

# CHEMICAL KINETICS

**Chemical kinetics** is the study of the rates of chemical reaction, the factors affecting the rates of the reactions and the mechanism by which the reactions proceed.

The description of the step-by-step process  
by which reactants are changed into products  
is called the mechanism of the reaction.

**Chemical reaction rate** is the change in the concentration of any one of the reactants or products per unit time.

***Rate of reaction=***

$$= \frac{\text{Decrease in the concentration of a reactant}}{\text{Time interval}}$$

or

$$= \frac{\text{increase in the concentration of a product}}{\text{Time interval}}$$

For any reaction of the type  $A + B \rightarrow C + D$  .

$$\text{Rate of reaction} = -\frac{\Delta C_A}{\Delta t} = -\frac{\Delta C_B}{\Delta t} = +\frac{\Delta C_C}{\Delta t} = +\frac{\Delta C_D}{\Delta t}.$$

The unit of the rate of reaction is  $\text{mol}/L \cdot s$

$(\text{mol} \cdot L^{-1} s^{-1})$ .

For heterogeneous reactions:

*Rate of reaction =*

*Change in amount of a substance*

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*Surface area of the reactants · Time interval*

**Factors affecting  
the Reaction Rate**

**Concentration of the reactants.**

Greater are the concentration of the  
reactants, faster is the reaction.

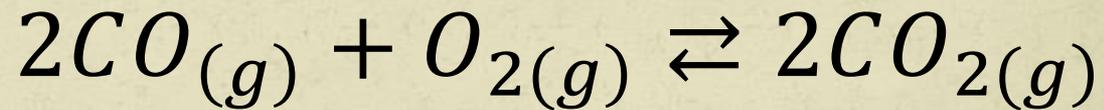
The concentration effect is described by the Law of Mass Action: at a constant temperature the rate of the chemical reaction at each moment is directly proportional to the concentration of the reacting substances.

For reaction  $aA + bB \rightarrow dD$  dependence of a homogeneous reaction on the concentration of reacting substances can be represented as:

$Rate = kC_A^a \cdot C_B^b$ , where  $k$  - is reaction rate constant

In kinetic equations only concentration of substances in gaseous or liquid form are written, because concentrations of solid substances are constant, thus, as included in the reaction rate constant.

For reactions  $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$



Kinetic equations are as follows:

$$rate = kC_{O_2}$$

$$rate = kC_{CO}^2 C_{O_2}$$

**Temperature.** The rate of reaction increases with increase of temperature.

In 1879 Van't-Hoff formulated an empirical rule:  
with temperature elevation by 10 degrees the rate of  
the chemical reaction increases 2-4 times:

$$Rate_{T_2} = Rate_{T_1} \cdot \gamma^{\frac{T_2 - T_1}{10}},$$

where  $Rate_{T_2}$  and  $Rate_{T_1}$  - the reaction rate at  
temperatures  $T_2$  and  $T_1$  respectively,  $\gamma$  - temperature  
coefficient showing how many times the rate increases  
at temperature elevation by 10 degrees.

**The nature of the reacting substances.** The decisive is the type of the chemical bond. For organic substances, main types of bonds are nonpolar or low-polar covalent and  $\pi$ -bonds.

The reaction with the substances having  $\sigma$  bonds are slower than with those having  $\pi$ -bonds. Inorganic substances which have ionic or polar covalent bond react faster.

**Surface area of the reactants.** For a reaction involving a solid reactant or catalyst, the smaller is the particle size, the greater is the surface area, the faster is the reaction.

**Pressure.** For reactions involving gases, increasing the pressure of a gas increases its concentration. A given volume contains a greater amount in moles of the gas.

Presence of Catalyst. A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing a permanent change.

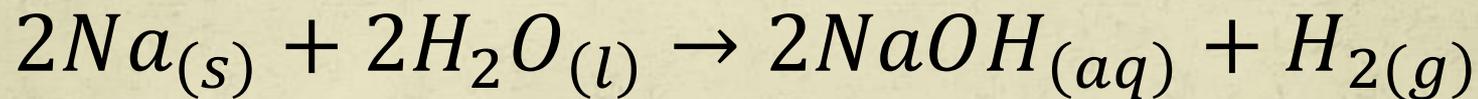
In case of reversible reactions, a catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

# Chemical equilibrium

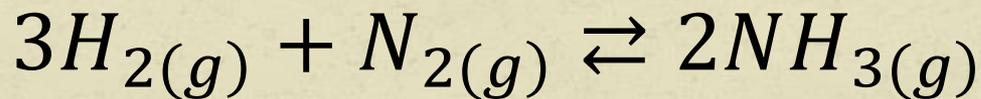
**A chemical equilibrium** is a state in which the concentrations of reactants and products remain constant over time.

**A chemical equilibrium is dynamic in nature in which the forward reaction proceeds at the same rate as the backward reaction.**

Reactions that go to completion are **irreversible**.



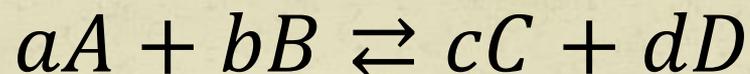
Reactions that do not proceed to completion are **reversible**.



The sign  $\rightleftharpoons$  represents the reversibility of a reaction. The reaction from left to right ( $\rightarrow$ ) is called the **forward** reaction while the reaction from right to left ( $\leftarrow$ ) is called the **backward** reaction (**reverse**).

A mathematical relationship derived from experiment and verified by theory which describes the equilibrium state is called the **equilibrium constant** expression.

For a reversible reaction at equilibrium:



in which A and B are reactants C and D are products and a, b, c, d are the stoichiometric coefficients.

The equilibrium constant is written as:

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

**Le Chatelier's Principle states**

When a change is introduced into a chemical system at equilibrium, the system will shift in the direction that counteracts that change.