

Topic 6: Chemical kinetics

6.1 Collision theory and rates of reaction

U1	Species react as a result of collisions of sufficient energy and proper orientation.
U2	The rate of reaction is expressed as the change in concentration of a particular reactant/product per unit time.
U3	Concentration changes in a reaction can be followed indirectly by monitoring changes in mass, volume and colour.
U4	Activation energy (E_a) is the minimum energy that colliding molecules need in order to have successful collisions leading to a reaction.
U5	By decreasing E_a , a catalyst increases the rate of a chemical reaction, without itself being permanently chemically changed.
A1	Description of the kinetic theory in terms of the movement of particles whose average kinetic energy is proportional to temperature in Kelvin.
A2	Analysis of graphical and numerical data from rate experiments.
A3	Explanation of the effects of temperature, pressure/concentration and particle size on rate of reaction.
A4	Construction of Maxwell–Boltzmann energy distribution curves to account for the probability of successful collisions and factors affecting these, including the effect of a catalyst.
A5	Investigation of rates of reaction experimentally and evaluation of the results.
A6	Sketching and explanation of energy profiles with and without catalysts.

Collision theory

According to collision theory, for a reaction to occur three criteria must be met:

- the particles must collide
- they must collide with the **appropriate geometry** or orientation so that the reactive parts of the particles come into contact
- they must collide with **sufficient energy** (the activation energy)

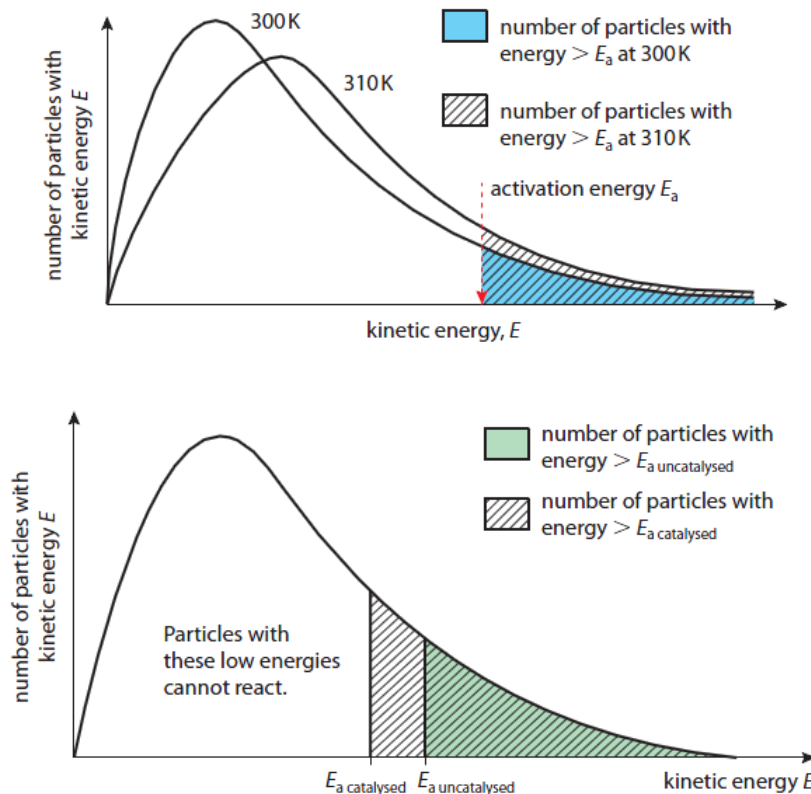
Quantity	Effect of increasing quantity	Explanation
particle size (surface area)	decreases rate	The greater the particle size, the smaller the exposed surface area. Reduced frequency of successful collision . So the rate of reaction decreases
temperature	increases rate	Increase temperature leads to an increase in average kinetic energy , so particles move faster. More particles have energy above the activation energy. Therefore, there is an increase frequency of successful collision.
concentration	increases rate	Increased concentration leads to an increase in frequency of successful collision. So the rate of the reaction increases without a change in activation energy.
pressure	increases rate	In gas, increased pressure means decrease in volume, leading to a increase in concentration. So the frequency of successful collision increases.
catalysts	increases rate	Catalyst will decrease the activation energy , providing an alternative route for the reaction. More particles will have energy beyond the activation energy. So the frequency of successful collision will increase.

Catalyst:

- Catalyst is able to decrease the activation energy
- Heterogeneous catalyst:** different state between catalyst and reactants
- Homogeneous catalyst:** same state between catalyst and reactants

The Maxwell-Boltzmann distribution

It represents fixed numbers of moles of gas in a given volume. It tells us fraction of molecules with a given value of kinetic energy. Only if the molecules have energy beyond activation energy, can they perform successful collision.



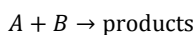
- Increasing the temperature lowers the peak of the curve and moves it to the right, more particles have enough energy to react
- Adding a catalyst reduces the activation energy, more particles have enough energy to react

Topic 16: Kinetics (HL)

16.1 Rate expression and reaction mechanism

U1	Reactions may occur by more than one step and the slowest step determines the rate of reaction (rate determining step/RDS).
U2	The molecularity of an elementary step is the number of reactant particles taking part in that step.
U3	The order of a reaction can be either integer or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step.
U4	Rate equations can only be determined experimentally.
U5	The value of the rate constant (k) is affected by temperature and its units are determined from the overall order of the reaction.
U6	Catalysts alter a reaction mechanism, introducing a step with lower activation energy.
A1	Deduction of the rate expression for an equation from experimental data and solving problems involving the rate expression.
A2	Sketching, identifying, and analysing graphical representations for zero, first and second order reactions.
A3	Evaluation of proposed reaction mechanisms to be consistent with kinetic and stoichiometric data.

Rate expression



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

The **rate constant** (k) is the constant of proportionality in the rate expression. It has a specific value for a specific reaction at a specific temperature. The units vary depending on the expressions.

The **overall order** of the reaction is $m + n$

The order with respect to a reactant is the power it is raised to in the rate expression.

Rate constant is only affected by **temperature**.

Rate expression is only focused on **reactants**.

Units of rate constant

Zero order	First order	Second order	Third order
Rate = k	Rate = k[A]	Rate = k[A] ² or Rate = k[A][B]	Rate = k[A] ³ or Rate = k[A][B] ² or Rate = k[A][B][C]
units of rate = mol dm ⁻³ s ⁻¹	$\frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$ = s ⁻¹	$\frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^2}$ = mol ⁻¹ dm ³ s ⁻¹	$\frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^3}$ = mol ⁻² dm ⁶ s ⁻¹

First, second and third order reactions

Zero order reactants (A→B)

$$\text{rate} = -\frac{dA}{dt} = k$$

$$-\frac{dA}{dt} = k$$

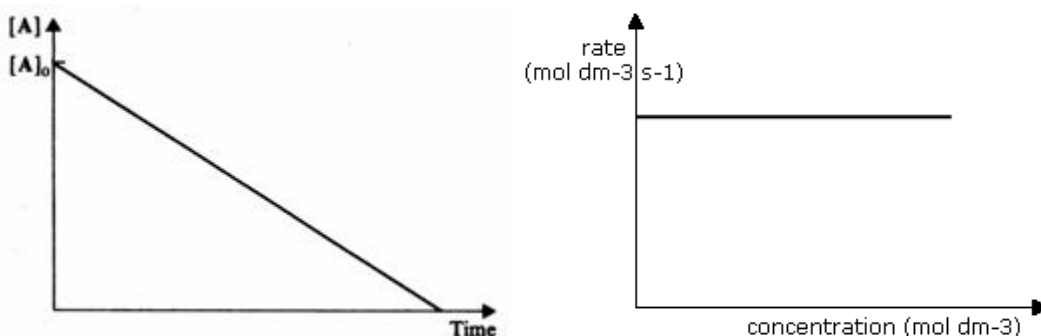
$$dA = -k \times dt$$

$$\int_{A_0}^{A_f} dA = -\int_0^t k dt$$

$$A_f - A_0 = -k \times t$$

$$A_f = A_0 - kt$$

- In zero order reaction: **Final concentration (A_f) = Initial concentration (A₀) – kt**



First order reaction:

$$\text{rate} = k[A] = -\frac{dA}{dt}$$

$$\frac{1}{A} \times dA = -k \times dt$$

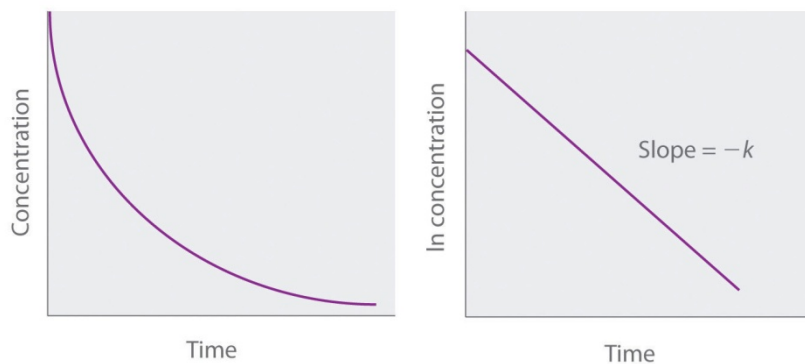
$$\int_{A_0}^{A_f} \frac{1}{A} dA = -\int_0^t k dt$$

$$\ln(A_f) - \ln(A_0) = -kt$$

$$\ln\left(\frac{A_f}{A_0}\right) = -kt$$

$$A_f = A_0 \times e^{-kt}$$

- In first order reaction: **Final concentration (A_f) = Initial concentration (A_0) $\times e^{-kt}$**



Second order reaction:

$$\text{rate} = k[A]^2 = -\frac{dA}{dt}$$

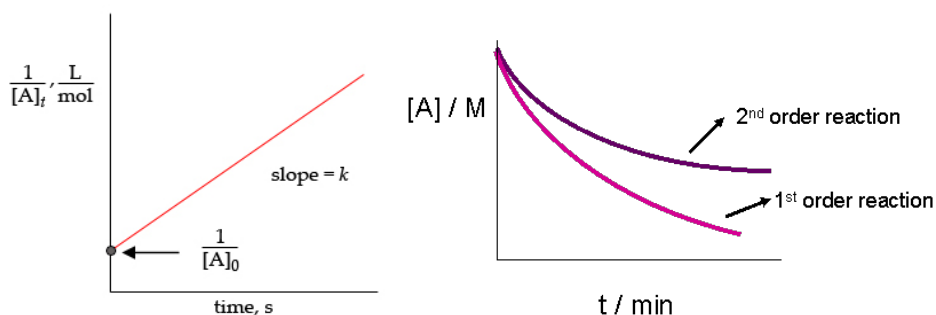
$$\frac{1}{A^2} \times dA = -k \times dt$$

$$\int_{A_0}^{A_f} \frac{1}{A^2} dA = -\int_0^t k dt$$

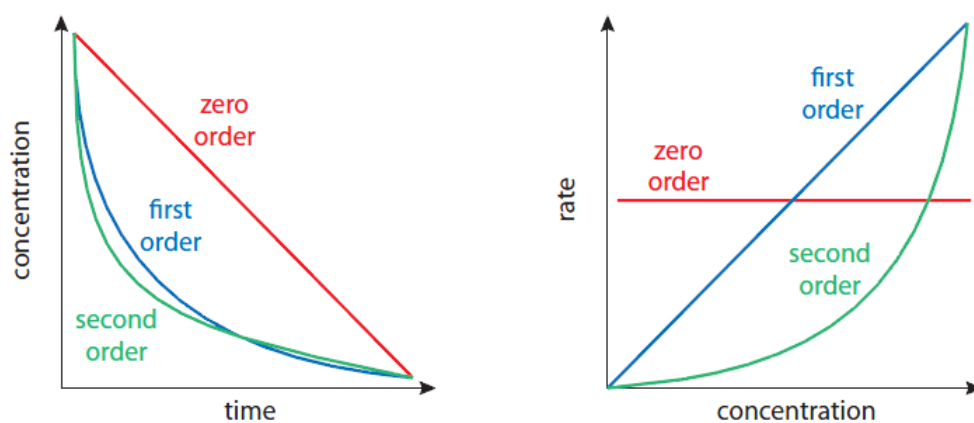
$$-\frac{1}{A_f} + \frac{1}{A_0} = -kt$$

$$\frac{1}{A_f} = \frac{1}{A_0} + kt$$

- In second order reaction: $\frac{1}{\text{final concentration } (A_f)} = \frac{1}{\text{initial concentration } (A_0)} + kt$



Combined graph



Half life: amount of time required for the final concentration to become half of the original amount

Zero order reaction:

$$A_f = \frac{1}{2}A_0$$

$$\frac{1}{2}A_0 = A_0 - kt$$

$$kt = \frac{1}{2}A_0$$

$$t_{\frac{1}{2}} = \frac{A_0}{2k}$$

First order reaction:

$$A_f = \frac{1}{2}A_0$$

$$\frac{1}{2}A_0 = A_0 \times e^{-kt}$$

$$-kt = \ln\left(\frac{1}{2}\right)$$

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Second order reaction:

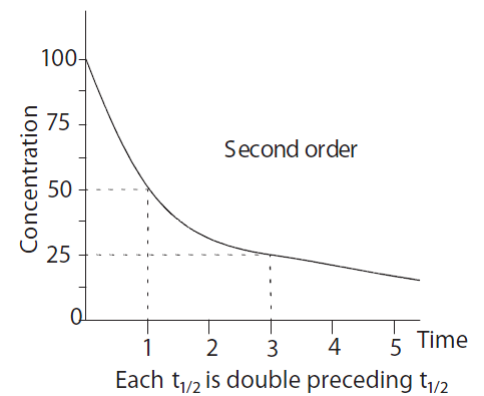
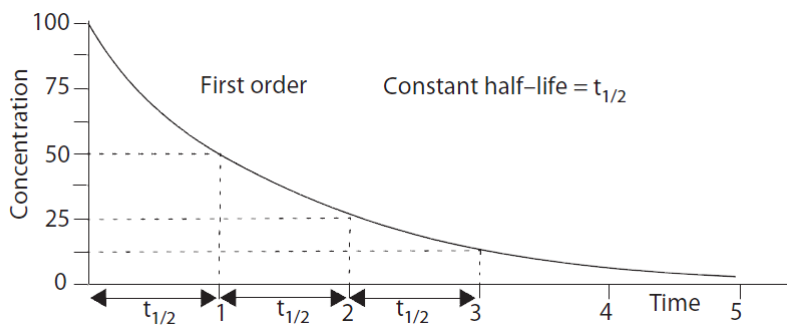
$$A_f = \frac{1}{2}A_0$$

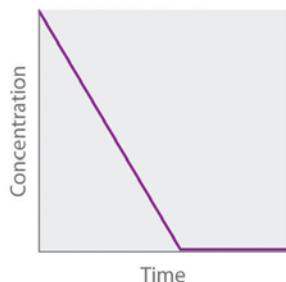
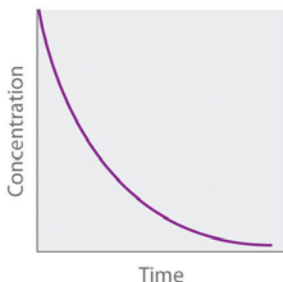
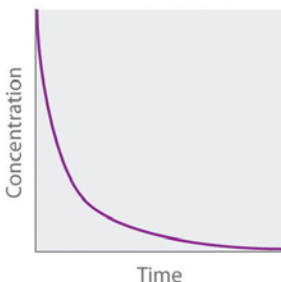
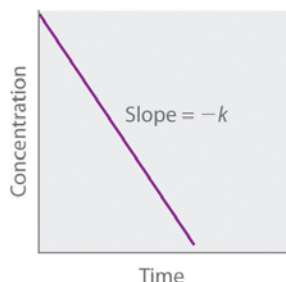

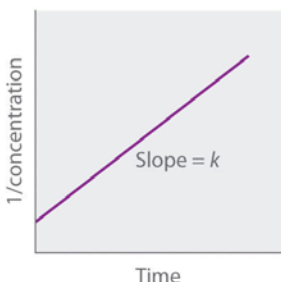
$$\frac{1}{\frac{1}{2}A_0} = \frac{1}{A_0} + kt$$

$$2 = 1 + kt \times A_0$$

$$t_{\frac{1}{2}} = \frac{1}{k \times A_0}$$

The concentration vs. time graphs for first and second orders look quite similar however, first order reactions have a **constant half-life**, whereas with second order reactions each half-life is twice the preceding one.



	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><tr><th>$[A], M$</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	$[A], M$	Rate, M/s	1	1	2	1	3	1	<table><tr><th>$[A], M$</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	$[A], M$	Rate, M/s	1	1	2	2	3	3	<table><tr><th>$[A], M$</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	$[A], M$	Rate, M/s	1	1	2	4	3	9
$[A], M$	Rate, M/s																										
1	1																										
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3	1																										
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3	9																										
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k , rate constant	M/s	1/s	$M^{-1} \cdot s^{-1}$																								

Reaction mechanism

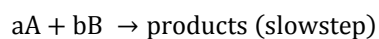
Most reactions that occur at a measurable rate occur as a series of simple steps. The sequence of steps is known as the **reaction mechanism**. The individual steps (**elementary steps**) usually cannot be observed directly. **Intermediates** are substances that are made in one step and used up in another. The sum of the elementary steps should cancel to give the original equation. The term **molecularity** is used in reference to an elementary step to indicate the number of reactant species involved. If a reaction has three, four or more species combining, it is likely that it can be split into steps.

The rate-determining step

The rate equation can be known by knowing the reaction mechanism, specifically the **slowest step**, which acts as a limit on the rate and is therefore called the **rate-determining step**.

The rate equation is also equal to the rate constant (k) multiplied by the concentrations of the substances raised to the power of their respective coefficients in the rate-determining step.

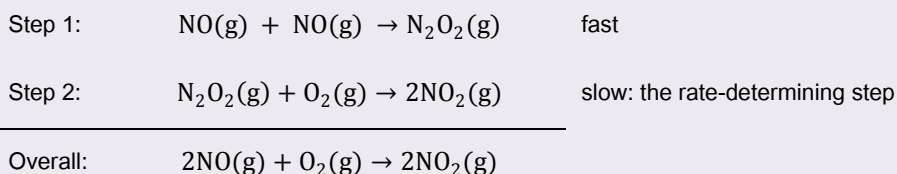
The **order of reaction** is the exact numbers of molecules involved in the rate determining step.



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

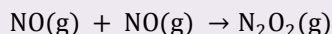
Problem solving

A noteworthy example is the following



$$\text{rate} = k[\text{N}_2\text{O}_2][\text{O}_2]$$

But



therefore:

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

If a species is both on the reactant and product side of the overall equation, it is probably a catalyst.

16.2 Activation energy

- U1 The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.
- U2 A graph of $1/T$ against $\ln k$ is a linear plot with gradient $-E_a/R$ and intercept, $\ln A$.
- U3 The frequency factor (or pre-exponential factor) (A) takes into account the frequency of collisions with proper orientations.
- A1 Analysing graphical representation of the Arrhenius equation in its linear form
- A2 Using the Arrhenius equation
- A3 Describing the relationships between temperature and rate constant; frequency factor and complexity of molecules colliding.
- A4 Determining and evaluating values of activation energy and frequency factors from data.

The rate of reaction increases with temperature (we know this already because of collision theory). A common relationship is that 10°C increase doubles the rate. Looking back at the Maxwell-Boltzmann distribution curve, an increase in temperature means that more particles have an energy greater or equal to the activation energy. This means that the value of the activation energy will determine temperature's effect. When the E_a is larger a temperature rise will make a larger difference, and when the E_a is smaller the temperature change will have a less significant effect.

The Arrhenius equation

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

A = the **Arrhenius constant**– taking account of frequency of collision with correct geometry

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

When temperature increases, k increases exponentially, speed of reaction increases exponentially.

The Arrhenius plot

