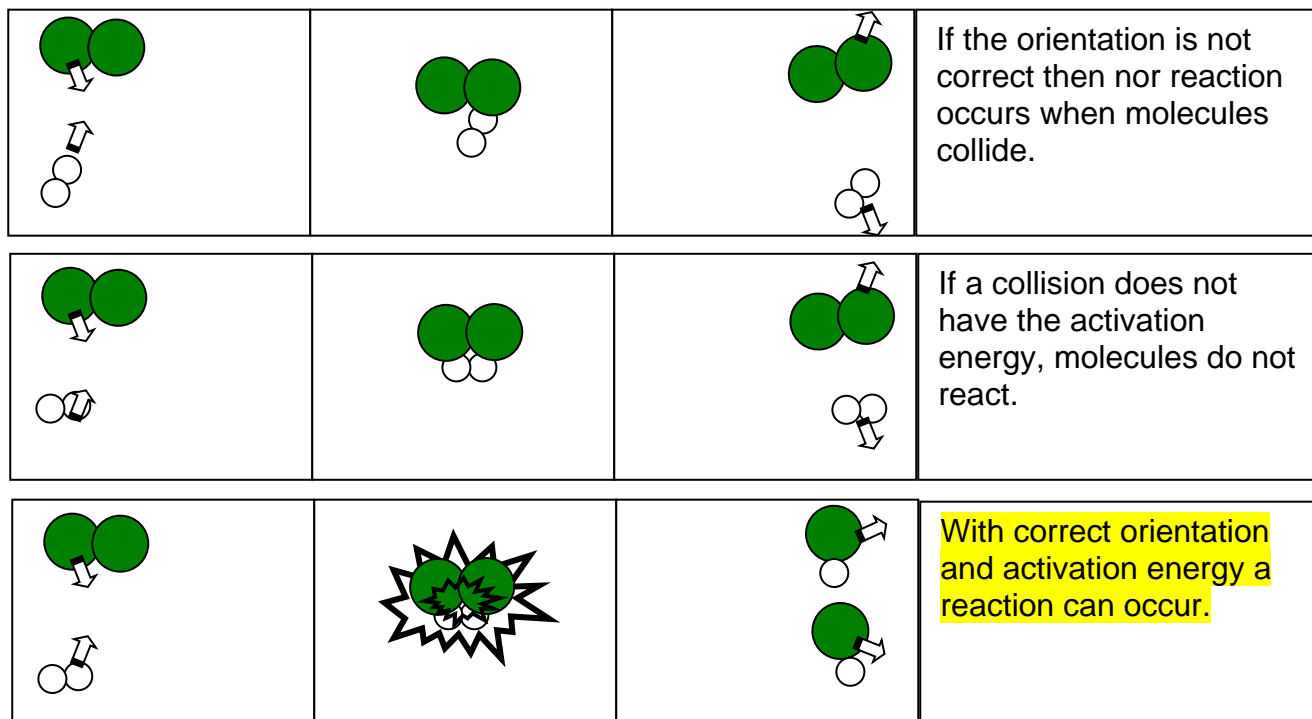


# RATES

## The Collision theory

The collision theory explains rates of reaction in terms of colliding particles. Essentially it says that before two particles can react they have to undergo a collision with each other. However, if the rate of a reaction is compared to the number of collisions which take place it is found that only certain collisions produce a reaction.

In order to produce a reaction, the molecules must have the correct orientation and sufficient energy;



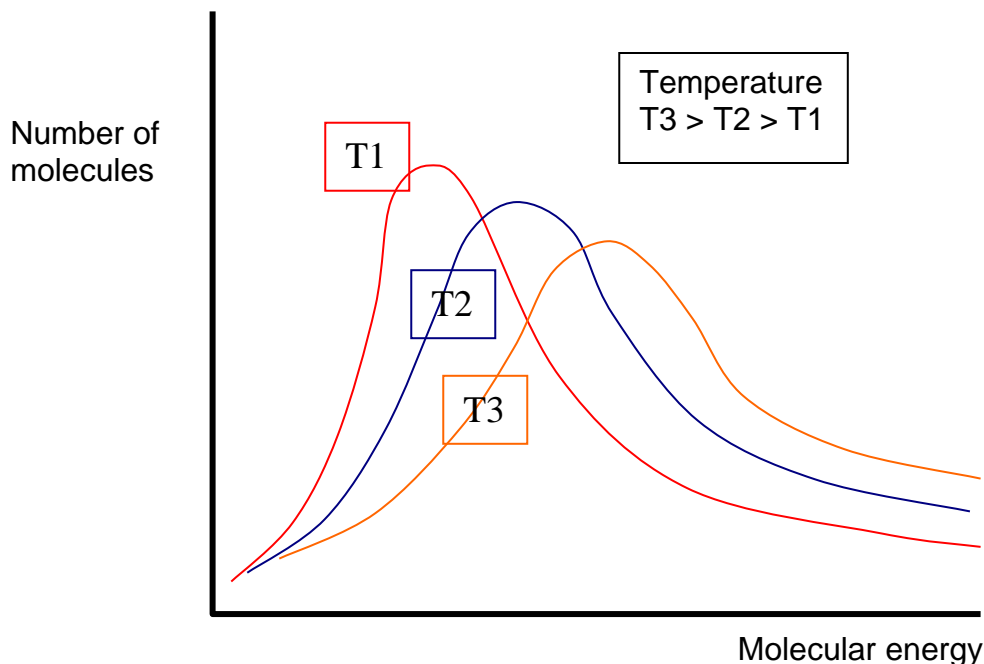
The factors which determine the rate of a chemical reaction are the following.

1. **Concentration**; the higher the concentration, the more there are in a given volume and so the more often the particles will collide in a set time.
2. **Pressure** in a gas; for a gas increase in pressure increases the number of particles in a given volume and so this is the same as concentration.
3. **Temperature**; the higher the temperature, the faster the particles move and so the greater the number of collisions in a set time. Also the energy of the particles increases, so more effective collisions take place.
4. **Surface area** for solid and liquid/gas; the reaction will occur where the two types of particle meet, at the surface, so the greater the surface area, the greater the number of collisions in a set time.
5. A **catalyst** provides an alternate reaction route of lower activation energy allowing more collisions in a set time to produce a reaction.

## Rate and Molecular Energy

The collision theory states that when two particles collide, they will only react if they have sufficient energy. Since, often only one collision in  $10^{14}$  produces a reaction, this factor is very significant.

A **Maxwell-Boltzmann graph** shows the distribution of molecular energies

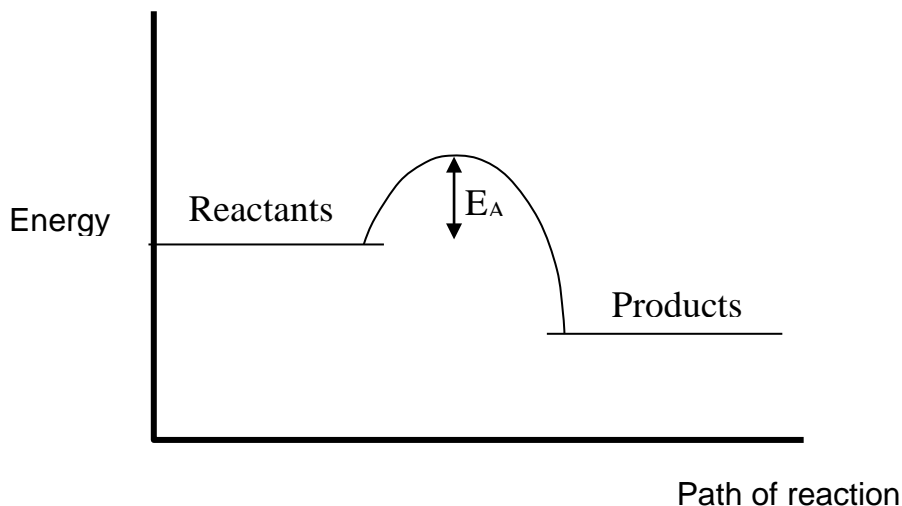


This type of graph is called a Maxwell-Boltzmann distribution. It shows the distribution of molecular energy within a gas. The horizontal axis shows the energy level and the vertical is the number of particles that have that energy.

At a higher temperature the average energy of the molecules increases. The area under each curve is the same, as this represents the total number of molecules, it does not of course change with temperature.

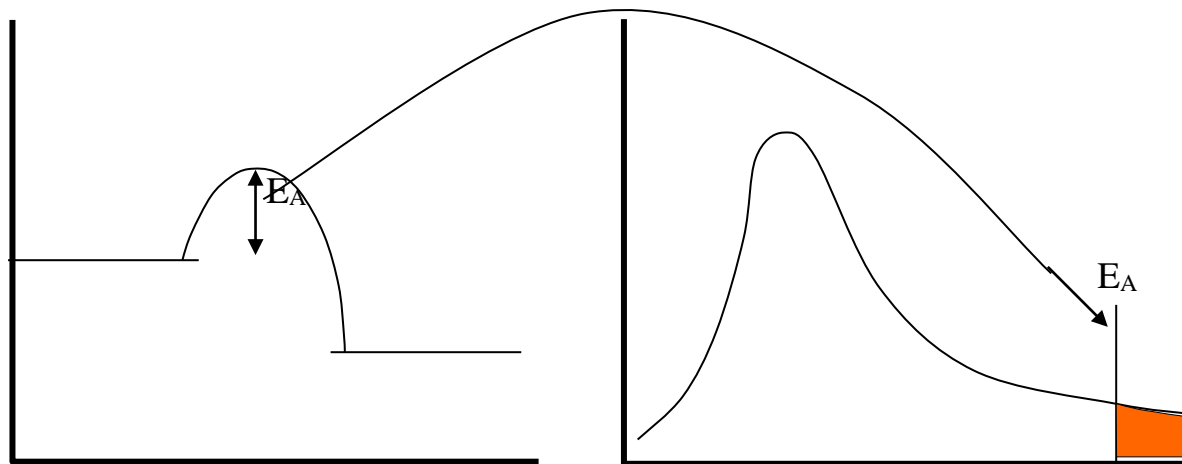
## Activation Energy

For molecules to react bonds have to first be broken. This means energy is taken in. When molecules collide and react, they move through a state of high potential energy. This can be pictured as an energy barrier. The energy required for a reaction to take place is called the **activation energy,  $E_A$** .



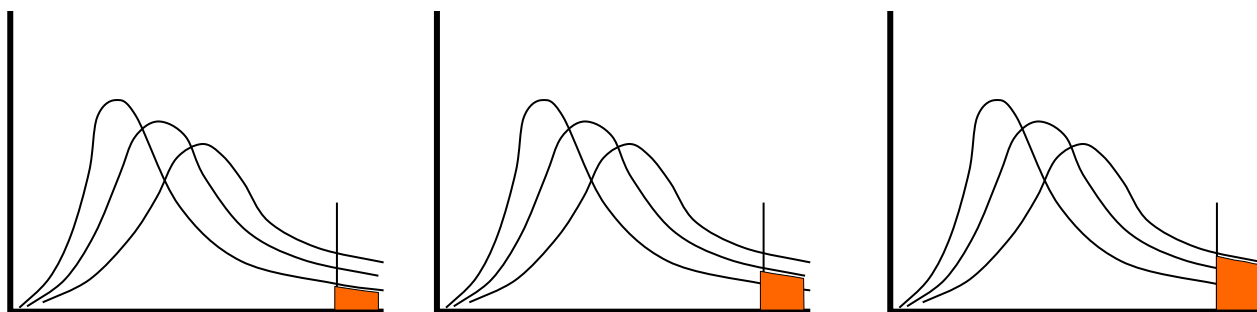
Products of a reaction will only form if the particles have sufficient energy to overcome this energy barrier, the size of this barrier being the activation energy. **The higher the value of the activation energy, the lower the number of effective collisions and so the lower the rate of reaction.**

The activation energy can be shown on the Maxwell-Boltzmann distribution graph.



Only molecules with energy equal to or higher than the activation energy can react. This is represented by the area under the line to the right of the Activation Energy line.

This means that as the temperature is increased many more molecules can react.



## Catalysts

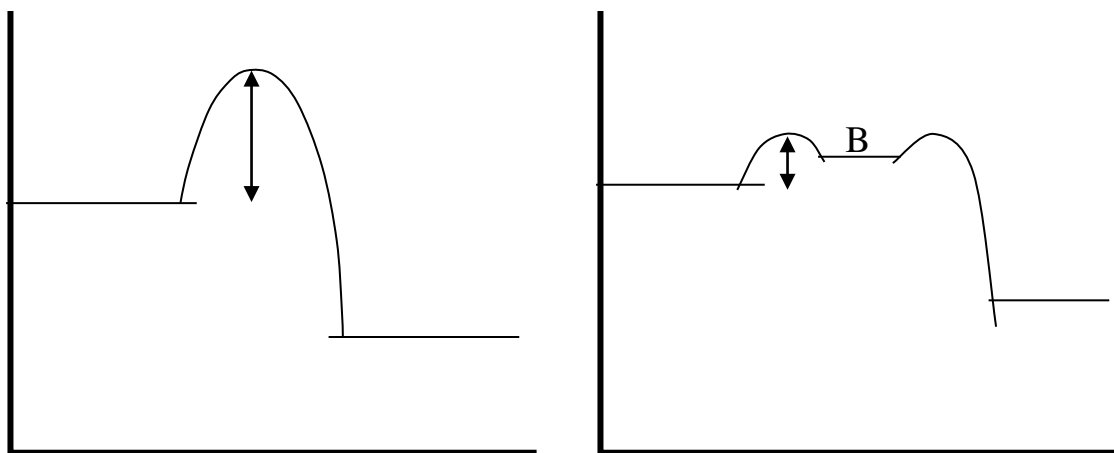
A **catalyst** is a substance which, when added to a reaction (normally in a small amount) will increase the rate of reaction. The substance does not take part in the reaction, but if it changes it is normally reformed by the end of the reaction, so it can perform its task again.

Catalysts are of great economic importance, because many of the chemical reactions used in industry will not take place (or require too much energy) without a catalyst.

Examples:

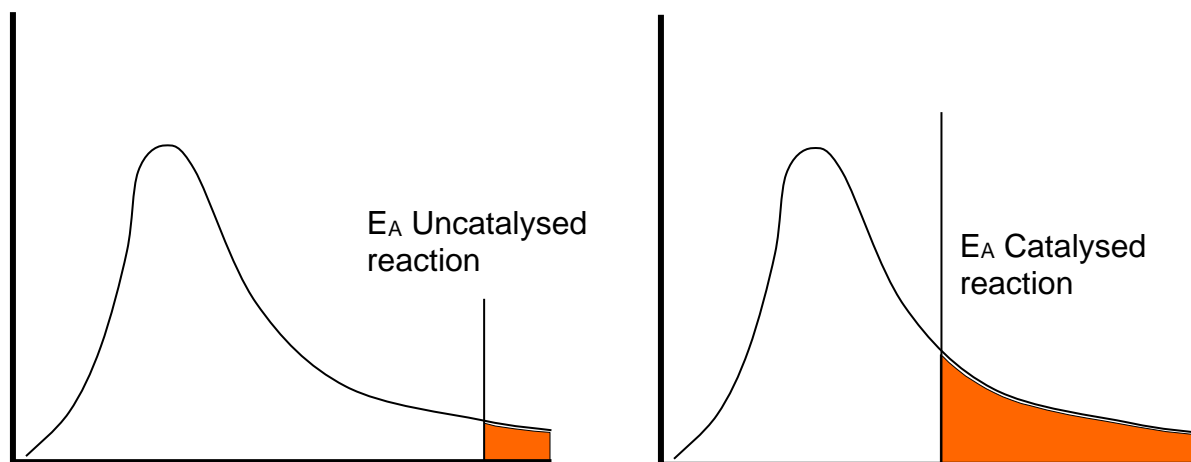
- Making fertilisers: Fe in Haber process (see below) to make ammonia; Pt for oxidation of ammonia to make nitric acid
- Petroleum processing:  $\text{Al}_2\text{O}_3$  in cracking; Pt in isomerisation; Pt/Re and Pt/Ir in reforming
- Margarine production: Ni in hydrogenation of unsaturated oils.

Catalysts do not generally affect the original pathway for a reaction, but provide a different pathway in addition, which requires a lower **activation energy**. Because of this, more molecules will have enough energy to react, and so there will be more successful collisions.



B represents the intermediate formed on interaction of reactant and catalyst.

This lower energy can be shown on a Maxwell-Boltzmann distribution curve.



As the activation energy is lowered, more molecules have sufficient energy to react.

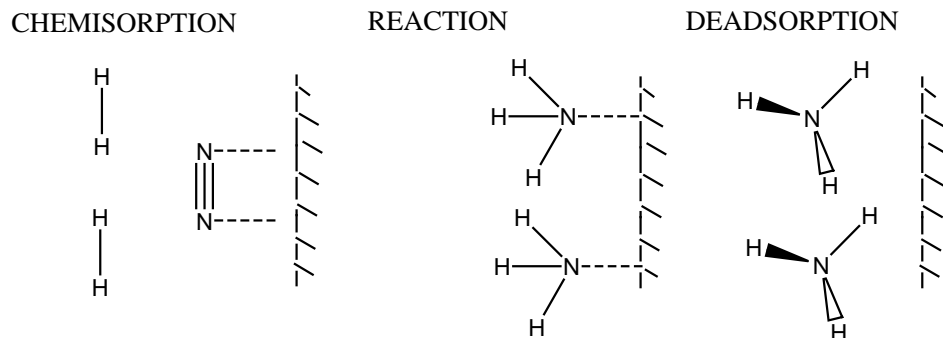
The lower activation energy also applies to the reverse reaction, so both forward and reverse reactions are speeded by the same amount. Hence there is no change in the equilibrium yield, although equilibrium is attained more rapidly.

### Homogeneous and heterogeneous catalysts

Catalysts are divided into **homogeneous** (in the same phase as the reactants, e.g. in solution for liquid-phase reaction; or all in gas phase) and **heterogeneous** (different phase – usually a solid catalyst for gas-phase or liquid-phase reactants) catalysts.

**Heterogeneous catalysts** such as surface catalysts involve steps such as; diffusion to surface, adsorption on surface, reaction at surface, desorption from surface, diffusion from surface.

If two reactant molecules collide they may react if they have enough energy. If they are brought together on the surface of a catalyst the activation energy may be lower so at a given temperature the reaction will be faster.



**Homogeneous catalysts** can form intermediates which contain the catalyst but then decompose to form products.

e.g. The reaction;  $A \rightarrow B + C$  high activation energy

Catalysed reaction  $A + \text{catalyst} \rightarrow \text{A-catalyst}$  low activation energy  
**Intermediate**

$\text{A-catalyst} \rightarrow B + C + \text{catalyst}$  low activation energy

Note - The catalyst may change oxidation state during the reaction.