(P1) Sec 8) Reaction kinetics

9701 Chemistry Syllabus requirements:

Sec 8: Reaction Kinetics

8.1 Rate of reaction

Learning outcomes

Candidates should be able to:

- explain and use the term rate of reaction, frequency of collisions, effective collisions and non-effective collisions
- explain qualitatively, in terms of frequency of effective collisions, the effect of concentration and pressure changes on the rate of a reaction
- Use experimental data to calculate the rate of a reaction.

8.2 Effect of temperature on reaction rates and the concept of activation energy

Learning outcomes

Candidates should be able to:

- define activation energy, *E*A, as the minimum energy required for a collision to be effective
- sketch and use the Boltzmann distribution to explain the significance of activation energy
- explain qualitatively, in terms both of the Boltzmann distribution and of frequency of effective collisions, the effect of temperature change on the rate of a reaction

8.1 Rate of reaction:

The study of rates of chemical reactions is called **reaction kinetics.**

Remember!
The balanced chemical equation gives us no information about the rate of a reaction. Experiments are needed to measure the rate at which reactants are used up or products are formed.

The rate of a reaction can be defined as follows:

$$\text{rate} = \frac{\text{change in amount of reactants or products}}{\text{time}}$$

The units of rate of reaction are normally moldm^{-3}s^{-1}.

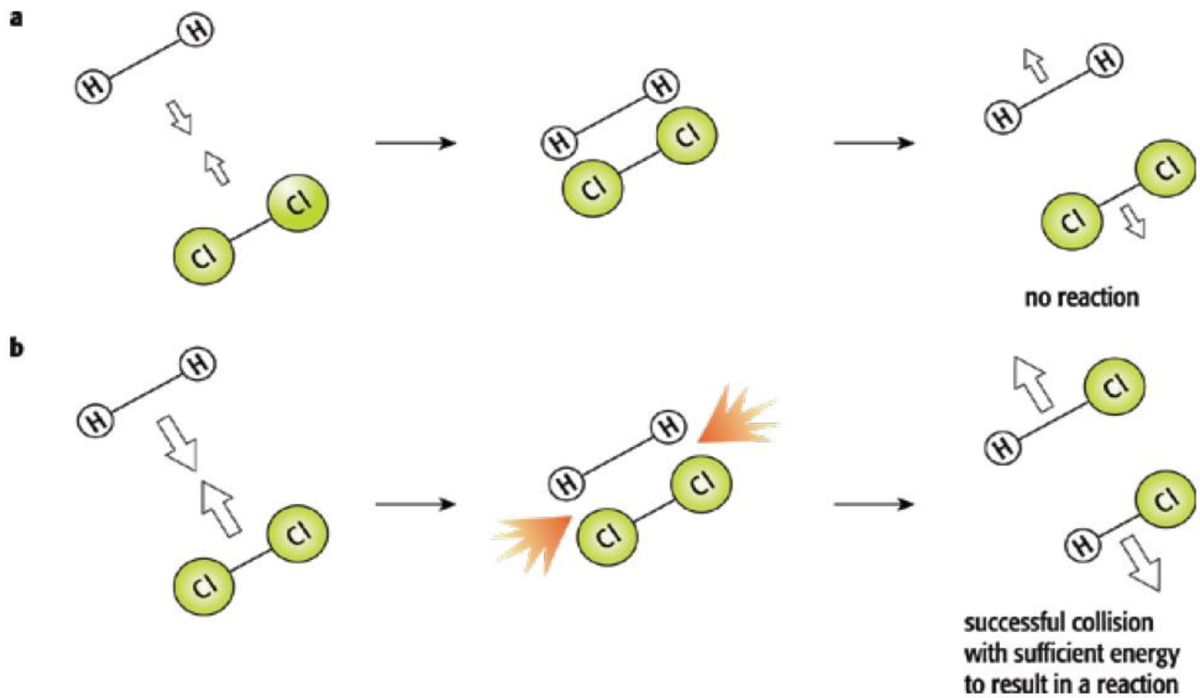
Collision Theory:

The collision theory states that in order to react with each other, particles (atoms, ions or molecule) must collide in the correct orientation and with the sufficient energy.

When reactant particles collide they may simply bounce off each other, without changing. This is called an in effective collisions.

An ineffective collision takes place if the colliding particles do not have enough energy to react. No reaction occurs.

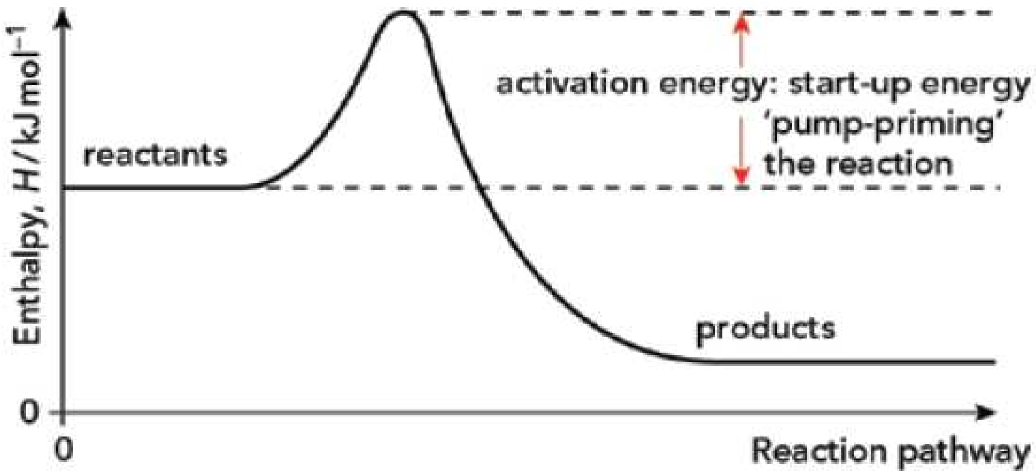
If the reactant particles do have enough energy to react, they may change into product particles when they collide. This is called an effective collision.



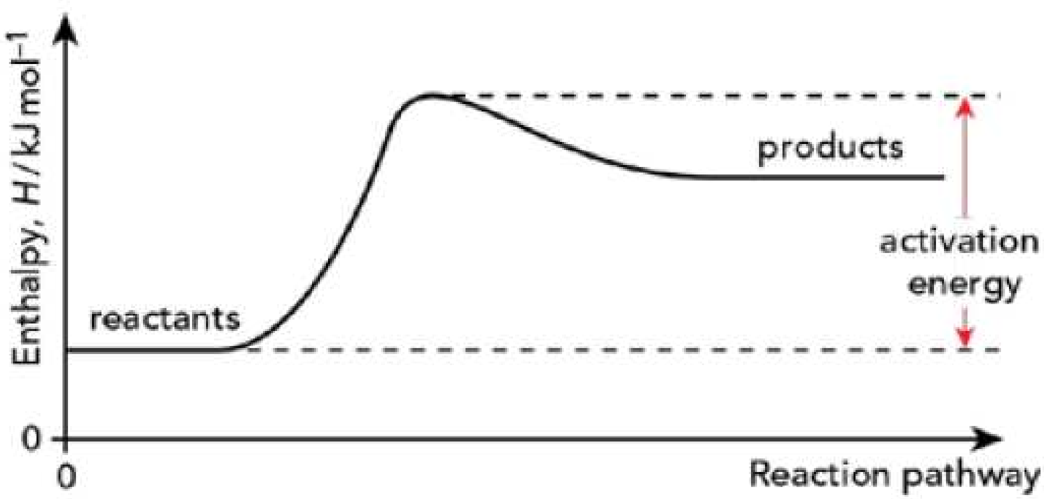
a) Ineffective (unsuccessful) collision
b) Effective (successful) collision

The minimum energy that colliding particles must possess for a collision to be effective is called the activation energy, Ea, for that particular reaction.

We can show the activation energy for an exothermic reaction and an endothermic reaction on reaction pathway diagrams.

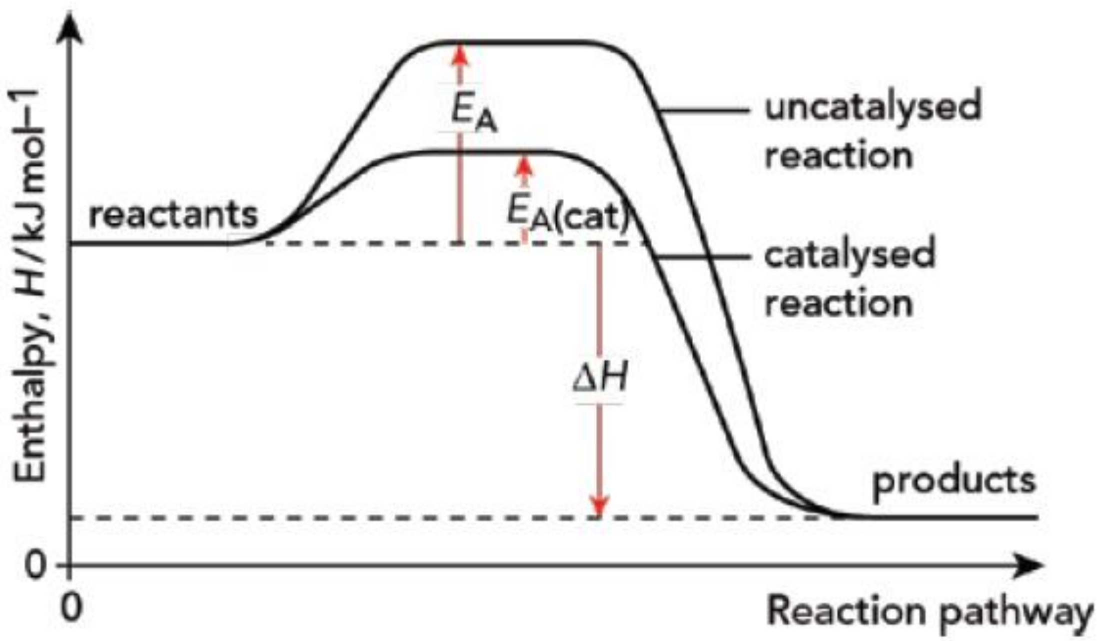


The activation energy in an exothermic reaction.



The activation energy in an endothermic reaction.

According to the collision theory, a reaction will speed up if: the frequency of collisions increases the proportion of particles with energy greater than the activation energy increases. The frequency of collisions is the number of collisions per unit time, e.g. number of collisions per second. A catalyst is a substance that increases the rate of a reaction but remains chemically unchanged itself at the end of the reaction. A catalyst does this by making it possible for the particles to react by an alternative mechanism.



The effect of a catalyst on the activation energy in an exothermic reaction.

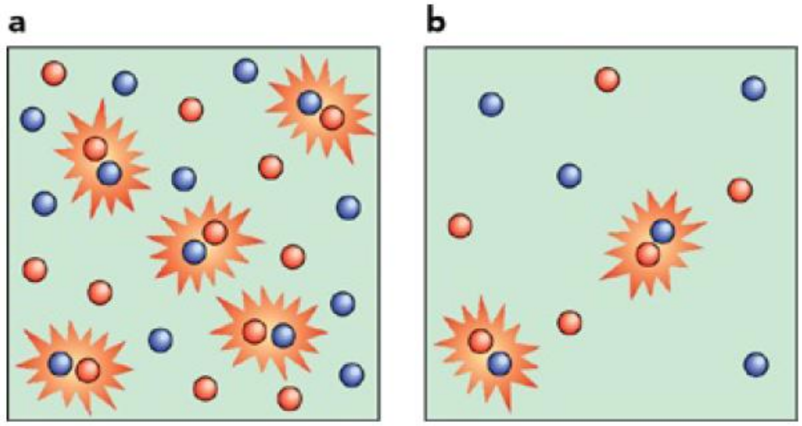
The effect of concentration on rate of reaction

In chemistry, we usually measure the concentration of solutions in moles per decimetre cubed: **mol dm^{-3}**.

The more concentrated a solution, the greater the number of particles of solute dissolved in a given volume of solvent. In reactions involving solutions, more concentrated reactants have a faster rate of reaction.

This is because the random motion of the particles in solution results in more frequent collisions between reacting particles.

This is shown in figure below:



The particles in box a are closer together than those in box b. There are more particles in the same volume, so the chances and frequency of collisions between reacting particles are increased. Therefore, the rate of reaction is greater in box a than in box b.

The effect of pressure in reactions involving gases is similar to the effect of concentration in solutions. As we increase the pressure of reacting gases, there are more gas molecules in a given volume.

This results in more collisions in any given time, and a faster rate of reaction.

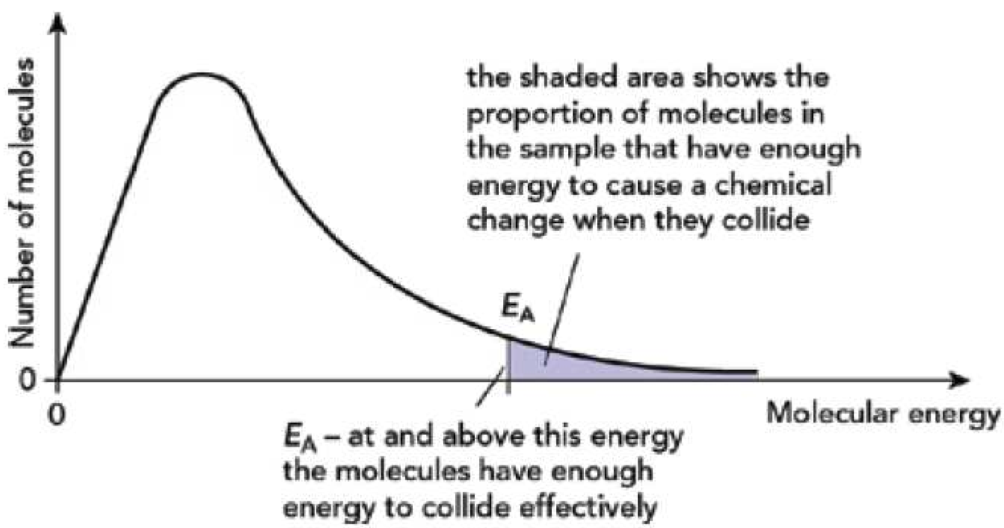
The effect of temperature on rate of reaction

To fully understand rates of reaction, we need to look more closely at the energy possessed by the reactant particles. In a sample of any substance, at a given temperature, the particles will not all possess the same amount of energy as each other.

A few particles will have a relatively small amount of energy. A few particles will have a relatively large amount of energy.

Most particles will have an amount of energy somewhere in between. The distribution of energies at a given temperature can be shown on a graph (see below).

This is called the **Boltzmann distribution.**



The Boltzmann distribution of molecular energies, showing the activation energy The activation energy, EA, is **labelled**. We have seen that the activation energy is defined as the minimum energy required for colliding particles to react. **When we raise the temperature of a reaction mixture, the average kinetic (movement) energy of the particles increases.**

Particles in solution and in gases will move around more quickly at a higher temperature, resulting in more frequent collisions.

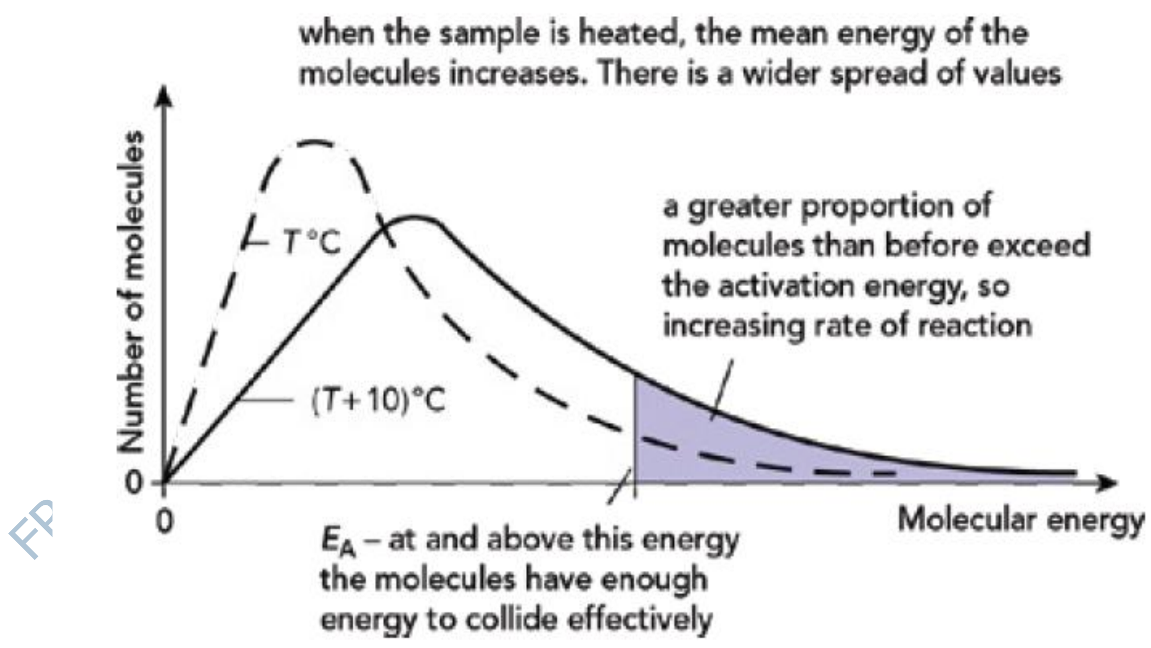
However, experiments show us that the effect of temperature on rate of reaction cannot be totally explained by more frequent collisions.

The key factor is that the proportion of successful collisions increases greatly as we increase the temperature.

The distribution of molecular energies changes as we raise the temperature, as shown in figure below.

The curve showing the **Boltzmann distribution** at the higher temperature flattens and the peak shifts to the right. The area under the curve represents the number of particles. The shaded area shows the number of particles with energy greater than the activation energy, EA.

For a **10 °C** rise in **temperature** this area under the **curve approximately doubles**, as does the rate of many reactions.



The Boltzmann distribution of molecular energies at temperatures T °C and (T + 10) °C, showing the activation energy.

Therefore, increasing the temperature increases the rate of reaction because:

- the increased energy results in particles moving around more quickly, which increases the frequency of collisions
- the proportion of successful collisions (i.e. those that result in a reaction) increases because the proportion of particles exceeding the activation energy increases. This is the more important factor.

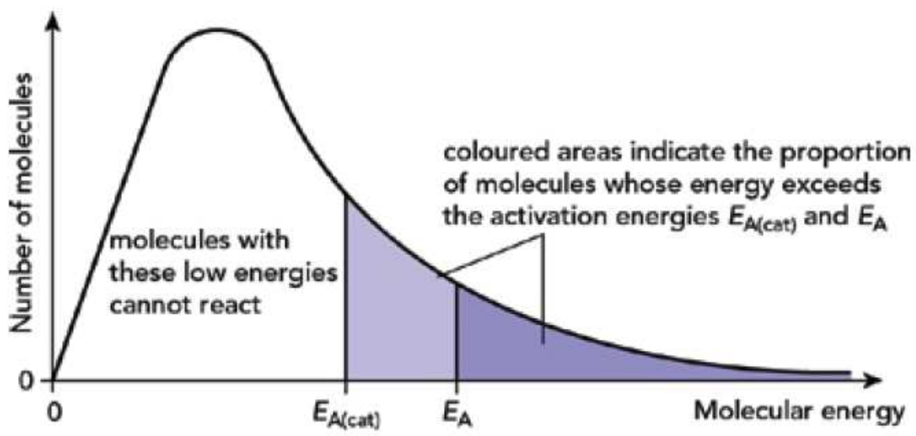
Catalysis:

Note that the presence of a catalyst does not affect the shape of the **Boltzmann distribution.**

However, by providing a lower activation energy, a greater proportion of molecules in the reaction mixture have sufficient energy to react. The shaded area under the curve represents the numbers of molecules that have energy greater than the activation energy of the reaction.

The total shaded area (including both the light and dark shading) under the curve shows the number of particles with energy greater than the activation energy with the catalyst present (EA(cat)). This area is much larger than the dark shaded area for the reaction without a catalyst.

Therefore, the rate at which effective collisions occur, and so the rate of the catalysed reaction, is greatly increased compared with the rate of the uncatalysed reaction.



The **Boltzmann distribution of molecular energies**, showing the change in activation energy with and without a catalyst.