		
0.80	[D] ÷ 2		
10.3	[A] x 2, [B] x 2		
6.5	[B] x 2, [C] x 3		
12.5	[A] x 2, [B] ÷ 3		
4.8	[B] x 3, [C] ÷ 2		
12.5	[A] x 6, [B] ÷ 4, [C] x 2		
2.9	[A] x 2, [B] x 10, [C] ÷ 1.5		
15.5	[B] x 3, [C] x 10, [D] ÷ 10		

2 Consider this reaction: $P + Q \rightarrow R$ T acts as catalyst

The rate equation is: $\text{rate} = k [P]^2 [T]$

Complete the table to show how changing the concentrations affects the rate.

Initial rate ($\text{mol dm}^{-3} \text{ s}^{-1}$)	Change in concentration of reagents	Effect on rate	New initial rate ($\text{mol dm}^{-3} \text{ s}^{-1}$)
6.0	[P] x 2		
5.0	[Q] x 5		
10.0	[R] x 3		
0.80	[T] x 4		
8.0	[P] ÷ 3		
12.5	[Q] ÷ 2		
60	[R] ÷ 5		
50	[T] ÷ 10		
12	[P] x 2, [Q] x 2		
10	[P] x 2, [T] x 3		
40	[Q] x 2, [T] ÷ 3		
25	[R] x 3, [T] ÷ 2		
10	[P] x 4, [Q] ÷ 2, [T] x 2		
20	[P] x 2, [Q] x 10, [T] ÷ 1.5		
30	[P] x 3, [Q] x 10, [T] ÷ 10		
5	[P] ÷ 2, [Q] ÷ 2, [T] ÷ 3		
12	[P] x 2, [Q] ÷ 10, [T] x 5		
16	[P] ÷ 3, [Q] ÷ 2.5, [T] x 3		
8	[P] x 2.5, [Q] ÷ 4, [T] ÷ 2		

TASK 3 – Finding the units of the rate constant

Work out the units for the rate constant in each of the following examples.

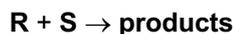
	Rate equation	Rearrange to give k	Working	Units for k
1)	rate = k [A]	$k = \frac{\text{rate}}{[A]}$	$k = \frac{(\text{mol dm}^{-3}) \text{ s}^{-1}}{(\text{mol dm}^{-3})}$	s ⁻¹
2)	rate = k [C] [H]			
3)	rate = k [S] ²			
4)	rate = k [J] ² [H] ²			
5)	rate = k [T]			
6)	rate = k [S] [E] [G] ²			
7)	rate = k [D] ² [C]			
8)	rate = k [A] [B] [C]			
9)	rate = k [J] [G]			
10)	rate = k [H ⁺] [Br]			

SECTION 4 – Find orders using initial rates data

The order with respect to each reagent, and so the rate equation, can be found by doing a series of experiments where the initial concentration of each reagent is changed to see how it affects the initial rate.

Example 1

Imagine a reaction where **R** reacts with **S** to make some products:



Experiment	Initial [R] (mol dm ⁻³)	Initial [S] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	1.0	1.0	0.200
2	2.0	1.0	0.400
3	1.0	2.0	0.200

If we compare experiments 1 and 2:

- The concentration of **R** has been doubled, but the concentration of **S** remains the same. The rate has doubled.
- Therefore the effect of doubling the concentration of **R** is to double the rate, and so therefore the reaction is **first order** with respect to the concentration of **R**

If we compare experiments 1 and 3:

- The concentration of **S** has been doubled, but the concentration of **R** remains the same. The rate has stayed the same.
- Therefore doubling the concentration of **S** has no effect on the rate, and so therefore the reaction is **zero order** with respect to the concentration of **S**

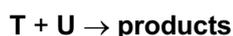
Therefore, the rate equation is: **rate = k[R]**

We can then work out the rate constant using any of the experiments:

$$\text{Using experiment 2: } k = \frac{\text{rate}}{[\text{R}]} = \frac{0.400}{2.0} = 0.200 \text{ s}^{-1} \quad \therefore \text{rate} = 0.200 [\text{R}]$$

Example 2

Imagine a reaction where **T** reacts with **U** to make some products:



Experiment	Initial [T] (mol dm ⁻³)	Initial [U] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
4	1.0	1.0	0.500
5	0.5	1.0	0.250
6	2.0	2.0	4.000

If we compare experiments 4 and 5:

- The concentration of **T** has been halved, but the concentration of **U** remains the same. The rate has halved.
- Therefore the effect of halving the concentration of **T** is to halve the rate, and so therefore the reaction is **first order** with respect to the concentration of **T**

There is no pair of experiments where only the concentration of **U** has been changed, so we will have to use the fact that we have just worked out that the reaction is first order with respect to the concentration of **U** to do this.

If we compare experiments 4 and 6:

- The concentration of **T** has been doubled, and this on its own would double the rate to 1.000 mol dm⁻³ s⁻¹.
- The concentration of **U** has also been doubled, and this has effectively increased the rate from 1.000 to 4.000 mol dm⁻³ s⁻¹ – in other words it has made it 4 times bigger.
- Therefore the effect of doubling the concentration of **U** is to make the rate 4 times faster, and so therefore the reaction is **second order** with respect to the concentration of **U**

Therefore, the rate equation is: **rate = k[T][U]²**

We can then work out the rate constant using any of the experiments:

$$\text{Using experiment 6: } k = \frac{\text{rate}}{[\text{T}][\text{U}]^2} = \frac{4.00}{2.0 \times 2.0^2} = 0.500 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1} \quad \therefore \text{rate} = 0.500 [\text{T}][\text{U}]^2$$

TASK 4 – Finding rate equations using initial rates data

1 Deduce the rate equation for each of the following reactions.

a) A reacts with B to form C. $A + B \rightarrow C$

Experiment	Initial [A] (mol dm ⁻³)	Initial [B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	3	1	10
2	6	1	40
3	3	2	10

b) D reacts with E to form F and G. $D + 2E \rightarrow F + G$

Experiment	Initial [D] (mol dm ⁻³)	Initial [E] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
4	0.1	0.1	5
5	0.4	0.1	20
6	0.8	0.2	80

c) J reacts to form K and L in the presence of an acid catalyst. $J \rightarrow K + L$

Experiment	Initial [J] (mol dm ⁻³)	Initial [H ⁺] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
7	0.2	0.5	12
8	0.2	0.25	3
9	0.1	1.0	24

d) S reacts with T to form U. $S + T \rightarrow 2U$

Experiment	Initial [S] (mol dm ⁻³)	Initial [T] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
10	0.005	0.2	300
11	0.001	0.3	450
12	0.010	0.2	300

e) P reacts with Q in the presence of an acid catalyst. $P + Q \rightarrow 2R$

Experiment	Initial [P] (mol dm ⁻³)	Initial [Q] (mol dm ⁻³)	Initial [H ⁺] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
13	0.01	0.01	0.2	8
14	0.01	0.04	0.4	64
15	0.01	0.02	0.4	32
16	0.02	0.08	0.1	32

f) W reacts with X to form Y and Z. $2W + X \rightarrow Y + Z$

Experiment	Initial [W] (mol dm ⁻³)	Initial [X] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
17	0.02	0.05	0.016
18	0.05	0.05	0.100
19	0.10	0.15	0.400

g) M reacts with N to make O. $M + N \rightarrow 2O$

Experiment	Initial [M] (mol dm ⁻³)	Initial [N] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
20	0.1	0.2	0.15
21	0.3	0.2	1.35
22	0.4	0.3	2.40

h) HI dissociates to form hydrogen and iodine: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Experiment	23	24	25	26
Initial [HI] (mol dm ⁻³)	1.64	3.28	4.92	6.56
Initial rate (mol dm ⁻³ s ⁻¹)	0.41	1.64	3.69	6.56

2 For each of the rate equations you deduced in question 1, calculate the rate constant and deduce its units.

TASK 5 – Using initial rates data

1 G reacts with H: $G + 2H \rightarrow \text{products}$ $\text{rate} = k[G][H]$

Complete the table with initial rates data.

Experiment	Initial [G] (mol dm ⁻³)	Initial [H] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.200	0.100	0.400
2		0.050	0.200
3		0.200	0.400
4	0.050	1.000	
5	0.150	0.100	
6	0.800		0.800
7	0.300		1.200
8	0.250		0.400

2 J reacts with K: $J + K \rightarrow \text{products}$ $\text{rate} = k[J]^2$

Complete the table with initial rates data.

Experiment	Initial [J] (mol dm ⁻³)	Initial [K] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
9	0.500	0.200	0.360
10		0.100	0.360
11		0.200	1.440
12		0.200	0.180
13	0.100	0.100	

3 L reacts with M: $2L + 2M \rightarrow N + 2P$ $\text{rate} = k[L][M]^2$

Complete the table with initial rates data.

Experiment	Initial [L] (mol dm ⁻³)	Initial [M] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
14	0.100	0.100	0.0500
15	0.100	0.300	
16	0.100		0.1500
17		0.200	0.0500
18	0.200		0.0500

4 In each of the following questions, use the initial rate data to find:

- the rate equation
- the rate constant k (including its units) at the experiment's temperature

a) A reacts with B to form C. $A + B \rightarrow C$

Experiment	Initial [A] (mol dm ⁻³)	Initial [B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
19	1	1	2
20	1	2	8
21	2	2	16

b) D reacts with E to form various products. $D + E \rightarrow \text{products}$

Experiment	Initial [D] (mol dm ⁻³)	Initial [E] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
22	1	1	0.20
23	2	1	0.20
24	4	4	0.80

c) P reacts with Q to form various products. $P_{(g)} + Q_{(g)} \rightarrow \text{products}$

Experiment	Initial [P] (mol dm ⁻³)	Initial [Q] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
25	0.1	0.1	0.00200
26	0.2	0.1	0.00398
27	0.3	0.1	0.00603
28	0.4	0.2	0.01598

d) The reaction between iodine and propanone is catalysed by H⁺_(aq) ions.



Experiment	Initial [H ⁺] (mol dm ⁻³)	Initial [CH ₃ COCH ₃] (mol dm ⁻³)	Initial [I ₂] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
29	0.5	6.0	0.02	9.0 x 10 ⁻⁵
30	0.5	8.0	0.04	1.2 x 10 ⁻⁴
31	1.0	6.0	0.02	1.8 x 10 ⁻⁴
32	1.0	8.0	0.02	2.4 x 10 ⁻⁴

SECTION 5 – Rate determining step

- The mechanism for a reaction may only involve one step, or could actually involve a series of steps.
- If a reaction mechanism has a series of steps, then the overall rate is dependent on the rate of slowest step.
- The slowest step is called the **rate determining step (RDS)**.
- In any mechanism, species that are only involved in steps after the RDS do not appear in the rate equation. However, species that appear in the steps up to and including the RDS are in the rate equation.
- The rate equation gives us clues about the mechanism and which is the rate determining step.
- We find the rate equation by experiment and then use the rate equation to deduce possible mechanisms (we do not use the mechanism to work out the rate equation!).
- A substance that acts as a catalyst will appear in the rate equation but not in the overall chemical equation for the reaction.

E.g. 1	<i>Overall equation</i> $A + 2B \rightarrow C + D$	<i>Rate equation</i> $\text{rate} = k[A][B]$	<i>Possible mechanism that fits rate equation</i> Step 1 $A + B \rightarrow P$ slow, RDS Step 2 $P + B \rightarrow C + D$ fast Up to and including the RDS: one particle of A and one particle of B are involved.
E.g. 2	<i>Overall equation</i> $A + 2B \rightarrow D + E$	<i>Rate equation</i> $\text{rate} = k[B]^2$	<i>Possible mechanism that fits rate equation</i> Step 1 $2B \rightarrow B_2$ slow, RDS Step 2 $B_2 + A \rightarrow D + E$ fast Up to and including the RDS: two particles of B are involved.
E.g. 3	<i>Overall equation</i> $A + 2B \rightarrow D + E$	<i>Rate equation</i> $\text{rate} = k[A][B]^2$	<i>Possible mechanism that fits rate equation</i> Step 1 $2B \rightarrow B_2$ fast Step 2 $B_2 + A \rightarrow D + E$ slow, RDS Up to and including the RDS: one particle of A and two particles of B are involved.
E.g. 4	<i>Overall equation</i> $A + 2B \rightarrow D + E$ <i>H⁺ acts as a catalyst</i>	<i>Rate equation</i> $\text{rate} = k[A][H^+]$	<i>Possible mechanism that fits rate equation</i> Step 1 $A + H^+ \rightarrow AH^+$ slow, RDS Step 2 $AH^+ + B \rightarrow AB + H^+$ fast Step 3 $AB + B \rightarrow D + E$ fast Up to and including the RDS: one particle of A and one particle of H ⁺ are involved. Note that H ⁺ is a catalyst as it appears in the rate equation but not the overall reaction equation.

TASK 6a – Rate determining step 1

In each of the following reactions, deduce which step is the rate determining step.

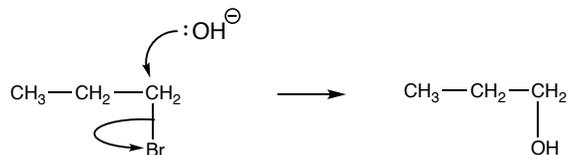
- 1** Overall reaction: $A + 2 B \rightarrow D$
 Rate equation: $\text{rate} = k [B]^2$
 Mechanism:
 step 1 $2 B \rightarrow C$
 step 2 $C + A \rightarrow D$
- 2** Overall reaction: $E + 2 F \rightarrow G$
 Rate equation: $\text{rate} = k [E] [F]^2$
 Mechanism:
 step 1 $E + F \rightarrow EF$
 step 2 $EF + F \rightarrow G$
- 3** Overall reaction: $J + K \rightarrow L$
 Rate equation: $\text{rate} = k [J] [H^+]$
 Mechanism:
 step 1 $J + H^+ \rightarrow JH^+$
 step 2 $JH^+ + K \rightarrow L + H^+$
- 4** Overall reaction: $M_2 + 2 N \rightarrow 2 MN$
 Rate equation: $\text{rate} = k [M_2]$
 Mechanism:
 step 1 $M_2 \rightarrow 2 M$
 step 2 $M + N \rightarrow MN$
- 5** Overall reaction: $2 A + C \rightarrow D$
 Rate equation: $\text{rate} = k [A]^2 [C]$
 Mechanism:
 step 1 $2 A \rightarrow B$
 step 2 $B + C \rightarrow D$

In each of the following reactions, state which of the proposed mechanisms **could be** a possible mechanism and which **could not be** a correct mechanism. Do **not** assume that there is one answer in each case!

- 6** Overall reaction: $P + 2 Q \rightarrow R$
 Rate equation: $\text{rate} = k [P]$
 Possible mechanism 1:
 step 1 (rds) $P + Q \rightarrow PQ$
 step 2 $PQ + Q \rightarrow R$
 Possible mechanism 2:
 step 1 $2 Q \rightarrow Q_2$
 step 2 (rds) $Q_2 + P \rightarrow R$
- 7** Overall reaction: $X + Y \rightarrow Z + B$
 Rate equation: $\text{rate} = k [X] [Y]$
 Possible mechanism 1:
 step 1 $X \rightarrow A + B$
 step 2 (rds) $A + Y \rightarrow Z$
 Possible mechanism 2:
 step 1 (rds) $X + Q \rightarrow P + B$
 step 2 $Y + P \rightarrow A + Q$
- 8** Overall reaction: $2 C + D \rightarrow F$
 Rate equation: $\text{rate} = k [C]^2 [D]$
 Possible mechanism 1:
 step 1 $C + D \rightarrow E$
 step 2 (rds) $C + E \rightarrow F$
 Possible mechanism 2:
 step 1 $2 C \rightarrow C_2$
 step 2 (rds) $C_2 + D \rightarrow F$

TASK 6b – Rate determining step 2

- 1 a** The mechanism for the reaction of 1-bromopropane with aqueous sodium hydroxide is shown.

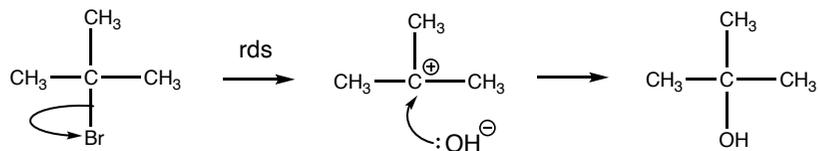


- i** Give the rate equation for this reaction.

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- ii** State the overall order of this reaction.

- b** The mechanism for the reaction of 2-bromo-2-methylpropane with aqueous sodium hydroxide is shown.



- i** Give the rate equation for this reaction.

.....

- ii** State the overall order of this reaction.

- 2** For this reaction: $P + 2Q \rightarrow R + S$

The mechanism involves three steps:

- | | |
|--------|----------------------------|
| Step 1 | $2Q \rightarrow Q_2$ |
| Step 2 | $Q_2 + P \rightarrow PQ_2$ |
| Step 3 | $PQ_2 \rightarrow R + S$ |

Give the rate equation if the rate determining step is:

- a** step 1
- b** step 2
- c** step 3

SECTION 6 – The Arrhenius Equation

The Arrhenius equation shows the link between the rate constant, activation energy and temperature.

$$k = Ae^{-\frac{E_a}{RT}} \qquad \ln k = \ln A - \frac{E_a}{RT}$$

k = rate constant (units vary depending on order of reaction)

A = Arrhenius constant (same units as k) (also called pre-exponential or frequency factor)

E_a = activation energy (J mol^{-1})

R = gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)

T = temperature (K)

[Note that **e** is a very special number in maths. It can be used on a calculator by using the **SHIFT** **ln** buttons.]

We can do various calculations using the equation, including some to show how changes in temperature and the addition of a catalyst affects the rate constant (and remember – the bigger the rate constant, the faster the reaction).

Example 1 – Finding the activation energy for a reaction

Calculate the activation energy for a reaction in kJ mol^{-1} given the Arrhenius constant (A) = $5.25 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the rate constant (k) = $3.36 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 298 K.

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\frac{E_a}{RT} = \ln A - \ln k$$

$$E_a = RT (\ln A - \ln k)$$

$$E_a = (8.31 \times 298) (13.17 + 8.00)$$

$$E_a = 52425 \text{ J mol}^{-1}$$

$$E_a = 52.4 \text{ kJ mol}^{-1}$$

Example 2 – Finding the rate constant at two different temperatures

- a) Calculate the rate constant at 20°C and 30°C in a reaction where the Arrhenius constant (A) = $2.5 \times 10^6 \text{ s}^{-1}$ and the activation energy (E_a) = 50 kJ mol^{-1} .
- b) Show that the rate of reaction is roughly twice as fast at 30°C than at 20°C

$$\begin{aligned} \text{At } 20^\circ\text{C:} \quad k &= Ae^{-\frac{E_a}{RT}} \\ &= 2.5 \times 10^6 \times e^{-\frac{50000}{8.31 \times 293}} \\ &= 2.5 \times 10^6 \times 1.21 \times 10^{-9} \\ &= 3.02 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{At } 30^\circ\text{C:} \quad k &= Ae^{-\frac{E_a}{RT}} \\ &= 2.5 \times 10^6 \times e^{-\frac{50000}{8.31 \times 303}} \\ &= 2.5 \times 10^6 \times 2.38 \times 10^{-9} \\ &= 5.94 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

k at 30°C is $\frac{5.94 \times 10^{-3}}{3.02 \times 10^{-3}}$ times greater, i.e. 1.97 times greater

and so the reaction is 1.97 times faster

Example 3 – Finding the rate constant with and without a catalyst

- a) Calculate the rate constant with and without a catalyst in a reaction where the Arrhenius constant, $A = 5.00 \times 10^7 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the activation energy is 100 kJ mol^{-1} without a catalyst and 80 kJ mol^{-1} with a catalyst at 298 K .
- b) How many times faster is the rate of reaction with a catalyst than without a catalyst?

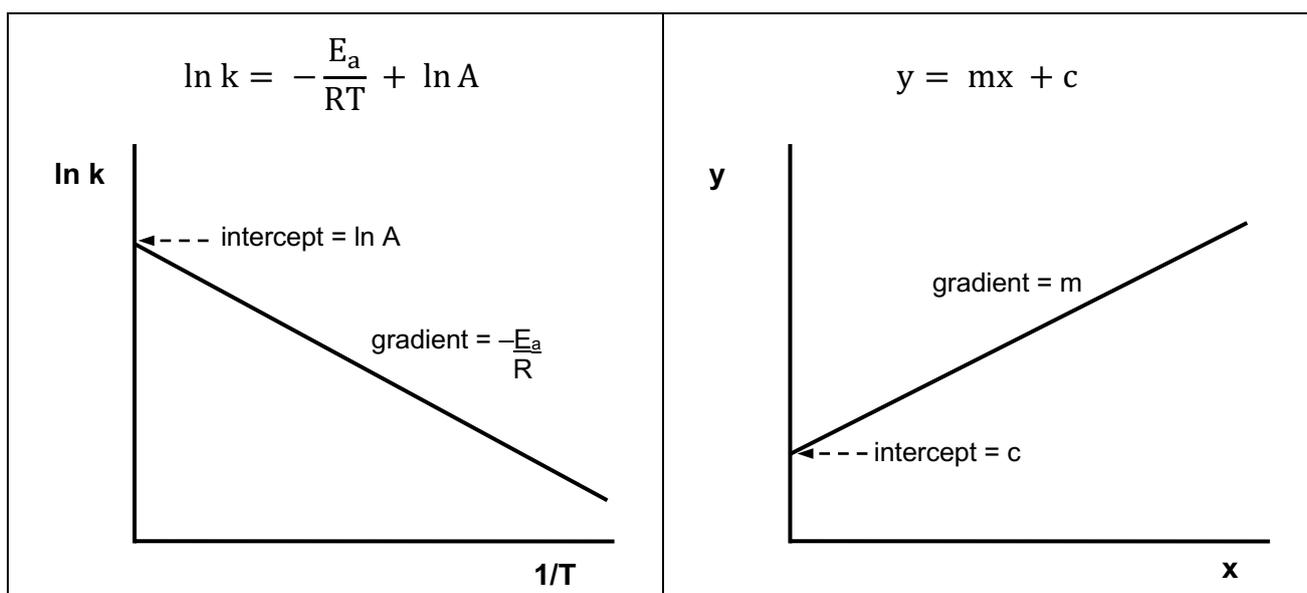
No catalyst:	$k = Ae^{-\frac{E_a}{RT}}$	With catalyst:	$k = Ae^{-\frac{E_a}{RT}}$
	$= 5.00 \times 10^7 \times e^{-\frac{100000}{8.31 \times 298}}$		$= 5.00 \times 10^7 \times e^{-\frac{80000}{8.31 \times 298}}$
	$= 5.00 \times 10^7 \times 2.91 \times 10^{-18}$		$= 5.00 \times 10^7 \times 9.33 \times 10^{-15}$
	$= 1.45 \times 10^{-10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$		$= 4.67 \times 10^{-7} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

k with a catalyst is $\frac{4.67 \times 10^{-7}}{1.45 \times 10^{-10}}$ times greater, i.e. 3220 times greater than without a catalyst,

and so the reaction is 3220 times faster

Graphical analysis

The natural log form of the Arrhenius equation equates to the equation of a straight line graph.



This means that the activation energy (E_a) and the Arrhenius constant (A) can be found from plotting a graph of $\ln k$ versus $1/T$.



Finding activation energy for a reaction (Chemsheets A2 1002)



TASK 7 – Using the Arrhenius equation

1 Rearrange the Arrhenius equation to show each of the following as the subject:

- a) k b) E_a c) A d) T

2 Calculate the activation energy for a reaction in kJ mol^{-1} given the Arrhenius constant (A) = $3.62 \times 10^7 \text{ s}^{-1}$ and the rate constant (k) = $8.92 \times 10^{-3} \text{ s}^{-1}$ at 298 K.

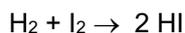
3 a) Calculate the rate constant at 20°C and 40°C in a reaction where the Arrhenius constant (A) = $5.18 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the activation energy (E_a) = 75 kJ mol^{-1} .

b) How many times greater is the rate constant and so the rate of reaction at 40°C compared to 20°C ?

4 a) Calculate the rate constant with and without a catalyst in a reaction where the Arrhenius constant, A = $6.92 \times 10^6 \text{ s}^{-1}$ and the activation energy is 150 kJ mol^{-1} without a catalyst and 50 kJ mol^{-1} with a catalyst at 298 K.

b) How many times greater is the rate constant and so the rate of reaction with a catalyst compared to without?

5 The table below shows how the rate constant varies with temperature in the reaction shown:

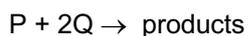


Temperature (K)	556	575	629	666	700	781
k ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	4.45×10^{-5}	1.34×10^{-4}	2.52×10^{-3}	0.0141	0.0643	1.34

a) Draw a table to show the values of $\ln k$ and $1/T$.

b) Plot a graph of $\ln k$ versus $1/T$ and use it to determine the activation energy (E_a) for this reaction.

6 The table below shows how the rate constant varies with temperature in the reaction shown:



Temperature ($^\circ\text{C}$)	20	50	100	150	200	250
k ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	0.0147	0.0675	0.497	2.29	7.61	20.1

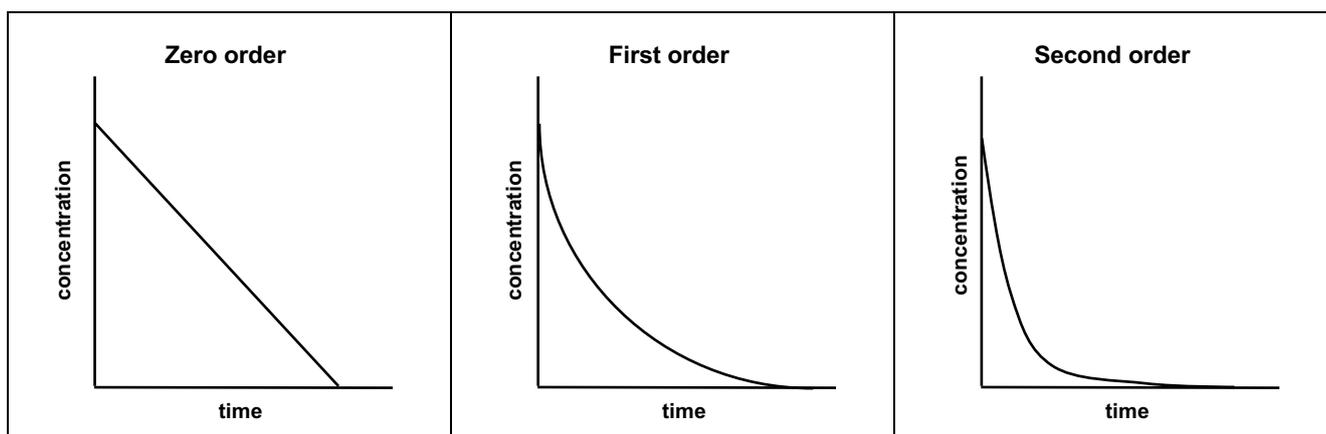
a) Draw a table to show the values of $\ln k$ and $1/T$.

b) Plot a graph of $\ln k$ versus $1/T$ and use it to determine the activation energy (E_a) for this reaction.

SECTION 7 – Concentration-time & rate-concentration graphs

Concentration-time graphs

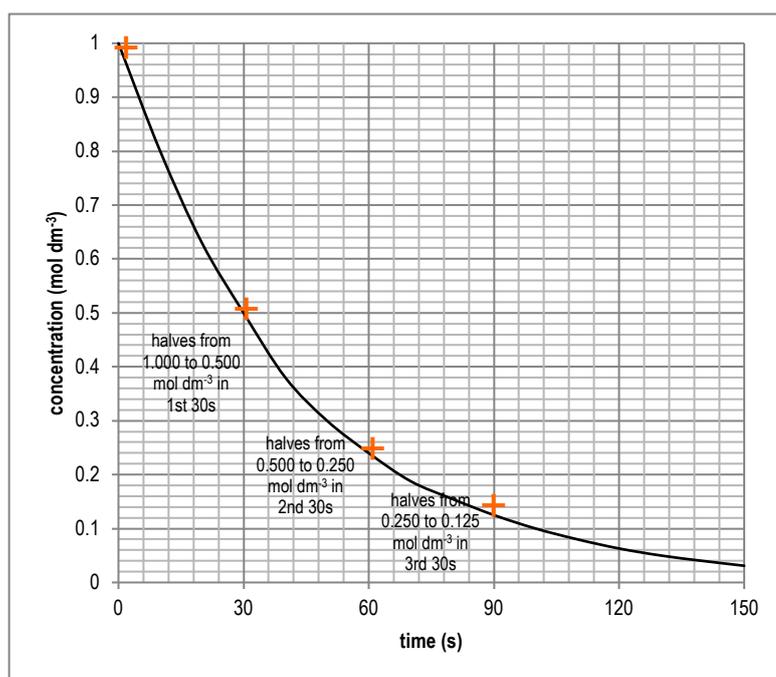
- Graphs of concentration of a reactant against time can give some clues to the order of that reagent in the rate equation.
- A straight-line graph shows that the reaction is zero order.
- A curve could mean it is first or second order.
- When producing graphs such as these of concentration against time for a reagent, the concentration of all other reagents should be kept constant. This is straightforward to do in a series of initial rates experiments, but in a continuous rates experiment it is done by ensuring the other reagents are in a large excess and so are effectively constant (if this is not done, then there will always be a downwards curve of some type depending whether the reaction is overall first, second, third, etc. order).



- In a zero order reaction, $\text{rate} = k$, and therefore gradient of the line in a zero order reaction gives the rate constant for the reaction.

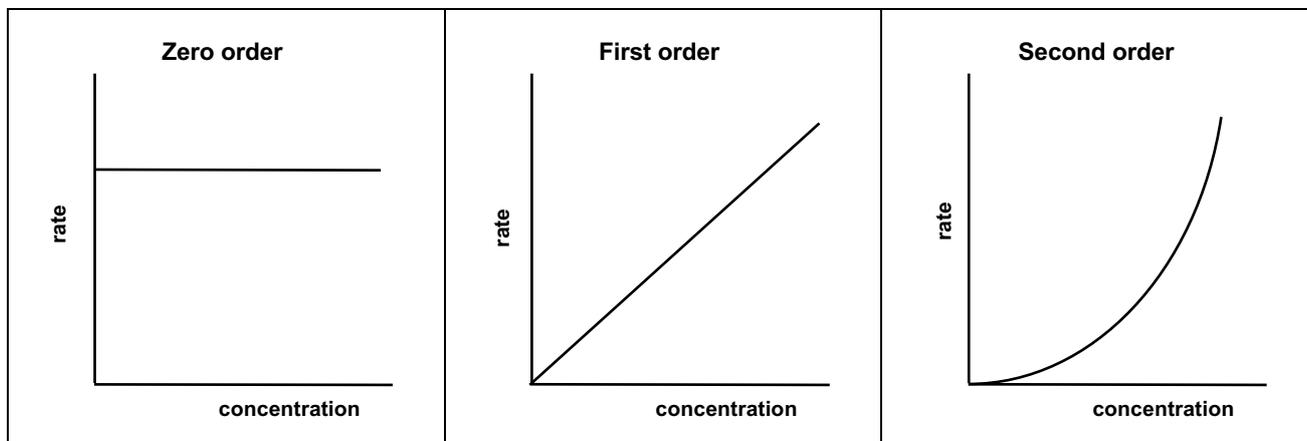
HALF LIFE (not on AQA) – for first order reagents ONLY

- If the rate of reaction is first order with respect to a reagent, then the time for half the reagent to be used up (this time is called the half life of that reagent) is always the same.
- For example, if it takes 30 seconds for the concentration to fall from $1.000 \text{ mol dm}^{-3}$ to $0.500 \text{ mol dm}^{-3}$, it will take another 30 seconds to halve again to $0.250 \text{ mol dm}^{-3}$, and another 30 seconds to halve to $0.125 \text{ mol dm}^{-3}$.
- This is not the case for a reagent when its order is zero or two.

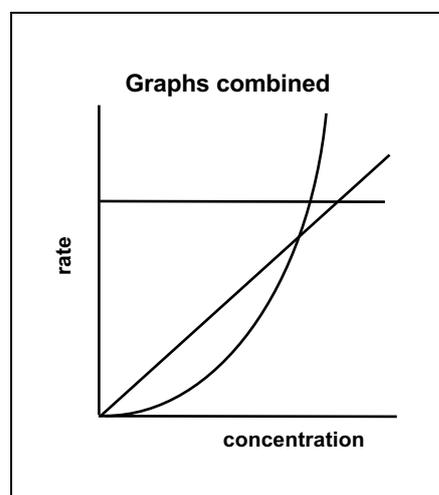


Rate-concentration graphs

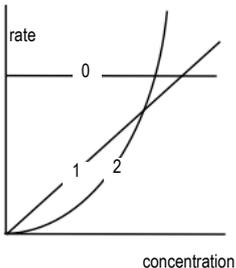
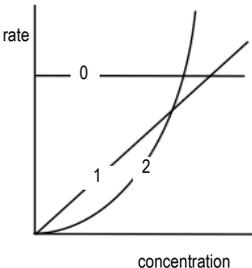
- Graphs of rate against concentration of a reactant are more useful and give the order directly.
- When producing graphs such as these of rate against concentration for a reagent, the concentration of all other reagents should be kept constant. This is straightforward to do in a series of initial rates experiments, but in a continuous rates experiment it is done by ensuring the other reagents are in a large excess and so are effectively constant (if this is not done, then it will always be the shape of the overall order of reaction rather than that for an individual reagent).



- A horizontal line shows that the reaction is **zero order** with respect to the concentration of that reagent.
- A rising straight line shows that the reaction is **first order** with respect to the concentration of that reagent.
- An upwards curve shows that the reaction is **second order** with respect to the concentration of that reagent.
- These graphs can be produced using experimental data (see section 7) by either:
 - Doing several experiments where the initial rate is measured and the initial concentration of a reagent is changed (**initial rates method**), with all other concentrations kept constant, or
 - Doing one experiment where the rate and concentration of a reagent is measured at several times during that one reaction (**continuous rates method**) – the other reagents must be in a large excess so they are effectively constant.



Using experiments to get data for rate-concentration graphs

	Initial rates method	Continuous rates method
Principle	<p>Do several reactions starting with different concentrations. Measure the initial rate of each one.</p> <p>Plot rate (or something proportional to it) v concentration (or something proportional to it) and see which type of line it is.</p> 	<p>Measure the rate at several points during one reaction</p> <p>Plot rate (or something proportional to it) v concentration (or something proportional to it) and see which type of line it is.</p> 
Gas production	<p><i>Either:</i></p> <p>Measure the volume or mass of gas produced v time and plot a graph. Find the gradient at the start – the rate is proportional to the gradient.</p> <p><i>or</i></p> <p>Time how long it takes to reach a specific point early in the reaction – the rate is proportional to volume or mass divided by time.</p>	<p>Measure the volume or mass of gas produced v time. Find the gradient at several points throughout the experiment – the rate is proportional to the gradient.</p>
Colour change	<p>Use a colorimeter to measure the time it takes to reach a specific point early in the reaction (e.g. when absorbance reaches a certain amount) – rate is proportional to 1/time.</p>	<p>Use a colorimeter to measure absorbance (how much light is absorbed) at various times during the reaction. Absorbance is proportional to concentration.</p> <p>Plot a graph of absorbance (or concentration) v time and find the gradient at various points – the rate is proportional to the gradient</p> <p>[the actual concentration can be found using a calibration curve which is a graph of absorbance v concentration]</p>
Turbidity (cloudiness)	<p>Time how long it takes to reach a point where you can no longer see through a reaction mixture – rate is proportional to 1/time.</p>	<p>Not possible.</p>
Quenching	<p>Stop a reaction – often done by add a lot of water to dilute it. It may be possible to measure the concentration of a reactant/product at that point (e.g. by titration) and calculate the rate by dividing the change in concentration by the time.</p>	<p>At regular time intervals take a sample out of the reaction mixture and stop it by quenching it which is often done by adding a lot of water to dilute it. It may be possible to measure the concentration of a reactant/product at that point (e.g. by titration).</p> <p>A graph of concentration v time can be plotted and the gradient measured at various points – the gradient is the rate.</p>
Chemsheets experiments	 <p>Initial rates 1 - Iodine clock (Chemsheets A2 1010)</p>	 <p>Continuous rates 1 – Decomposition of hydrogen peroxide (Chemsheets A2 1006)</p> <p>Continuous rates 2 – Magnesium + hydrochloric acid (Chemsheets A2 1108)</p>

TASK 8 – Plotting concentration-rate graphs to determine orders

- 1 A solution of hydrogen peroxide decomposes as shown: $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

A series of initial rates experiments was carried out to find the rate of decomposition at different initial concentrations of hydrogen peroxide solution.

Plot a graph of rate against concentration of hydrogen peroxide and use the shape of the graph to find the order with respect to the concentration of hydrogen peroxide.

$[\text{H}_2\text{O}_2]$ (mol dm ⁻³)	0.10	0.20	0.30	0.40	0.50
rate (mol dm ⁻³ s ⁻¹)	4.20×10^{-5}	8.30×10^{-5}	1.22×10^{-4}	1.75×10^{-4}	2.06×10^{-4}

- 2 When placed in solution, the blue substance **M** reacts with colourless **N** to form colourless **P**.



The progress of a reaction was followed using a colorimeter which measured the absorbance of **M**(aq). The results are shown in the table. The concentration of **M** is proportional to the absorbance measured.

time (s)	0	5	10	15	20	30	40	50	60	70
absorbance	1.00	0.60	0.47	0.38	0.32	0.24	0.18	0.15	0.12	0.11

- a) Plot a graph of absorbance against time.
b) Calculate the gradient at 0, 5, 10, 20, 30 and 40 seconds.
c) Plot a graph of these gradients against (absorbance) to determine the order of the reaction with respect to **[M]** by looking at the type of line produced.
- 3 a) A student reacted halogenoalkane **X** with warm aqueous sodium hydroxide to form an alcohol. The student took samples out the reaction and quenched the samples and found the concentration of sodium hydroxide each time by titration. The student's results are in the table.

Time (s)	0	60	120	180	240	300	360	420	480	540	600
$[\text{NaOH}]$ (mol dm ⁻³)	1.00	0.80	0.63	0.50	0.40	0.31	0.25	0.20	0.16	0.13	0.10

- i) Plot a graph of $[\text{NaOH}]$ against time.
ii) Calculate the gradient at $[\text{NaOH}]$ values of 1.00, 0.80, 0.60, 0.40 and 0.20 mol dm⁻³.
iii) Plot a graph of these gradients against $[\text{NaOH}]$ to determine the order of the reaction with respect to $[\text{NaOH}]$ by looking at the type of line produced.
- b) The student reacted halogenoalkane **Y** with warm aqueous sodium hydroxide to form a different alcohol. The student again took samples out the reaction and quenched the samples and found the concentration of sodium hydroxide each time by titration. The student's results are in the table.

Time (s)	0	60	120	180	240	300	360	420	480	540	600
$[\text{NaOH}]$ (mol dm ⁻³)	1.00	0.93	0.86	0.80	0.73	0.67	0.60	0.54	0.48	0.41	0.34

- i) Plot a graph of $[\text{NaOH}]$ against time.
ii) Calculate the gradient at $[\text{NaOH}]$ values of 1.00, 0.80, 0.60, 0.40 and 0.30 mol dm⁻³.
iii) Plot a graph of these gradients against $[\text{NaOH}]$ to determine the order of the reaction with respect to $[\text{NaOH}]$ by looking at the type of line produced.
- c) Explain whether these two halogenoalkanes react with sodium hydroxide by the same mechanism?