Collision theory

Learning objectives

- ❑ Calculate the rate of reaction from data and from a graph
- ❑ Know that reactions only occur when particles collide in the right orientation
- ❑ Know that reactions only occur when particles have enough energy
- ❑ Define the term activation energy
- ❑ Explain why most collisions do not lead to a reaction
- ❑ Be able to draw and interpret Maxwell-Boltzmann curves

Rate of reaction

The rate of a chemical reaction **varies**. Explosions happen quickly, in seconds, whereas rusting of iron occurs slowly over days, sometimes years and the formation of diamond takes millions of years. We can **calculate** the rate of reaction:

$$Rate = \frac{Change\ in\ mass, concentration\ or\ volume}{time}$$

Units

There are several units for rate of reaction, e.g. g s^{-1} , mol dm^{-3} s^{-1}

It depends on the units in the equations! So watch out in exams.

Examples

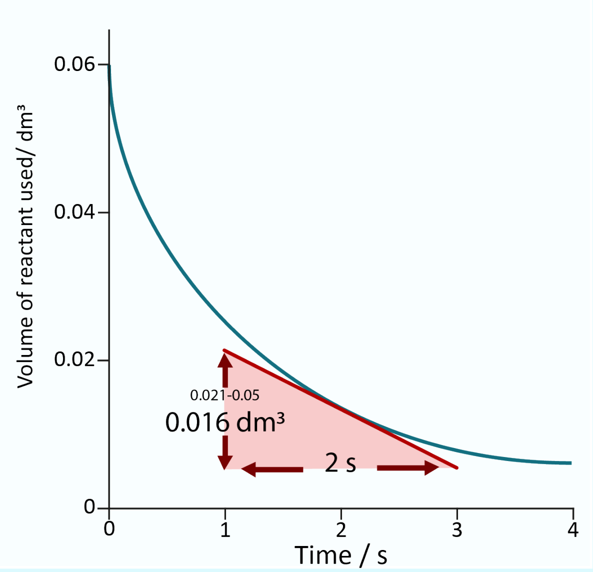
1. In a reaction 1.8 mol dm^{-3} of a product was formed in 37 seconds, calculate the mean rate of reaction:

Rate = $\frac{1.8}{37}$ 1 = 0.049 mol dm^{-3} s^{-1}

2. What is the rate of reaction at 2 seconds?

It is also possible to work out the rate of reaction from a graph.

1. Draw a tangent from the point where you want to find the rate – at 2 seconds here.
2. Calculate the gradient of that tangent ($\text{gradient} = \frac{\Delta y}{\Delta x} = \frac{\text{change in y}}{\text{change in x}}$)
3. In this case:
   Change in x = 3 -1 = 2 s
   Change in y = 0.021 – 0.005 = 0.016 dm^3
4. Rate = $\frac{0.016}{2} = 0.008$ dm^3 s^{-1}



There are a few factors that affect the rate of reaction:

- Temperature
- Pressure
- Concentration
- Surface area
- Whether a catalyst is present

Collision theory

Collision theory

Molecules can only react if they **collide**:

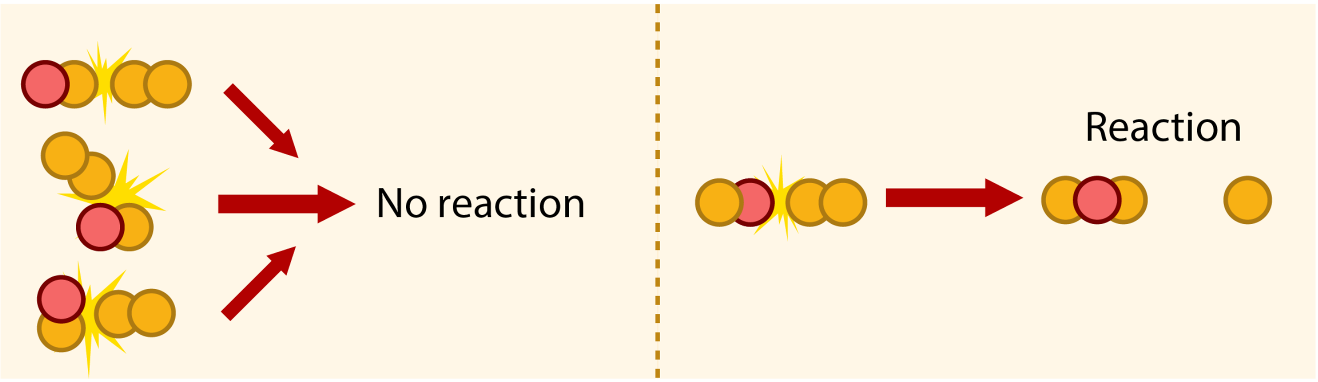
- in the right **orientation**

  AND

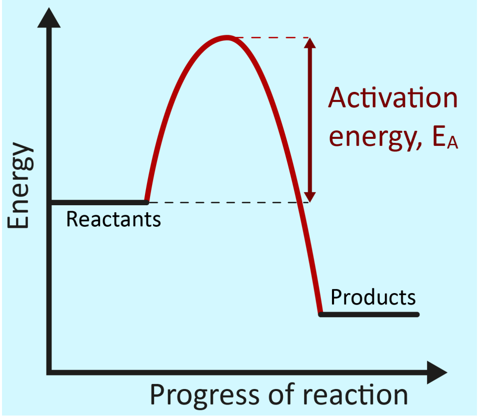
- have **enough energy** to overcome the **activation energy**

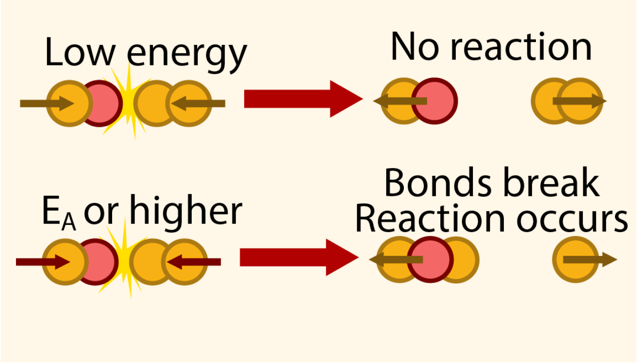
Most collisions **do not** have enough energy or happen in the **wrong orientation**, and so no reaction occurs.

More collisions happen in the wrong direction than the right direction, as there are more possible ways of colliding in the wrong direction.



Activation energy is the **minimum** amount of **kinetic energy** particles need to react. This energy is used to **break the bonds** of the reactants and start the reaction. So, even if the particles collide in the right way the reaction will **not happen unless** they have **enough energy.** If particles collide, in the right direction but without the activation energy, they will just **bound apart**. Reactions with low activation energies happen easily. However, reactions with high activation energies often need to be heated, so the particles have the energy to overcome the high activation energy.



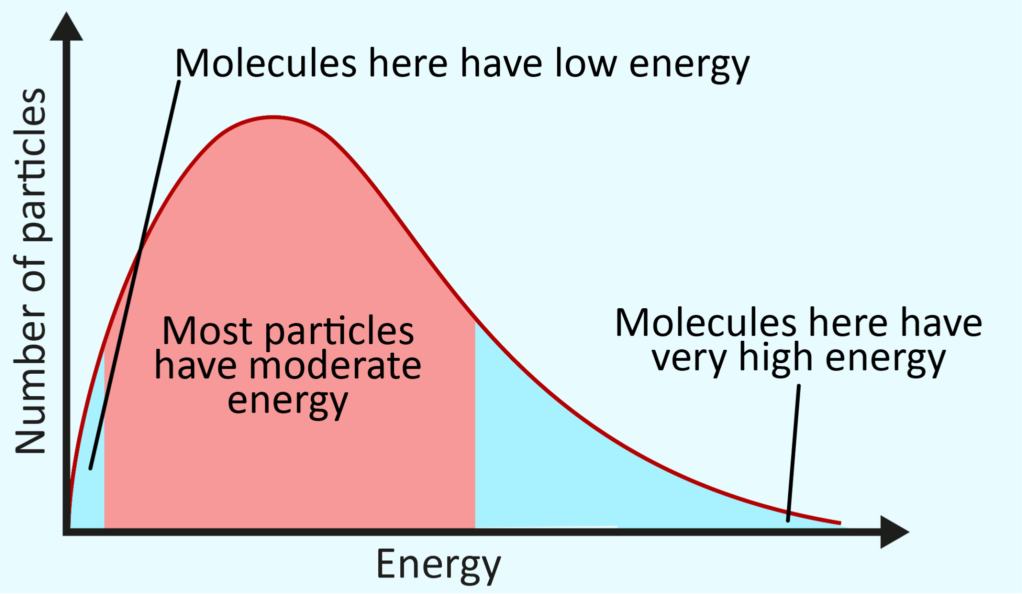


The **rate of reaction** is **dependent** on the **number of successful collisions**, aka collisions in the correct orientation with enough energy, E_A or higher, to break the bonds of the molecules.

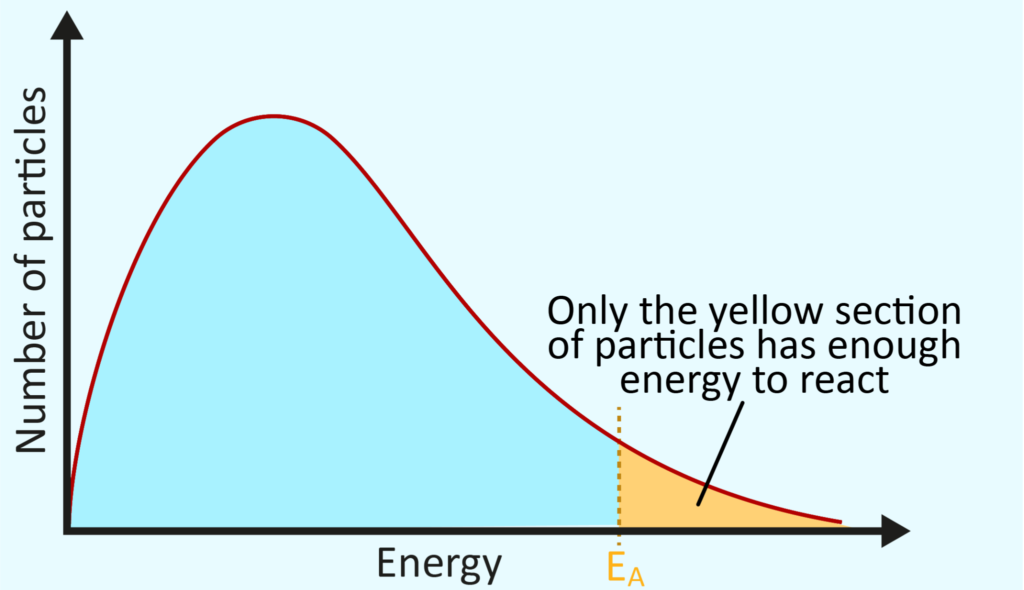
Collision theory

Boltzmann distribution curve

The **kinetic energy** a particular particle in a group of particles **varies**. Some will be going **very slowly**, and some will be going very **quickly**, but most will have a **similar speed**. The **Maxwell-Boltzmann distribution** curve is a graph showing the **kinetic energy of molecules** versus the **number of molecules**. The peak shows us the **mode (the most common) energy** of the particles. The **area** under the curve represents the **total amount of particles**. Most of the **area falls under the peak**, showing us that most particles have an energy near the **mode energy**.



We often mark where the **activation energy** is on the y-axis. It helps us visualise **how many particles** have an **energy equal to or higher energy** than the **activation energy.** The more particles that have the activation energy the more successful collisions will occur.



The **shape** of the Maxwell-Boltzmann distribution is the **same**, at a **given temperature** for a set number of molecules, regardless of what the molecule is.

Factors affecting rate

Learning objectives

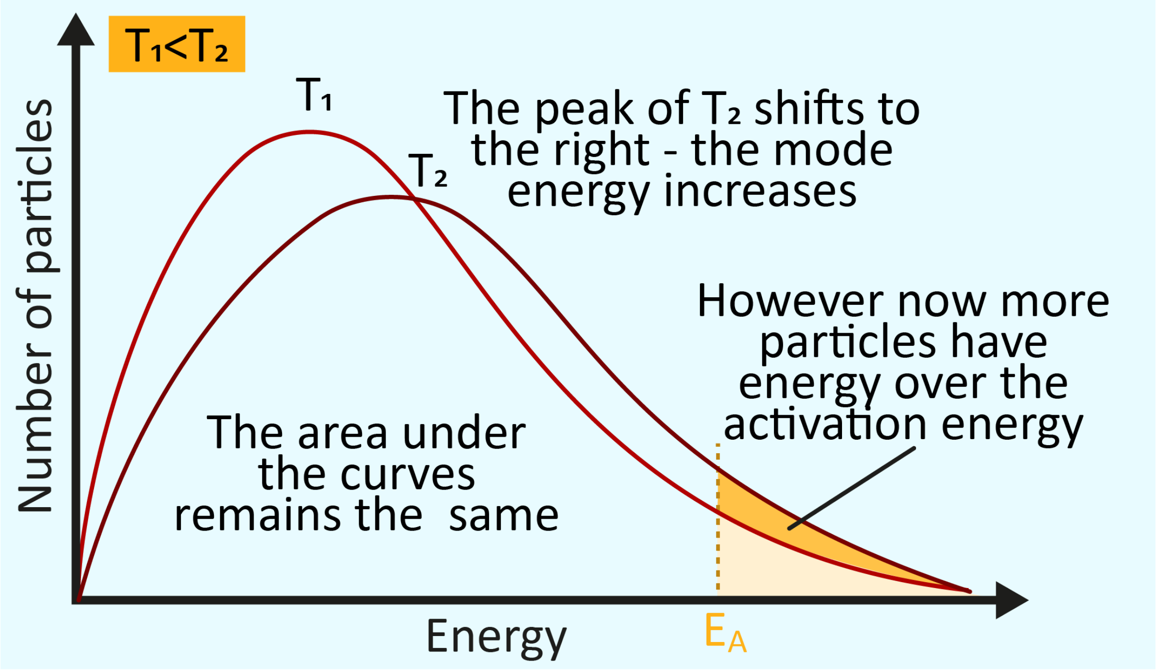
- ❑ Explain, using collision theory, how a change of temperature affects the rate of reaction
- ❑ Use Maxwell-Boltzmann distribution to explain how a small temperature increase affects yield
- ❑ Explain, using collision theory, how a change of pressure and concentration affect the rate of reaction
- ❑ Use Maxwell-Boltzmann distribution to explain show how pressure and concentration effects yield

Temperature

The temperature of a substance refers to the amount of kinetic energy that the substance has. **Increasing** temperature affects the **rate of reaction** in two ways:

1. **Particles can only react if they collide.**
   The **higher** the temperature, the **more kinetic energy** the particles have. This means the particles will be **moving around faster**, and so, **more collisions** will be happening per second. The **more collisions** there are means there will also be **more successful collisions**, and so the **rate of the reaction will increase**.
2. **Successful collisions require energy higher than the activation energy.**
   An **increase in temperature** also means that **more particles** will have an energy higher than the **activation energy**. This means that a **larger proportion of collisions** will be successful, and so the **rate of reaction will increase.**

Overall, when temperature increases, the number of successful collisions increases and so the rate of reaction increases.



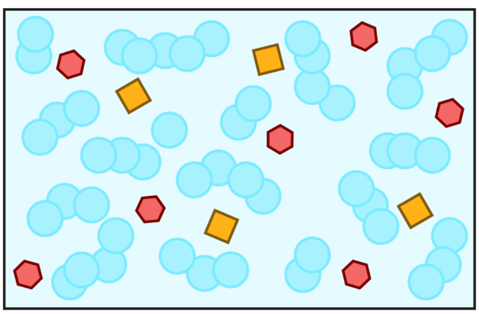
Factors affecting rate

A **change in temperature changes** the **shape** of the **Maxwell-Boltzmann** distribution. This is because **temperature is directly related to energy**. An increase in temperature causes the **peak to lower** and **shift to the right** – **increasing** the number of particles with the **activation energy**. A decrease in temperature **raises the peak and shifts it to the left** – decreasing the number of particles with the activation energy. The **area under the graphs** is equal to the number of molecules remains the same.

Reducing the temperature has the opposite effect, lowering the kinetic energy of the particles. Less collisions will occur per unit time and less particles will have energy higher than the activation energy. Overall the number of successful collisions decreases and the rate of reaction decreases.

Concentration and pressure

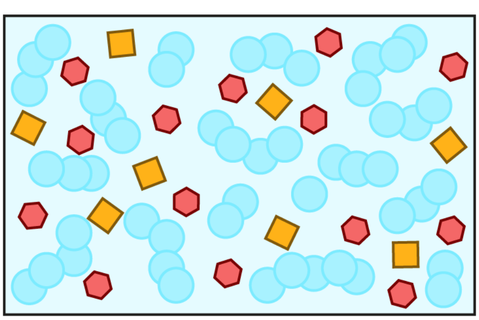
Changes in concentration (in aqueous solutions) and **pressure** (in gaseous reactions) affect rates of reaction similarly. This is because **an increase** in both pressure and concentration result in molecules becoming **more closely packed together**:



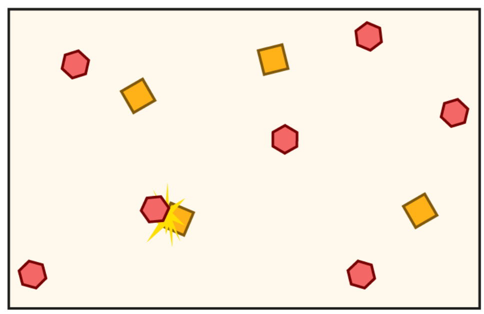
4 ■ per unit volume
7 ⬢ per unit volume

Increase in concentration

8 ■ per unit volume
14 ⬢ per unit volume



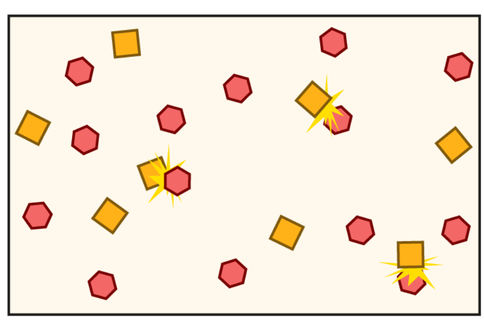
More reactants per unit volume of water means more collisions per unit time



4 ■ per unit volume
7 ⬢ per unit volume

Increase in pressure

8 ■ per unit volume
14 ⬢ per unit volume

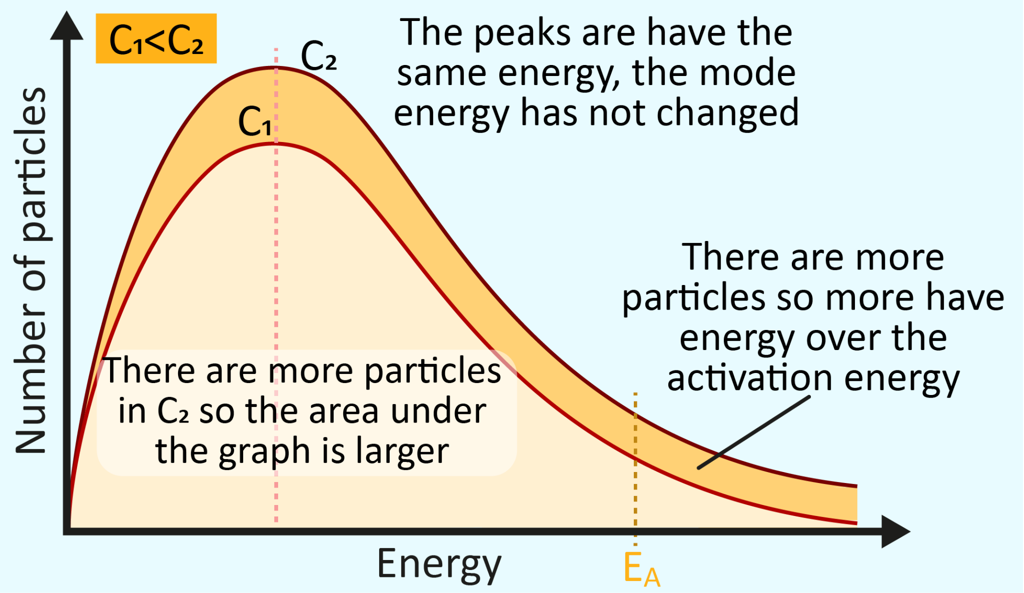


More reactants per unit volume means more collisions per unit time

Factors affecting rate

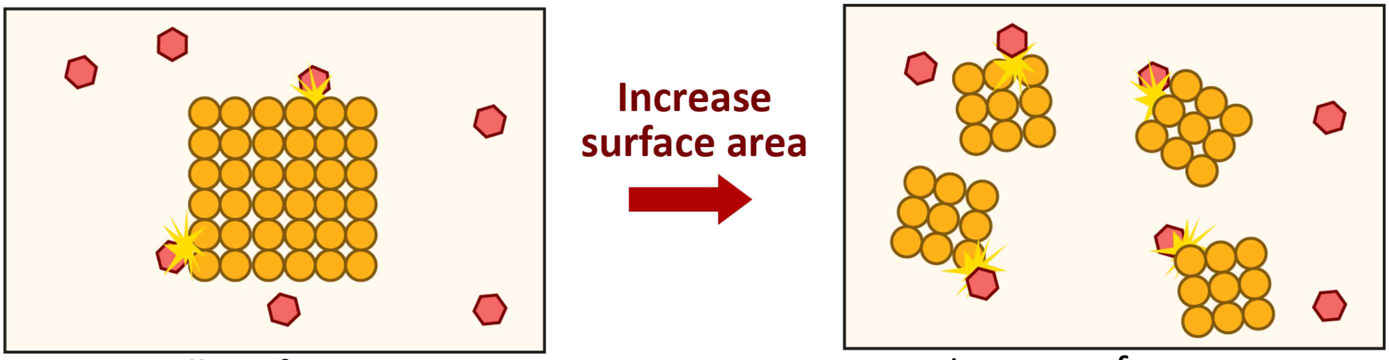
If the molecules are **closer together**, they are **more likely to collide** with each other. **More collisions** means **more successful collisions**. An increase in pressure or concentration also means there will be **more molecules per unit volume**; this means there will be **more molecules,** so **more molecules** will have energy higher than the **activation energy.**

A change in **pressure/concentration changes** the shape of the **Maxwell-Boltzmann distribution**. An increase in pressure or concentration means there are **more molecules (per unit volume)**, and so, **graph moves up**. There are more molecules, therefore more molecules will have the activation energy. There is an increase in the rate of reaction. A decrease in concentration or pressure means there are fewer molecules, and the graph moves down, so fewer molecules will have the activation energy.



Surface area

Surface area of a solid also **affects rate of reaction**. The **more surface area**, the **more particles are available to react**. With more particles exposed **more collisions** take place and so **more successful collisions** take place, **increasing the rate of reaction**.



Small surface area
20 available

Large surface area
32 available

5. (a) (i) State two factors other than a change in temperature or the use of a catalyst that influence the rate of a chemical reaction.

→ pressure of gas

→ amout of Surface area

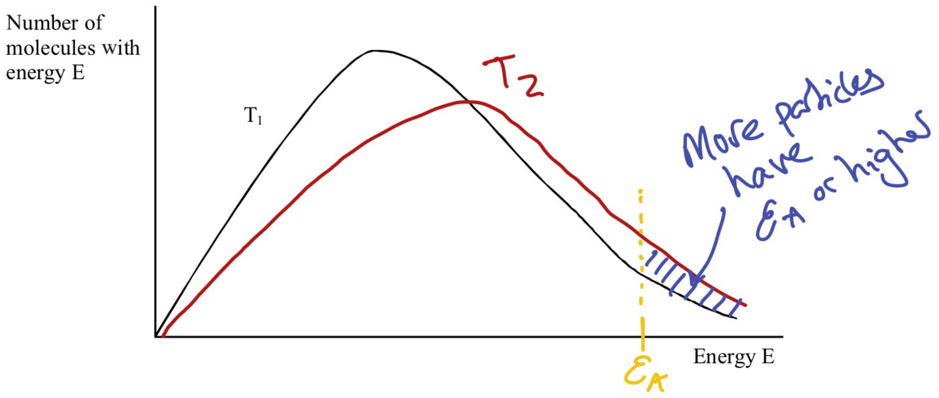
(2)

(ii) For one of the factors you have chosen explain the effect on the rate.

→ increase of surface area, means More molecules avalible to react. More collisions occur → More sucessful collision occur.

(2)

(b) The Maxwell–Boltzmann distribution of molecular energies at a given temperature T_1 is shown below.



(i) On the same axes draw a similar curve for a reaction mixture at a higher temperature T_2.

(2)

(ii) Place a vertical line marked E_a at a plausible value on the energy axis to represent the activation energy for a reaction.

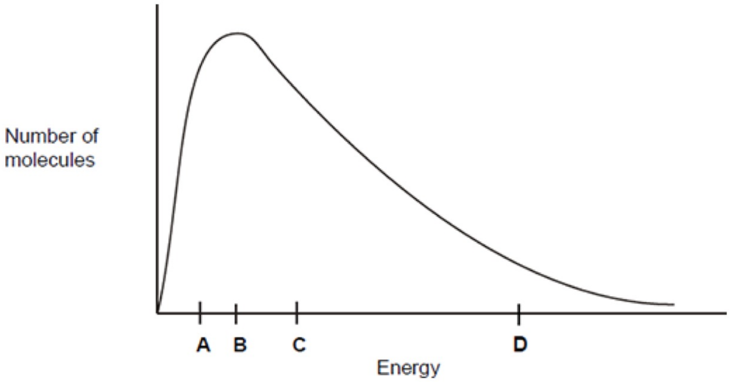
(1)

(iii) Use your answers to parts (i) and (ii) to explain why an increase in temperature causes an increase in the reaction rate.

At higher temperatures Molecules have more kinetic energy. There will be more collisions and more particles will have energy $\geq E_A$ ∴ more sucessful collisions

(3)
(Total 10 marks)

3. This question is about the Maxwell–Boltzmann distribution of molecular energies in a sample of a gas shown in the figure below.



Which letter best represents the mean energy of the molecules?

A ☐
B ☐
C ☒
D ☐

Mean, C is the average energy.
Mode, B is the most common
Mean is further to the right than mode as the particles moving very fast increase the mean.

(Total 1 mark)

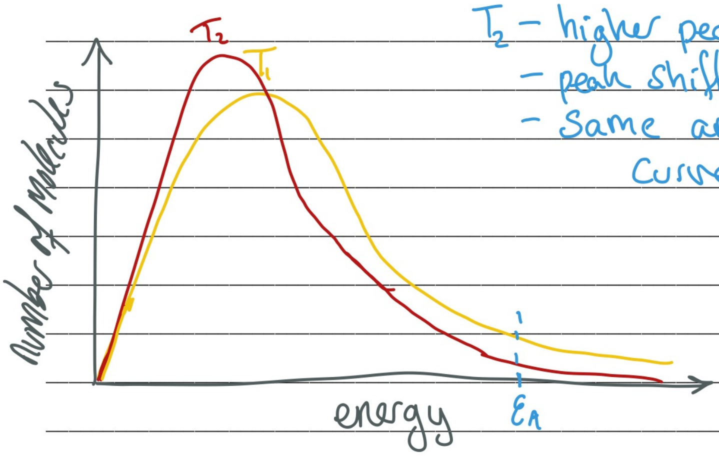
4. (a) Define the term *activation energy* for a chemical reaction.

The Minimum energy required for a reaction to start.

(2)

(b) Draw, with labelled axes, a curve to represent the Maxwell–Boltzmann distribution of molecular energies in a gas. Label this curve **T**$_1$. On the same axes, draw a second curve to represent the same sample of gas at a lower temperature. Label this curve **T**$_2$.

Use these curves to explain why a small decrease in temperature can lead to a large decrease in the rate of a reaction.



T_2 – higher peak
– peak shifted to left
– Same area under Curve.

A small decrease in temperature results in less molecules having E_A.

(c) Give **one** reason why most collisions between gas-phase reactants do not lead to a reaction. State and explain **two** ways of speeding up a gas-phase reaction other than by changing the temperature.

The orientation of the collision is wrong.

To increase rate

- Increase pressure
  - the molecules will be closer together
  - More collisions will happen
  - ∴ more sucessfull collisions
- Increase temperature
  - molecules faster - more collision
  - More kinetic energy - More particles have E_A.
  - ∴ more sucessfull collisions

(5)

(Total 15 marks)

Catalysts

Learning objectives

- ❑ Define the term catalyst
- ❑ Be able to draw the reaction profiles for uncatalysed and catalysed reactions
- ❑ Use a Maxwell-Boltzman distribution to help explain how a catalyst increases the rate of a reaction involving a gas
- ❑ Know the economic benefits of catalysts
- ❑ Understand the use of a solid catalyst for indusial reaction in the gas phase

Catalyst

A **catalyst** is a molecule that **speeds up a reaction without** being **chemically changed** itself. Although the catalyst **takes part in a reaction**, it is **remade** by the end of the reaction. So, at the end of the reaction you have the same amount of catalyst that you started with.

A catalyst **speeds up the rate of reaction** by providing **another chemical pathway** with a **lower activation energy**, this means **more molecules** will have enough **energy to react**, and so **more successful collisions happen**.

Example

Consider the reaction:

$$A + B \longrightarrow AB$$

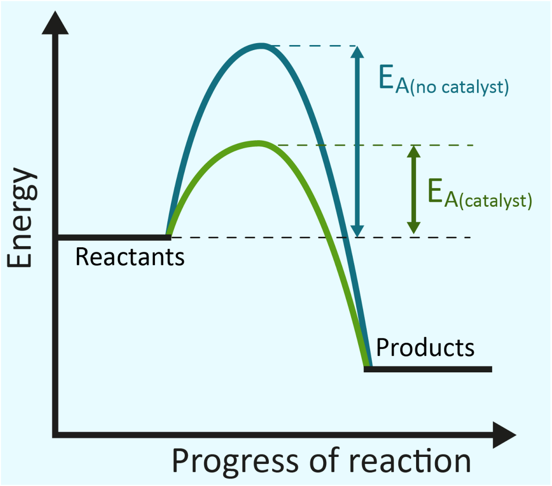
When we **add the catalyst C** to the reaction, the reaction can happen differently:

$$A + C \longrightarrow AC$$

$$AC + B \longrightarrow AB + C$$

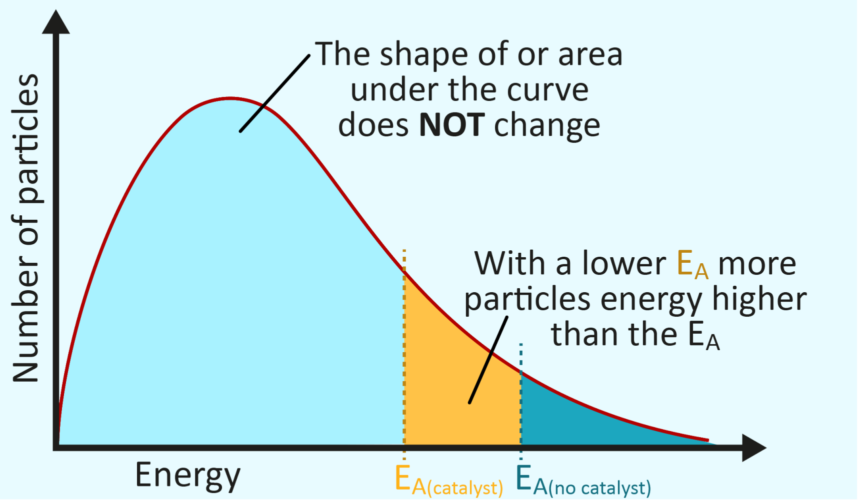
This **new pathway** has a **lower activation energy**, and so increases the rate of the reaction. (Or reduces the temperate and pressure needed to achieve the same rate of reaction.) The catalyst is reproduced at the end and can be used again

We can show the difference in activation energies using a reaction profile:



Catalysts

A catalyst **does not change the Maxwell-Boltzmann distribution**. However, it shifts the activation energy to the **left**. This means the area under the curve after the activation energy is larger and so **more molecules have energy above the activation energy.**

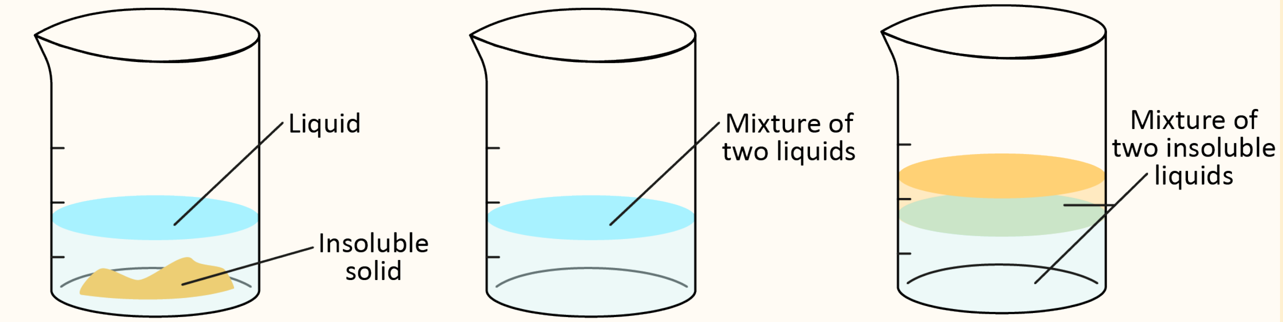


Types of catalysts

There are two main types of catalyst – **heterogeneous** and **homogeneous**. Heterogeneous catalysts are in a different phase than the reactants, and in a homogeneous, it is in the same phase.

Phases

A phase describes a mixture or a substance that has a boundary.
For example:



An isolable solid in a liquid, both the solid and liquid are their own phase.

A mixture of a dissolved solid and liquid is just one phase.

Some liquids that don't dissolve in each other have different phases, e.g. oil and water.

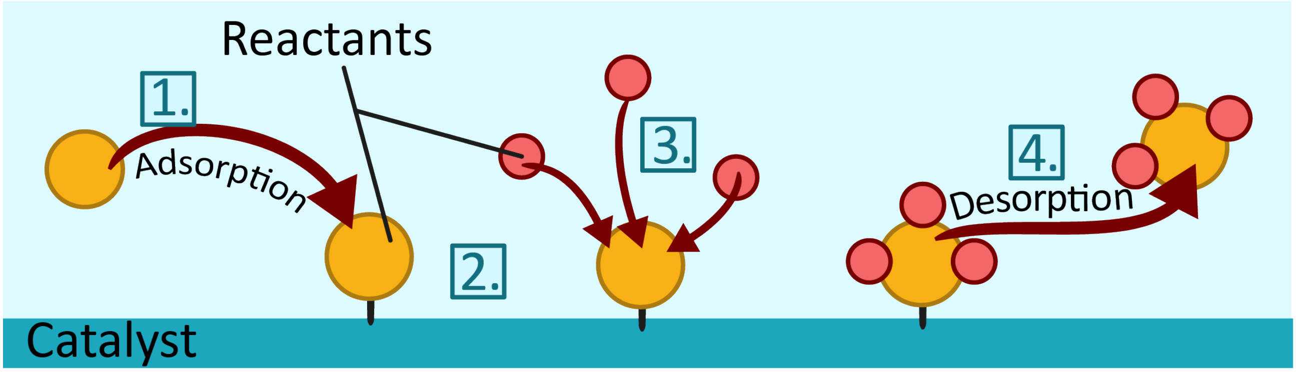
Heterogeneous catalyst

In most cases, the heterogeneous catalyst will be a **solid**, with either liquid or gaseous reactants. They work by **adsorption**. **Adsorption** (not to be confused with absorption) is where a **molecule sticks to a surface** of an solid. Absorption is when the molecule is taken within the structure of another substance.

Catalysts

How heterogeneous catalysts work:

1. One or more reactants are **adsorbed** onto the catalyst
2. This cause the reactant to be **more reactive** (for example the bonds might weaken)
3. The **reaction happens**
4. The product is **desorbed** (the opposite to adsorbed)



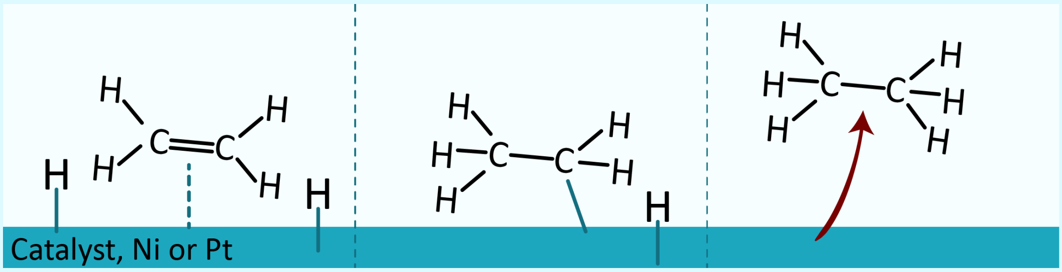
A useful catalyst will adsorb the reactant **strongly enough** for the reaction to take place but **desorbs easily** sufficient for the product to be collected.

A **catalyst** will typically only work on a **specific reaction**. Using catalyst can save lots of **money** in industrial processes. This is because a catalyst **will reduce the temperature and pressure** needed to achieve the same rate of reaction. This reduces the energy needed and so reduces cost of the reaction overall. Catalysts also **reduce carbon emissions** by reducing the energy needed.

Common catalysts

Reaction	Catalyst
Decomposition of hydrogen peroxide	Manganese(IV)oxide, MnO2
Nitration of benzene	Conc. Sulphuric acid
Haber Process (making ammonia)	Iron
Contract Process (making sulphuric acid)	Vanadium(V)oxide, V5O5
Hydrogenation of a C=C double bond	Nickle

Example: Hydrogenation



The alkene and H_2 are **adsorbed** on to the catalyst. H_2 **dissociates**. The **double bond breaks.** One end of the **alkene bonds wit a H atom** while the other carbon is still **attached to the catalyst**. The **second** carbon atom bonds to a H atom. The molecule is **desorbed**.

Catalysts

Example

Catalytic converters
Cars produce **poisonous** molecules, such as **carbon monoxide** and **nitrogen oxidises**. Catalytic converters **convert** these compounds into **less harmful molecules** such as **carbon dioxide** and **nitrogen**. They use catalysts like platinum, palladium and rhodium – all expensive metals.

$$2CO + 2NO \rightarrow \text{Gases travel through the catalytic converter} \rightarrow 2CO_2 + N_2$$

Toxic gases from engine — Non-toxic gases into air

Homogeneous catalyst

These are catalysts in the **same phase** as the reactants. You do not need to know as much about these. An example is the reaction between persulphate ions and iodide ion to form iodine. These ions are **both negative** so a collision is **very unlikely**. However, if we add iron(ii) the reaction can happen:

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

Enzymes

The body has evolved its **own catalysts**; we call them **enzymes**. Enzymes are large **complex molecules** with **active sites** that have evolved over billions of years for very **specific reactions**. These active sites are shaped to fit specific reactants in very specific reactions. Some **diseases** are caused when the **body produces faulty enzymes** or doesn't produce them at all. These diseases tend to be rare; some examples are below. **You do NOT need to know these.**

Name	Brief description
Gaucher Disease	An enzyme that breaks down fatty substances is faulty. It leads to a build-up in of fatty substances in liver, spleen and bone marrow.
Hunter Syndrome	An enzyme that breaks down harmful molecules is missing, leading to a build-up of damaging molecules that cause a numerous amount of symptoms, from stunted growth to white skin growths.
Wilson's Disease	An enzyme that helps remove copper from your body is missing or faulty. A build-up of copper is deadly. However, when diagnosed, this disease is easy to treat.

Humans have used **enzymes** as catalysts for **thousands of years**. For example, we use **enzymes in yeast** to make **bread rise**. Enzymes are very convenient catalysts they work best at **room temperature**, which makes **production cheaper**. Enzymes can be used to make drugs and are also useful for breaking down toxic substances.

Exam Questions

1 Catalysts speed up the rate of a reaction without being consumed by the overall reaction.

(a) Chlorine radicals in the stratosphere act as a catalyst for ozone depletion.

(i) Research chemists have proposed possible reaction mechanisms for ozone depletion. The equations below represent part of such a mechanism.

Complete the equations.

$Cl + O_3 \rightarrow$ ClO + O_2

$ClO +$ O $\rightarrow$ Cl $+ O_2$ **[2]**

(ii) Write an equation for the overall reaction in **(i)**.

$O_3 + O \rightarrow 2O_2$ **[1]**

(b) One of the catalysed reactions that takes place in a catalytic converter is shown below.

$$2CO(g) + 2NO(g) \rightarrow N_2(g) + 2CO_2(g)$$

The catalyst used is platinum/rhodium attached to a ceramic surface.

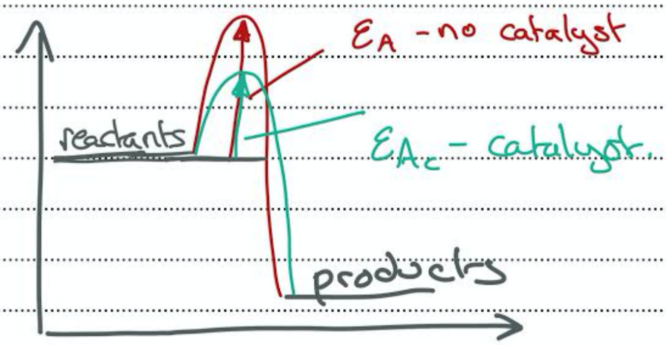
Outline the stages that take place in a catalytic converter to allow CO to react with NO.

1. CO and NO are adsorbed onto surface.
2. This weakens the reactants bonds
3. The chemical reaction occurs
4. Products are desorbed

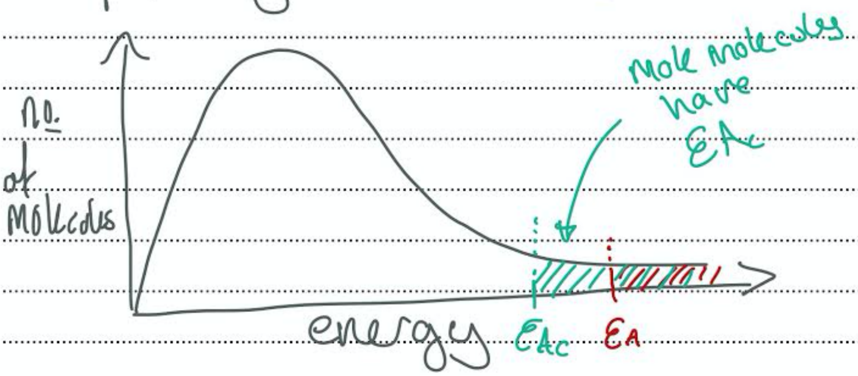
[4]

(c) Explain, using an enthalpy profile diagram and a Boltzmann distribution, how the presence of a catalyst increases the rate of reaction.

In your answer you should organise your answer and use the correct technical terms.



A catalyst will lower the activation energy. It does this by providing a alternative chemical pathway, (or mechanism). This new pathway has a lower E_A.



More molecules will have energy greater than or equal to E_{A_c} than the old E_A

[7]

(d) Explain why many industrial manufacturing processes use catalysts.

Include in your answer ideas about sustainability, economics and pollution control.

Catalyst can reduce temperatures and reduces pressures needed for a reaction to occur. This means LESS energy is used. Energy cost money and produces pollution. Reducing energy used reduces cost and is more sustainable