

Rates of Reaction

Rate of reaction refers to the amount of reactant used up or product created, per unit time. We can therefore define the rate of a reaction as:

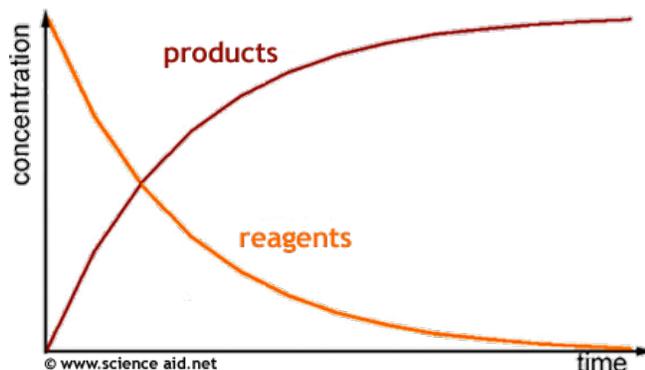
$$\text{Rate} = \frac{\text{change in concentration}}{\text{time}}$$

$$\text{units: mol dm}^{-3} \text{ s}^{-1}$$

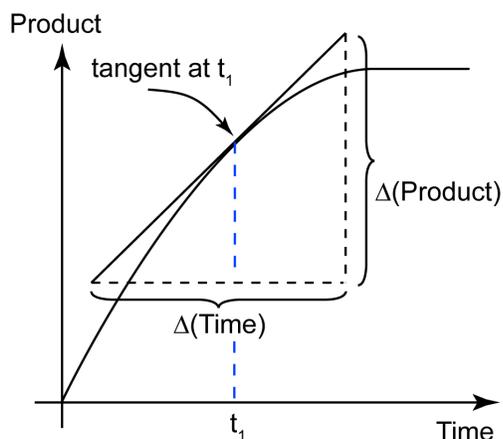
We will find in many rates experiments it is easier to measure changes in mass, or volume of gas, for example. In that case we would end up with units of rate such as g s^{-1} or $\text{cm}^3 \text{ s}^{-1}$.

If we measure the amount of reactant used, or product produced, as it changes during a reaction we can plot a graph with time on the x-axis and concentration (or mass, or volume) on the y-axis.

We should note that the definition of rate we used earlier means that the gradient (gradient = $\Delta y/\Delta x$) of such a graph at any time, t_1 , is equal to the rate of reaction at time t_1 .



We can find the value of the gradient at any time, t_1 , by drawing a **tangent** to the curve on a concentration vs. time graph. A tangent is a straight line drawn so that its gradient is the same as that of the curve at the point where it touches the curve. This is chosen to correspond to the time, t_1 , at which the rate of the reaction is to be found.



The rate is then found using the gradient of the tangent line, by constructing a triangle:

$$\text{Gradient} = \text{rate} = \frac{\Delta(\text{Product})}{\Delta(\text{Time})}$$

It is quite common to want to know the **initial rate** of the reaction. This is found by drawing a tangent to the curve at time = 0 and finding the gradient at this point in the same way.

From the shape of typical concentration vs. time graphs we can see that:

- The initial rate of reaction, at $t=0$, is the fastest rate of reaction, corresponding to when there is the maximum amount of the reactants present
- The rate of reaction decreases progressively as reactants are used up

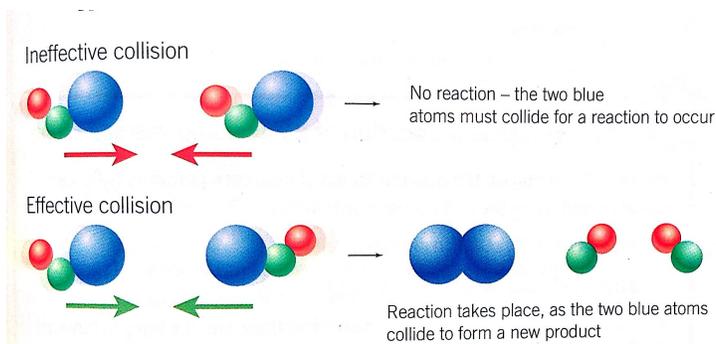
- When one of the reactants has been completely used up, the reaction finished: no more product is produced, the gradient becomes zero, and the rate of reaction becomes zero.

Collision Theory

For a reaction to take place, particles of the reactants must collide with one another. Some collisions are successful and some are unsuccessful.

To be successful, the particles must collide with energy sufficient to break the necessary bonds in the reactants; they must collide with energy greater than the **activation energy** for the reaction.

To be successful the particles must collide with the **correct orientation**, so that the atoms between which new bonds are formed will be next to each other:



Reaction conditions affect the rate of a reaction, and we use collision theory to explain this:

Concentration:

Increasing the concentration of a reactant means having more of that reactant per unit volume. Having more particles in the same volume means that collisions will take place more frequently. Each collision is just as likely to be successful regardless of the concentration, so increasing the frequency of collisions will increase the frequency of successful collisions, increasing the rate of reaction proportionally to the increase in concentration.

Pressure:

Increasing the pressure of a gas compresses the particles into a smaller volume – there are more gas particles per unit volume so the effect is the same as increasing the concentration of a reactant.

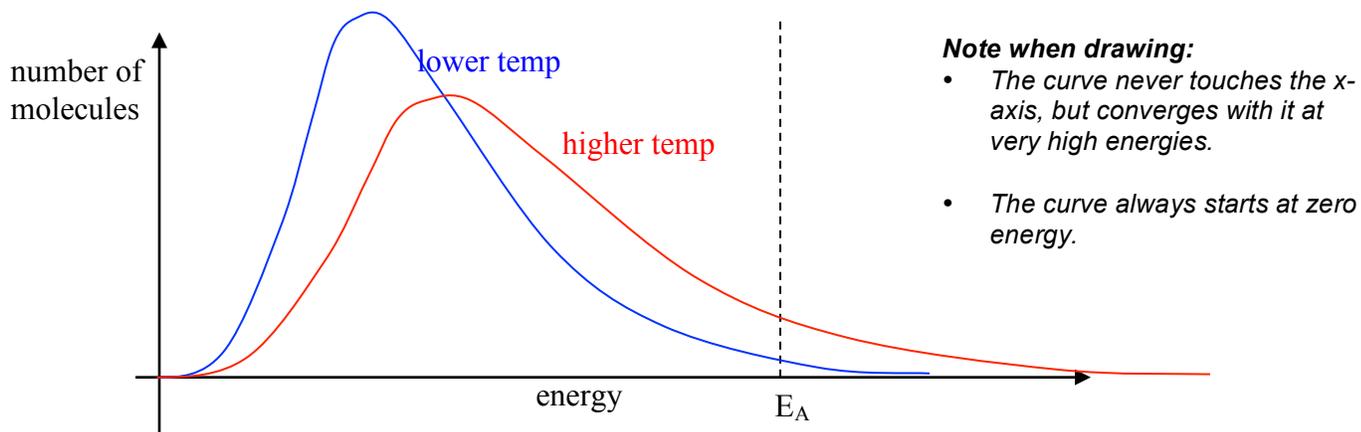
Temperature:

Increasing the temperature of a reactant increases the kinetic energy of the particles. The particles move more rapidly and therefore collide more frequently. In addition, the particles collide with greater energy, and so a higher proportion of the collisions which take place will be successful. These two effects in combination mean that a small increase in temperature can cause a large increase in rate of reaction.

Surface Area:

Only the surface of a solid reactant is exposed for collisions to take place with the other reactant(s) so the greater the surface area of a solid (i.e. the more powdered it is), the more frequently collisions between the solid reactant and the other reactant particles will take place, and the more frequently there will be successful collisions.

The Boltzmann distribution



The Boltzmann distribution shows the distribution of kinetic energies in a collection of particles (molecules) at a specific temperature.

The curve:

- starts at 0,0: no molecules have no energy
- shows that there are only a few very energetic molecules
- has a peak that shows the average energy the particles have

The **area under curve** is equal to the number of molecules in sample (so this mustn't change when the curve is redrawn to represent different temperatures).

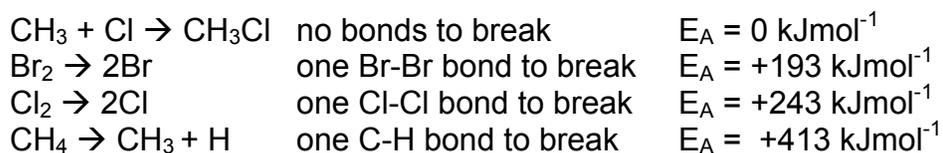
With increasing temperature:

- the curve still starts at 0,0: there are still no molecules with no energy
- the peak is wider and lower: there is a greater distribution of energies among the molecules
- the maximum moves to the right: the average energy of the molecules increases
- the area under the curve remains the same: there are the same number of molecules

Activation energy

The activation energy, E_A , is the **minimum** energy that the molecules/particles need to have in order to react when they collide. This is the same as the **minimum** energy needed to break the necessary bonds in the reactants, in order for new bonds to be formed in the products.

We can compare activation energies by looking at the bond enthalpies of the reactants and summing the bond enthalpies for the bonds that have to be broken:



For any reaction, there will be a value of the Activation Energy, E_A , which can be marked on the energy (x-) axis of the Boltzmann Distribution curve. Particles with energies above E_A have energy sufficient to react when they collide. Particles with energies below E_A do not.

We can expect that the lower the activation energy is, the faster the rate of reaction will be: the greater the proportion of all the particles with energy exceeding E_A , the higher the probability of collisions being successful.

Explaining the effect of temperature on rate

We can use the Boltzmann distribution to help us explain why rate increases with temperature. We need to mark the Activation Energy, E_A , for the reaction on the energy (x-) axis. We can then state that the area under the Boltzmann distribution curve and above E_A at a lower temperature (which is the same as the number of particles with energy greater than the activation energy) is lower than the area under the Boltzmann distribution curve above E_A at a higher temperature, and hence raising the temperature increases the proportion of particles with energy greater than E_A , which increases the proportion of collisions between reactants that will be successful and result in reaction. Hence the rate of reaction will increase at a higher temperature.

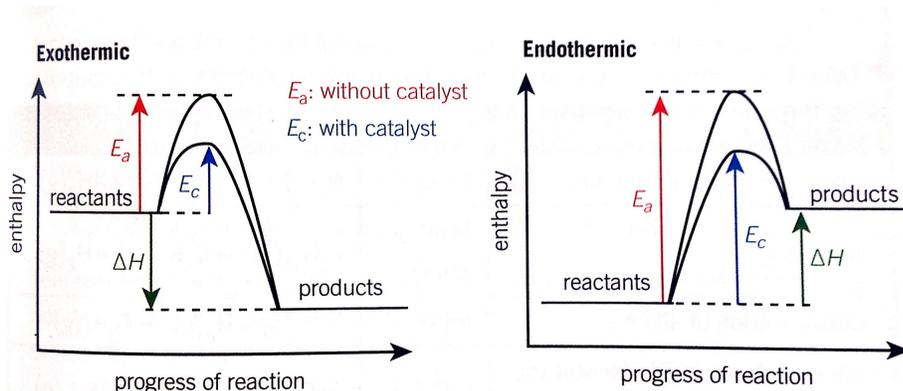
Catalysts

Catalysts increase the rate of a reaction, and are not permanently changed by the reaction. They do this by offering an alternative route (reaction pathway) which has a lower activation energy.

- A catalyst can do this by reacting with a reactant to form an **intermediate**.
- A catalyst can do this by providing a surface on which the reaction can take place.

Regardless of the mechanism of catalysis, the catalyst is always regenerated at the end of the reaction.

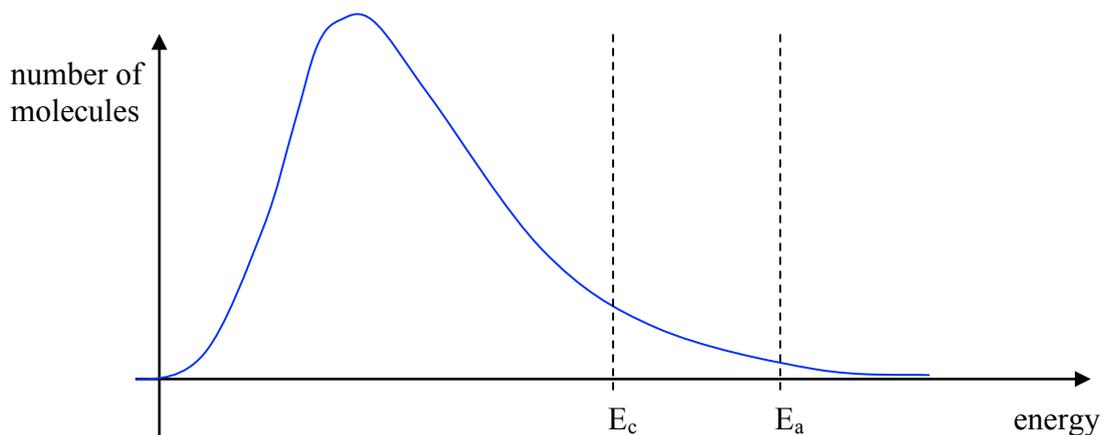
We can see the effect in enthalpy profile diagrams:



*Note:
 $E_c < E_a$ and hence rate
 faster in both cases*

*ΔH is the same
 regardless of whether a
 catalyst is used*

The Boltzmann distribution can also be used to show catalytic behaviour.



We can see that E_c is lower in energy than E_a , so the area under the curve at energy greater than E_c is larger than the area under the curve at energy greater than E_a . This in turn shows that a greater number of molecules have energy in excess of E_c , compared to E_a , and hence a greater proportion of the collisions that take place between the reactants will be successful when the catalyst is present. The rate of reaction will therefore be higher at the same temperature when a catalyst is used.

Alternatively, the same rate of reaction can be achieved at a lower temperature when a catalyst is used, which is important in industry as fuel costs can be saved and emissions reduced.

Types of Catalyst

Catalysts may be **heterogeneous** (different state as the reactants). The following examples are all solid catalysts with reactants in the gaseous state - the most common situation.

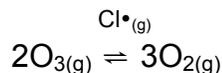
Reaction	Catalyst	Equation
Haber process	$\text{Fe}_{(s)}$	$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$
Reforming	$\text{Pt}_{(s)}$ or $\text{Rh}_{(s)}$	e.g. $\text{C}_6\text{H}_{14(g)} \rightarrow \text{C}_6\text{H}_{12(g)} + \text{H}_{2(g)}$
Hydrogenation	$\text{Ni}_{(s)}$	$-\text{CH}=\text{CH}_{(g)} + \text{H}_{2(g)} \rightarrow -\text{CH}_2-\text{CH}_2_{(g)}$
Contact process	$\text{V}_2\text{O}_{5(s)}$	$2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$

The process of heterogeneous catalysis involves **adsorption** of a reactant on the catalyst surface (formation of a weak bond between the reactant and the catalyst) as a result of which the reactant has its **bonds weakened**, reducing the energy needed to break them. With a lower activation energy, more molecules have energy $> E_A$, so more of the collisions which take place are successful in bringing about a reaction. **Desorption** of the product molecules then takes place - the weak bond to the catalyst surface breaks and the product is released. This is why catalysts are sometime described as places where reactions occur.

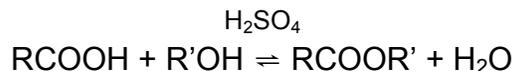
Gases may have to be passed over a gauze/porous heterogeneous quite catalyst slowly to allow time for the reaction to take place, or to allow adsorption to take place.

Other catalysts are **homogeneous** (in the same physical state as the reactants). It is common for homogeneous catalysts to work in aqueous solution

e.g. Chlorine radicals $\text{Cl}\cdot_{(g)}$ catalyse the breakdown of ozone in the upper atmosphere



Sulphuric acid (H^+) is the catalyst used during esterification:

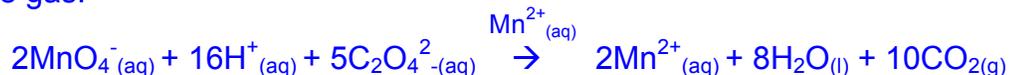


Homogeneous catalysis consists of two steps (often one is a reduction and one is an oxidation):

- The catalyst reacts with the reactants to form an **intermediate**.
- The intermediate then breaks down to give the products and regenerate the catalyst.

Application – you don't need to learn the details of this reaction, but you do need to understand the principles of how it works, and be able to identify the catalyst and intermediate in similar reactions.

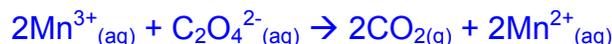
e.g. acidified permanganate ions react with ethanedioate ions, turning them into carbon dioxide gas.



In the first step the Mn^{2+} reduces $\text{MnO}_4^-_{(aq)}$ to $\text{Mn}^{3+}_{(aq)}$:



The intermediate $\text{Mn}^{3+}_{(aq)}$ ions then react with the ethanedioate ions, regenerating the Mn^{2+} catalyst:



In the above example, not only is Mn^{2+} the catalyst, but it is also one of the products – this is unusual. As this reaction proceeds, more of the catalyst is generated, so the rate of reaction will increase exponentially until one of the reactants has been used up. This is called **autocatalysis**.

Catalysts in Industry

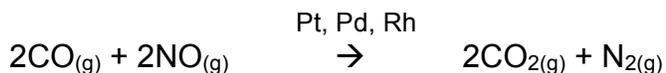
- Lowering the activation energy for a reaction by using a catalyst means that a lower operating temperature can be used to achieve the same rate of reaction. This in turn has benefits in terms of less fuel use and less emission of combustion products – i.e. better **sustainability**.
- Making a product faster and using less energy reduces the production costs and increases profitability – the economic advantages of using a catalyst will, in time, outweigh the costs associated with developing a catalytic process.
- The use of a catalyst may make an alternative reaction possible that has higher **atom economy** – less waste.

Application

The traditional synthesis of ibuprofen involves 6 steps and has an atom economy of 32%. Using catalysts it can be made in 3 steps with an atom economy of 77%.

Catalysts and the Environment

Catalysts are also used to transform harmful or toxic waste gases into more benign products. The most common example of this is the automotive catalytic converter. Incomplete combustion in the car engine, along with the high operating temperature results in the production of carbon monoxide and oxides of nitrogen. The catalytic converter converts these into CO₂ and N₂ respectively, and also converts any unburnt hydrocarbon fuel into CO₂ and H₂O.



Disposal

Catalysts eventually become poisoned and need to be replaced. Disposing of them in landfill may cause environmental problems as they may contain toxic heavy-metal compounds. They will need to be recycled or converted into less harmful forms. Some catalysts contain precious metals such as Pt, which needs to be recovered and recycled.