8 Velocità ed equilibrio nelle trasformazioni della materia

Summing-up

The average reaction rate can be calculated from the ratio between the amount or concentration of a reactant or a product and the time interval in which the reaction takes place.

$$v = \frac{\text{change in the amount of a reactant (or of a product)}}{\text{time interval}}$$

$$v = \frac{\text{variation in the concentration of a reactant (or of a product)}}{\text{time interval}}$$

For a chemical reaction to occur it is necessary that the particles of the reactants come into contact (**collision theory**). Collisions between particles of the reactants do not always result in a chemical transformation, collisions between particles must satisfy two conditions:

- The particles must be oriented correctly;
- The particles must have a sufficient amount of kinetic energy.

The collisions that meet these conditions are called **successful collisions**.

The surplus chemical energy that the system must possess in order for collisions between particles of the reactants to be successful is called the **activation energy**.

An increase in successful collisions per unit time results in an increase in the reaction rate.

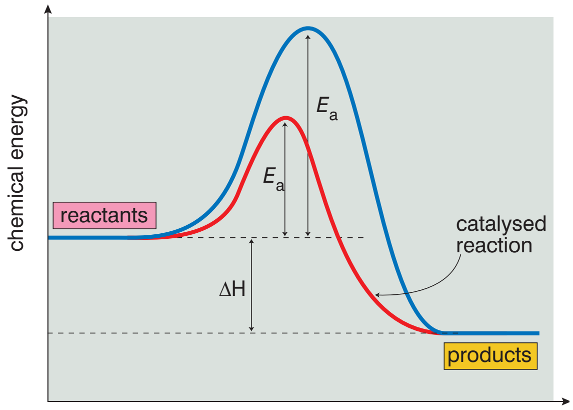
The rate increases with the increase in the *concentration of reactants*, since an increase in concentration leads, at the particle level, to an increase in collisions, and thus of successful collisions between particles of reactants.

For the same reason an increase in the *contact area* between the reactants increases the reaction rate.

An increase in the *temperature of the reactants* produces an increase in reaction rate as, at the particle level, a higher mean kinetic energy for the particles results in an increase in the percentage of successful collisions.

The sequence of transformations leading to the formation of the final products of a chemical reaction are called the **reaction mechanism**.

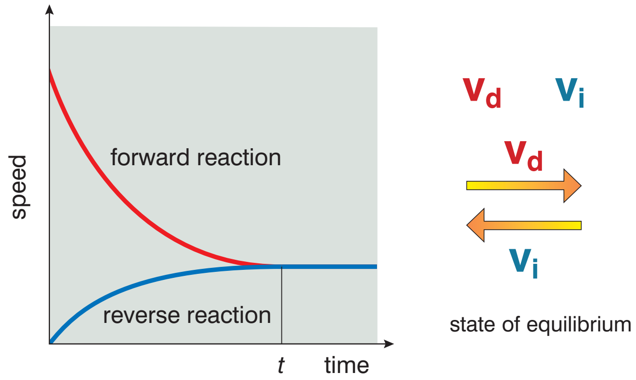
Catalysts can increase the reaction rate; whilst taking part in the reaction the catalysts do not feature in the chemical equation and do not change the nature of the products; catalysts help to increase reaction rates by determining a different reaction mechanism, characterised by a lower activation energy.



In biological processes the action of catalysts is of particular importance: these specific substances are called *enzymes*.

The transformations that take place in a closed system will stop before all the reactants are transformed into products; when the system properties that can be observed and measured remain constant over time the system is said to have reached a **state of equilibrium**.

The equilibrium achieved by a reaction is a **dynamic equilibrium**, which means that the reaction continues to take place but simultaneously, and at the same speed, with the reaction in the opposite direction: the state of equilibrium is reached when the rate of the *forward reaction* (i.e. the reaction which proceeds to the right) is equal to that of the *reverse reaction* (i.e. the one towards the left). To represent reactions that lead to the equilibrium state a double arrow symbol is used.



If we consider the equation of a generic chemical reaction,

$$aA + bB \rightleftarrows cC + dD$$

the expression for the **equilibrium constant** (**K_{eq}**), known as the **law of mass action**, is given by the ratio of the product of the molar concentrations of products raised to their stoichiometric coefficients divided by the product of the molar concentrations of the reactants also raised to their stoichiometric coefficients.

$$K_{eq} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$$

The concentrations of solids or liquids in equilibrium with gaseous substances or in solution must not be reported in the expression for the equilibrium constant.

The value of the equilibrium constant does not change if the temperature does not change and can provide valuable information on the *tendency of a reaction to occur*: the higher the value of K_{eq}, the greater the amount of products obtained when equilibrium is reached:

- if the value of K_{eq} is greater than 10^3 the balance is shifted to the right;
- if the value of K_{eq} is less than 10^{-3} the balance is shifted to the left.

It should be remembered that the value of K_{eq} does not make any prediction regarding the time a system takes to reach equilibrium.

Le Chatelier's principle establishes how one can *shift equilibrium*: when a system at equilibrium is disturbed it tends to counteract to reduce the effects of the disruption, creating new conditions of equilibrium.

- In practice, one can have the following cases: When, in a system at equilibrium, the *concentration* of a reactant increases, or that of one of the products decreases, equilibrium shifts to the right;
- When, in a system at equilibrium, the *temperature* is increased the equilibrium shifts in the direction of the endothermic reaction, but if the temperature decreases, the system favours the exothermic reaction;
- *Pressure* influences the equilibrium state of systems in which only gaseous substances are present: an increase in pressure shifts equilibrium in the direction that leads to a decrease in the total number of molecules of substances in the aeriform state.

To predict the direction, forward or reverse, in which a reaction proceeds to reach equilibrium we can calculate what is termed the **reaction quotient** (Q_c). The reaction quotient is calculated in the same way as the equilibrium constant but the concentrations used refer to any point in the reaction.

- If Q_c is smaller than K_{eq} the concentrations of reactants are higher and consequently a part of the reactants change into products: thus the direct reaction is faster than the reverse. The reaction will need to produce more products to reach equilibrium, which will shift equilibrium to the right.
- If Q_c is greater than K_{eq} the concentrations of products are greater and the excess products change into reactants and therefore the reverse reaction is faster than the forward reaction. The reaction will need to produce more reactants to reach equilibrium which will shift equilibrium to the left.