

CAIE Chemistry A-level

26: Reaction Kinetics (A-level only)

Notes

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Rate Equations, Orders of Reaction and Rate Constants

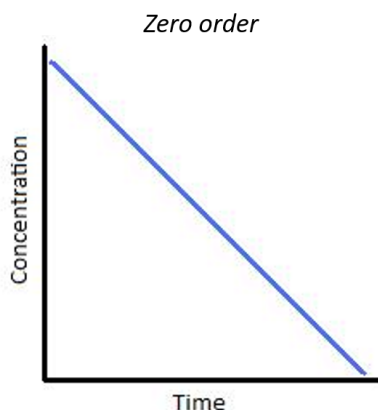
- **Rate equation:** for the reaction $A + B \rightarrow C$, the rate equation is $\text{rate} = k[A]^m[B]^n$ (m is the order of the reaction with respect to A, n is the order of reaction with respect to B).
- **Order of reaction:** the power to which the concentration of a reactant is raised in the rate equation (this could be 0, 1 or 2).
- **Rate constant:** the constant (k) linking rate of reaction and the concentration of reactants. This value changes with temperature and use of a catalyst but remains the same if only concentrations of reactants are changed.
- **Half-life:** the amount of time taken for the concentration of the reactants to halve.
- **Rate-determining step:** the stage with the slowest rate in a multi-step reaction.
- **Intermediate:** is a substance formed between the reactants and the product during a chemical reaction.

If a reaction is 0 order with respect to reactant P, the rate is **unaffected** by changing the concentration of P. If a reaction is first order with respect to reactant Q, doubling the concentration of Q will double the rate (**rate \propto [Q] or rate = k[Q]**). If a reaction is second order with respect to X, doubling the concentration of X will quadruple the rate (**rate \propto [X]² or rate = k[X]²**). The **overall order** of a reaction is equal to the sum of all the orders of the reactants (e.g. if a reaction is first order with respect to reactants A and B, the overall order is $1 + 1 = 2$).

The overall rate equation is in the form: **rate = k [A]^m[B]ⁿ** (for which m and n are 0, 1 or 2 - the order with respect to the compound in []).

Concentration-Time Graphs

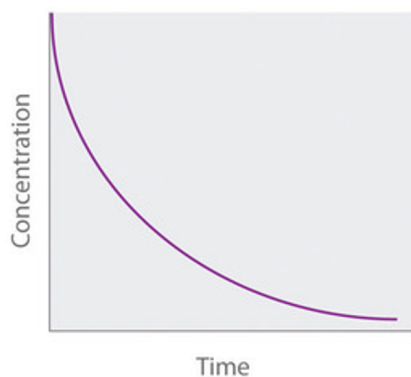
To determine the **order of a reaction**, observe the shape of the **shape of the concentration-time graph** and compare it to the graphs on the following page. The shape of the first and second order graphs appear very similar so to distinguish between these two, calculate the half-life of the reactant. The **half-life of a first order graph will be constant** (the concentration of the reactant will half at equal time intervals).



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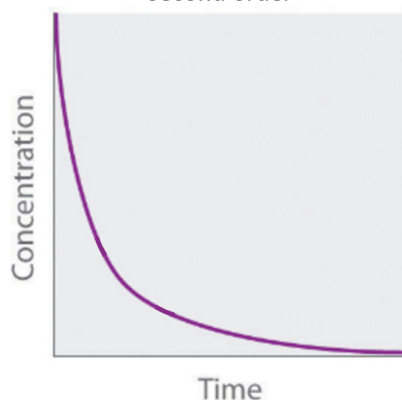


First order



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Second order



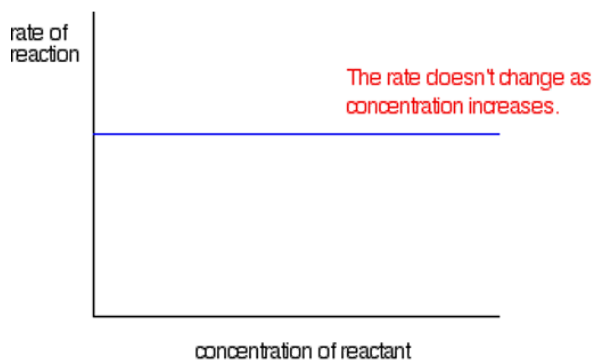
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The initial rate of reaction can be determined by drawing a **tangent** to the concentration-time graph $t = 0$ and calculating the **gradient** of this line (change in $y \div$ change in x).

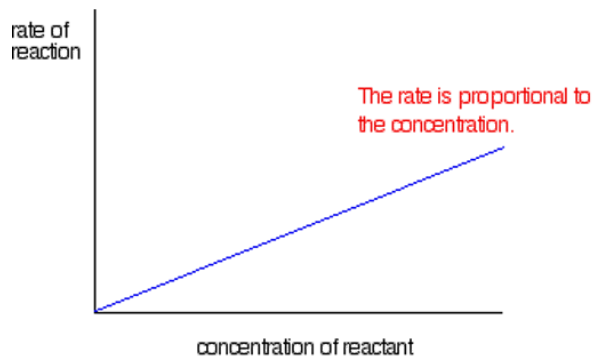
Rate-Concentration Graphs

The order can also be deduced using a rate-concentration graph. Observe the shape of the graph and compare to those shown below:

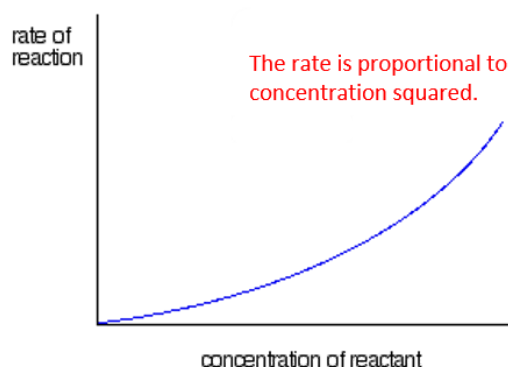
Zero order



First order



Second order



[Jim Clark, Chemistry Libre Texts, CC BY-NC-SA 3.0 US](#)

A **rate-concentration graph** showing a curve isn't necessarily second order (it may be third order or a fractional order for example). To prove that the reaction is second order with respect to reactant X, **rate would have to be plotted against $[X]^2$** (this would be a straight line graph if it was second order). Alternatively, a log graph could be plotted.

Initial Rate Experiments

The orders of reaction can also be determined using experimental data relating to initial rates. An example is shown below:

Experiment	[A] (mol dm ⁻³)	[B] (mol dm ⁻³)	Initial rate (mol dm ⁻³ s ⁻¹)
1	0.10	0.10	0.0015
2	0.20	0.10	0.0060
3	0.20	0.20	0.0120



Between experiments 1 and 2, the concentration of A doubles ([B] stays constant) and the rate quadruples. The reaction is second order with respect to A. Between experiments 2 and 3, the concentration of B doubles ([A] remains the same) and the rate doubles. The reaction is first order with respect to B.

From these results, the rate equation is: $\text{rate} = k[A]^2[B]$.

The rate equation can be used to calculate the rate constant:

- Substitute in experiment 1 values into the rate equation: $0.0015 = k \times 0.10^2 \times 0.10$.
- Rearrange to find k: $k = 0.0015 \div 0.001 = 1.5$.
- Work out units: $k = \text{mol dm}^{-3} \text{ s}^{-1} \div (\text{mol dm}^{-3})^3 = \text{mol}^2 \text{ dm}^{-6} \text{ s}^{-1}$.
- $k = 1.5 \text{ mol}^2 \text{ dm}^{-6} \text{ s}^{-1}$.

Half-life of First Order Reactions

The half life ($t_{1/2}$) of a first order reaction is constant. This means the time taken for the concentration of reactants to half is always the same.

The relationship between the rate constant (k) and the half-life of a first order equation is shown below:

$$k = \frac{\ln 2}{t_{1/2}} \approx \frac{0.693}{t_{1/2}}$$

If the half life of a first order reaction is 150 s, the rate constant would be:
 $k = 0.693 \div 150 = 0.00462 \text{ s}^{-1}$.

Reaction Mechanisms

A reaction mechanism describes the steps involved in making and breaking bonds during a reaction.

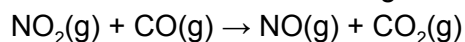
The **slowest step** of a reaction (or the **rate-determining step**) must include reactants which have an impact on the rate of reaction when their concentrations are changed. **Zero order reactants have no influence on the rate of a reaction** so they cannot be included in the rate-determining step.

When constructing a reaction mechanism, the **powers in the rate equation** indicate the number of molecules of each substance involved in the slowest step. Any **intermediates** generated in the slowest step must be reactants in another step as they are **not present** in the balanced overall equation.



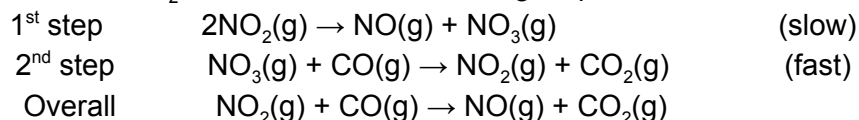
Example mechanism:

Nitrogen dioxide and carbon monoxide react to form nitrogen monoxide and carbon dioxide:



The rate equation for this reaction is: $\text{rate} = k[\text{NO}_2]^2$

- From the rate equation, the reaction is zero order with respect to $\text{CO}(\text{g})$ and second order with respect to $\text{NO}_2(\text{g})$.
- 2 molecules of NO_2 are in the rate-determining step



Temperature and Rate

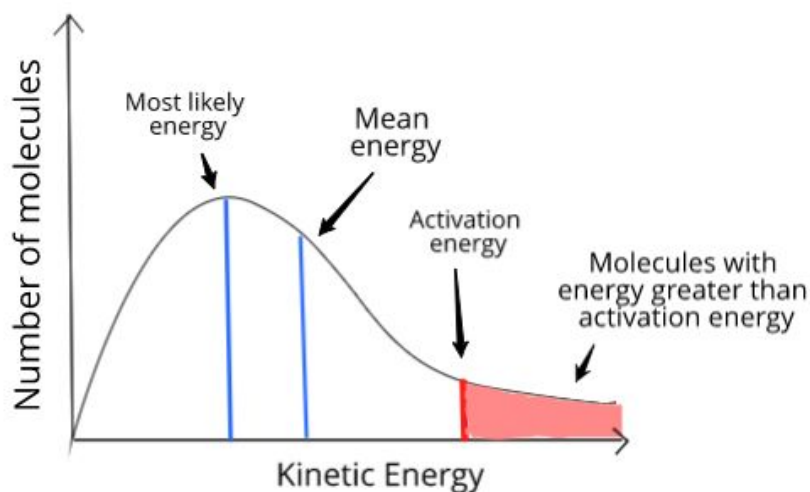
Activation Energy and the Boltzmann Distribution

Activation energy is the **minimum amount of energy required for a reaction to occur**.

Only molecules with energy above the activation energy will react when they collide at the correct orientation.

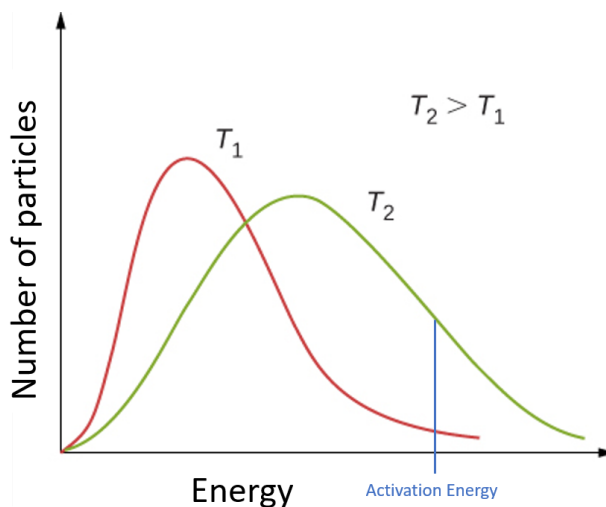
For gases, the relative energies of the particles can be plotted on a graph called the **Boltzmann distribution** (shown on the following page). There are several key points to remember about Boltzmann distributions:

- The area under the curve is equal to the total number of particles present.
- No particles have no energy.
- There is no maximum energy.
- Only particles with energy above the activation energy have sufficient energy to react when they collide.



Changing Temperature

Below is a Boltzmann distribution showing the **relative energies of particles** at 2 different **temperatures** (T_2 is a higher temperature):



[‘Distribution of molecular speeds’, OpenStax, Physics LibreTexts](#)
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Increasing the temperature means the particles have **more kinetic energy** so there will be more collisions in the same amount of time. Also, a greater proportion of the particles have **energy above the activation energy** (as seen in the Boltzmann above) meaning more of the collisions will result in a reaction. This means there will be **more frequent successful collisions** so the rate of reaction will **increase**.

Temperature and the Rate Constant

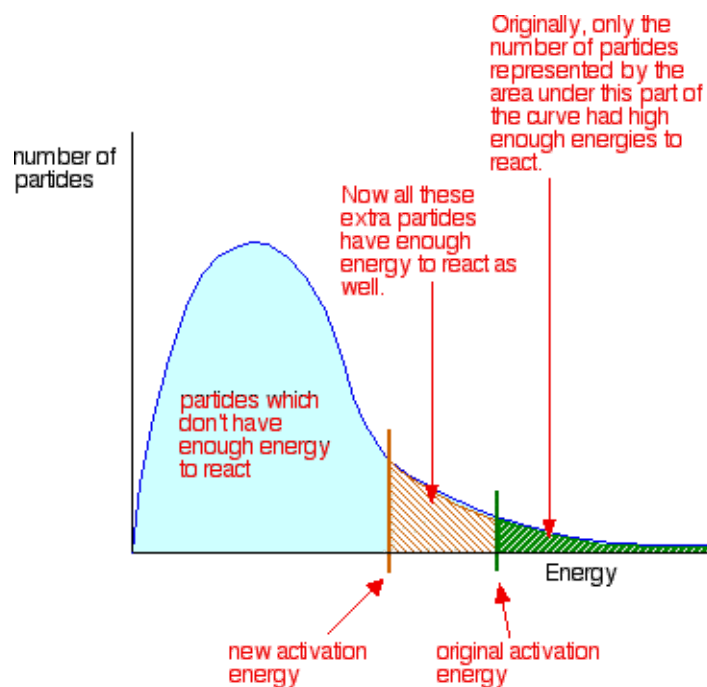
As temperature increases, the rate constant increases. This also means that the rate will increase. For example, the temperature of a reaction with the rate equation $\text{rate} = k[X]$ is increased. If the concentration of X remains the same, the rate of reaction will increase because k is increasing.

Catalysts

A catalyst is a substance which **speeds up the rate** of a reaction **without being chemically changed** at the end. A homogeneous catalyst is in the same phase as the reactants while a heterogeneous catalyst is in a different phase to the reactants (e.g. a solid catalyst with liquid or gaseous reactants). In the presence of a catalyst, a reaction has a **different mechanism**, with a **lower activation energy**.

The Boltzmann distribution on the following page shows the effect of catalysts:

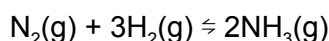




[The effect of catalysts on reaction rates](#). Chemguide
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Haber Process

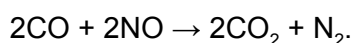
The Haber process produces ammonia from nitrogen and hydrogen:



Iron is the **heterogeneous catalyst** used in the Haber process. Nitrogen and hydrogen **adsorb** onto the surface of the iron. Bonds are broken and made to form ammonia which **desorbs** from the surface. The use of an iron catalyst **increases the rate** at which the equilibrium is established.

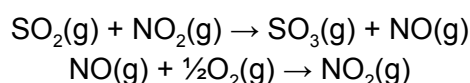
Catalytic Converters

Catalytic converters convert **carbon monoxide** and **nitrogen oxides** from car exhausts into less harmful compounds. Platinum, palladium and rhodium are used as **heterogeneous catalysts**. A ceramic honeycomb is coated in a thin layer of these metals to increase the surface area. The reactants **adsorb** to the catalyst and react. The products then **desorb**. The reaction that takes place is:



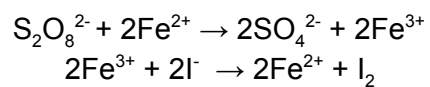
Oxides of Nitrogen and the Oxidation of Atmospheric Sulfur Dioxide

Sulfur dioxide is oxidised in the atmosphere to form sulfur trioxide, which causes acid rain. The reaction is catalysed by the **homogeneous catalyst** nitrogen dioxide. Nitrogen dioxide **reacts** with sulfur dioxide before being **regenerated**:



Iron ions and I⁻/S₂O₈²⁻

Iron(II) or iron(III) ions can be used as a **homogeneous catalyst** for the reaction between I⁻ and S₂O₈²⁻ ions. If Fe²⁺ ions are used, the following reactions occur:



The Fe³⁺ generated in the first reaction are used in the second reaction which regenerates the Fe²⁺ catalyst. If Fe³⁺ ions are used instead, the reactions occur the other way around - the Fe²⁺ ions generated in the reaction with iodide ions are used in the reaction with S₂O₈²⁻ ions.

