Topic 2.2

KINETICS

Rates of Reaction
Simple Collision Theory
Factors Affecting the Rate of Reaction

RATES OF REACTION

Some reactions take place instantly, but most are much slower and it is possible to measure how long these reactions take to reach a certain stage. As a chemical reaction proceeds, the concentration of the reactants decreases and the concentration of the products increases. **The decrease in the concentration of reactants per unit time, or the increase in the concentration of products per unit time, is known as the rate of reaction**. The study of rates of reaction is known as **kinetics**.

SIMPLE COLLISION THEORY

How do chemical reactions take place?

Substances in the liquid, aqueous and gaseous phase consist of particles in rapid and constant motion. The rate of a chemical reaction depends on three factors:

1. Collision frequency

If a chemical reaction is to take place between two particles, they must first collide. The number of collisions between particles per unit time in a system is known as the **collision frequency** of the system.

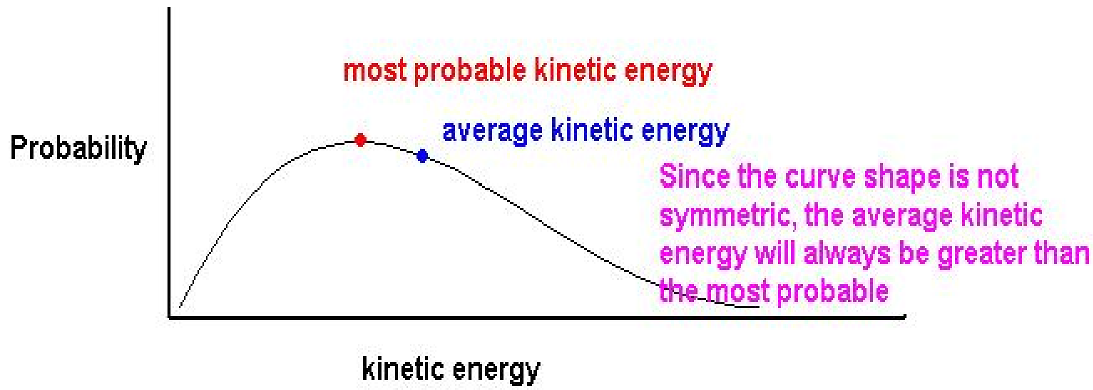
The collision frequency of a given system can be altered by changing the concentration of the reactants, by changing the total pressure, by changing the temperature or by changing the size of the reacting particles.

2. Collision energy

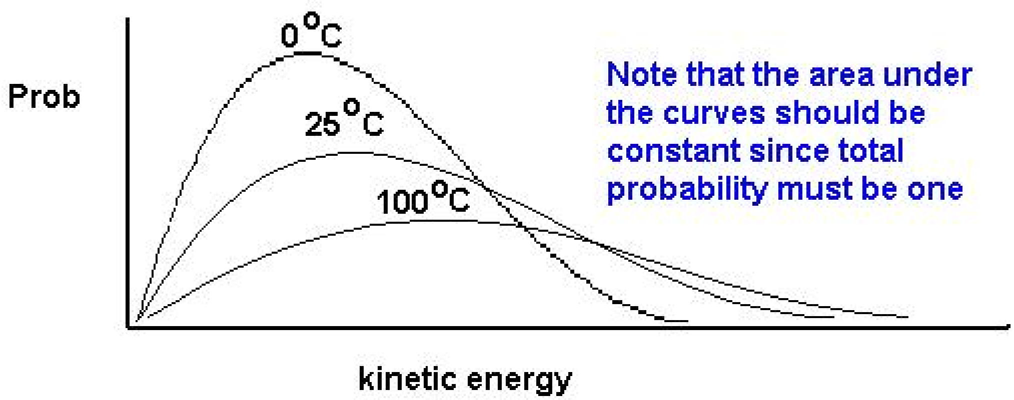
Not all collisions, however, result in a chemical reaction. Most collisions just result in the colliding particles bouncing off each other. Collisions which do not result in a reaction are known as **unsuccessful collisions**. Unsuccessful collisions happen when the colliding species do not have enough energy to break the necessary bonds. If they do not have sufficient energy, the collision will not result in a chemical reaction. If they have sufficient energy, they will react and the collision will be **successful**. The combined energy of the colliding particles is known as the **collision energy**.

Not all the particles in a given system have the same energy; they have a broad distribution of different energies. The shape of the distribution of energies depends on the temperature of the system: the higher the temperature, the greater the mean kinetic energy of the particles.

The distribution of molecular energies at a characteristic temperature T_1 can be represented graphically. It is known as a Maxwell-Boltzmann distribution:



At a higher temperature T_2 the distribution of energies will be different; the mean energy will be higher and the distribution will be broader:



The greater the mean kinetic energy of the particles, the greater the collision energy.

3. Activation energy

The minimum energy the colliding particles need in order to react is known as the **activation energy**. If the collision energy of the colliding particles is less than the activation energy, the collision will be unsuccessful. If the collision energy is equal to or greater than the activation energy, the collision will be successful and a reaction will take place.

The activation energy can be changed by the addition of a catalyst.

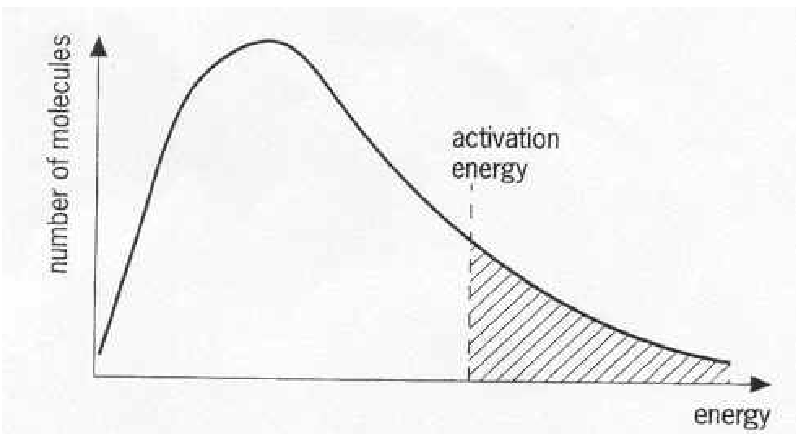
4. Summary

In reactions that do not happen instantaneously, most collisions are unsuccessful. Such reactions can be made faster in two ways:

- by increasing the collision frequency
  the more frequently the particles collide, the faster the reaction will be

- by increasing the fraction of successful collisions
  the greater the fraction of collisions that result in a chemical reaction, the faster the reaction will be. The fraction of successful collisions can be increased by increasing the collision energy or decreasing the activation energy.

The fraction of successful collisions can be shown graphically as the area under the curve to the right of the activation energy divided by the total area under the distribution curve:



FACTORS AFFECTING THE RATE OF REACTION

The rate of a chemical reaction can be changed in a number of ways:
- by changing the concentration of the reacting particles
- by changing the pressure of the system (if some of the reacting particles are in the gas phase)
- by changing the particle size (if some of the reacting particles are in the solid state)
- by changing the temperature of the system
- by adding a catalyst

Each of these factors can be considered in turn:

a) concentration

The greater the concentration of the species in a liquid or gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide. Hence an increase in concentration causes the rate of reaction to increase by increasing the collision frequency.

The collision energy, activation energy and hence the fraction of successful collisions are unaffected.

An increase in concentration increases the rate of reaction because

- **the number of particles per unit volume increases**
- **so the collision frequency increases**

b) pressure

The greater the pressure in a gaseous mixture, the greater the number of species per unit volume and the greater the frequency with which they will collide. Hence an increase in pressure causes the rate of reaction to increase by increasing the collision frequency. The pressure of a system is generally increased by reducing its volume.

The collision energy, activation energy and hence the fraction of successful collisions are unaffected.

An increase in pressure increases the rate of reaction because

- **the number of particles per unit volume increases**
- **so the collision frequency increases**

c) particle size

If a sample of a solid is crushed into smaller pieces, the surface area of the solid will increase. This means that more of the solid particles are exposed to the other reactants and there is more likely to be a collision. The collision frequency thus increases and the rate of reaction will increase.

The collision energy, activation energy and hence the fraction of successful collisions are unaffected.

A decrease in particle size increases the rate of reaction because

- **the surface area increases**
- **so the collision frequency increases**

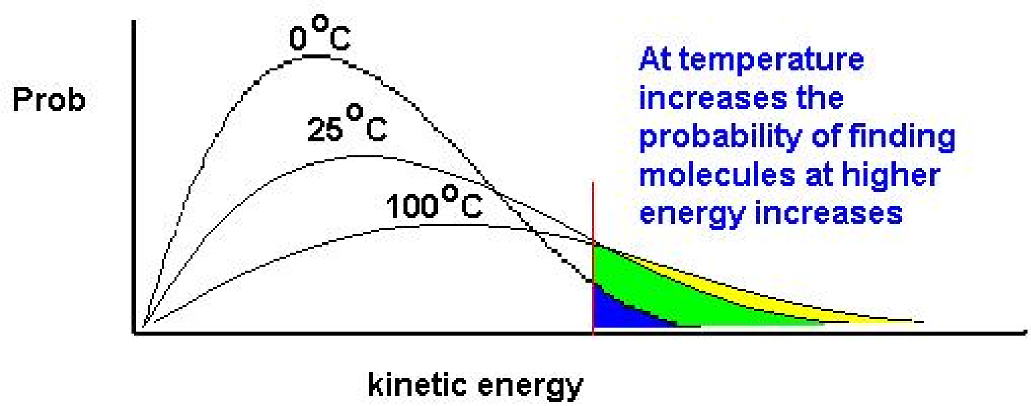
d) temperature

An increase in temperature increases the rate of a reaction for two reasons:

i) collision energy

It has been shown that an increase in temperature changes the distribution of molecular energies in such a way as to increase the mean kinetic energy of the particles and thus increase the collision energy.

For a given activation energy therefore, it follows that an increase in temperature will increase the number of colliding particles with an energy equal to or greater than the activation energy (ie the shaded area under the graph to the right of the activation energy):



It is clear that at a higher temperature, the fraction of particles with enough energy to react increases dramatically and the percentage of collisions which are successful thus also increases dramatically. The rate of reaction thus increases.

ii) collision frequency

At a higher temperature, the molecules have more kinetic energy and are thus moving faster. Thus they collide more often, and the collision frequency increases. Therefore the rate of reaction also increases.

The increase in rate due to the increase in collision frequency is actually quite small in comparison to the change due to the increase in collision energy.

Thus the rate of reaction increases when the temperature is increased because the collision frequency and the collision energy both increase. Of these two reasons, the increase in collision energy is the most important and accounts for about 95% of the increase in rate for a given reaction. The activation energy is unchanged.

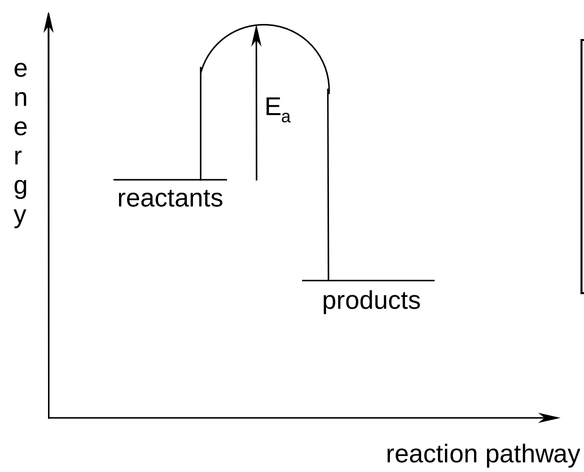
An increase in temperature increases the rate of reaction because
- **the mean collision energy of the particles increases**
- **so more of the particles have a collision energy greater than the activation energy**
- **so the fraction of successful collisions increases**
- **and the particles are moving faster**
- **so the collision frequency increases**

On average, a 10°C temperature rise approximately doubles the rate of reaction. The higher the activation energy, the greater the effect an increase in temperature will have.

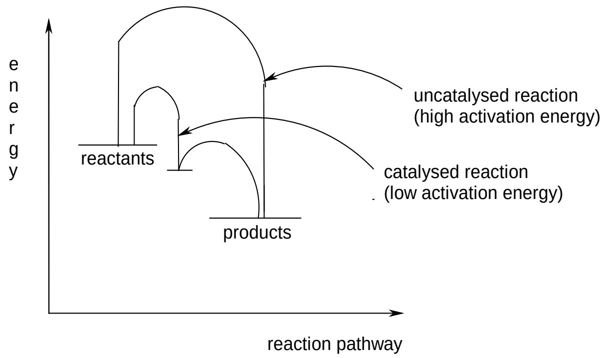
e) catalysts

A catalyst is a substance which changes the rate of a chemical reaction without itself being chemically altered at the end of the reaction.

Catalysts provide an alternative reaction pathway, usually by introducing an extra step into the reaction, which has a lower activation energy than the uncatalysed reaction. This effect can be illustrated with an enthalpy level diagram:

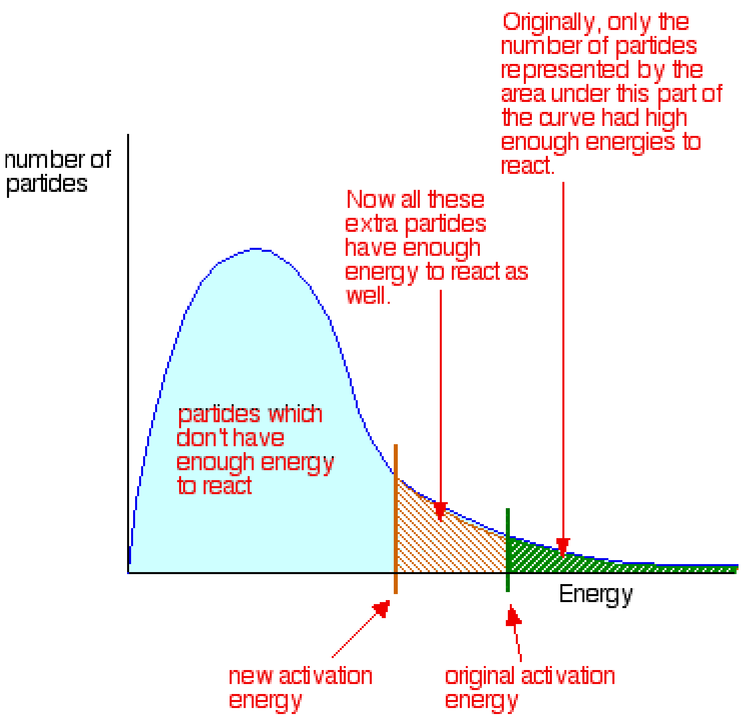


This energy diagram shows a simple one-step exothermic reaction. The activation energy E_a is the energy needed to break the bonds in the colliding particles and cause a successful collision.



This energy diagram shows a reaction taking place with and without a catalyst. The uncatalysed reaction has a high activation energy. The catalysed reaction proceeds via an alternative reaction pathway and has a lower activation energy.

Since catalysts reduce the activation energy of a chemical reaction, the number of particles which have sufficient energy to react will therefore increase. This can be shown graphically by considering the Maxwell-Boltzmann distribution of molecular energies:



A catalyst increases the rate of reaction because

- **the activation energy of the particles decreases**
- **so more of the particles have a collision energy greater than the activation energy**
- **so the fraction of successful collisions increases**

The collision frequency and collision energy are unchanged.

FACTORS AFFECTING RATE OF REACTION - SUMMARY

Effect:	On collision frequency	On collision energy	On activation energy	On fraction of successful collisions	On rate
Decrease particle size (solids only)	Increases	No effect	No effect	No effect	Increases
Increase concentration (liquids and gases)	Increases	No effect	No effect	No effect	Increases
Increase pressure (gases)	Increases	No effect	No effect	No effect	Increases
Increase temperature	Increases	Increases	No effect	Increases	Increases
Add a catalyst	No effect	No effect	Decreases	Increases	Increases