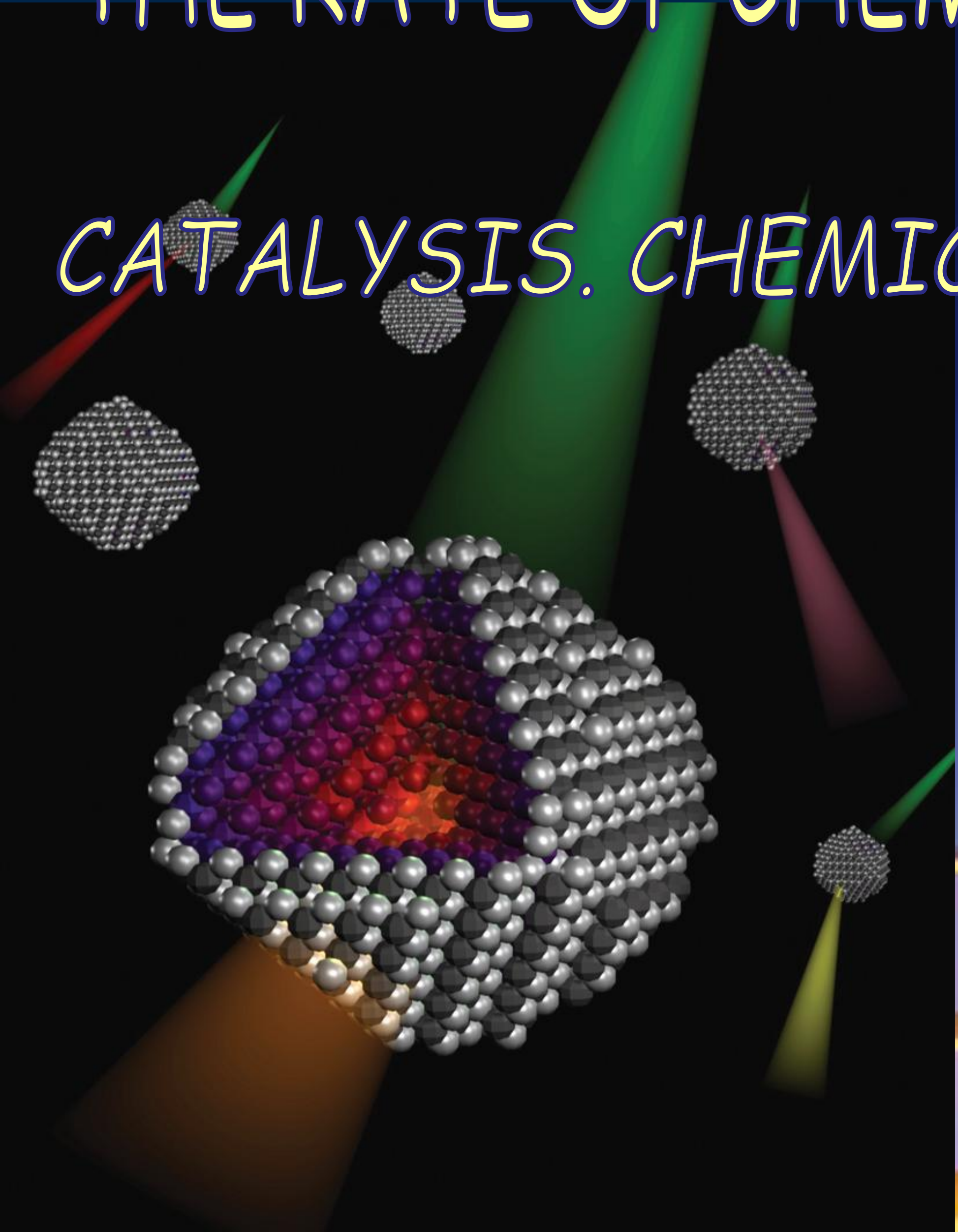
THE RATE OF CHEMICAL REACTIONS.

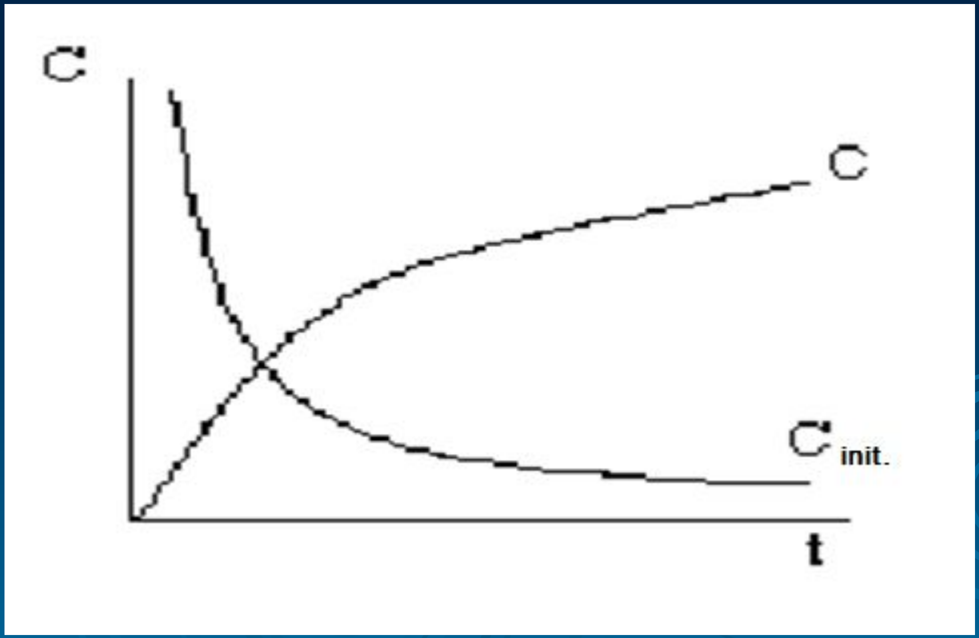
CATALYSIS. CHEMICAL EQUILIBRIUM.



Chemical kinetics studies the rate and mechanism of chemical processes.

$$v = \pm \frac{\Delta c}{\Delta t} \qquad v = \pm \frac{c_1 - c_0}{t_1 - t_0}$$

v=mole/L·sec



Factors affecting the rate of chemical reaction

The chemical reaction rate depends on:

1. <u>The nature of reacting substances:</u>

$$H_2 + F_2 \rightarrow 2HF$$

(in the dark, in cold with the explosion)

$$H_2 + Cl_2 \xrightarrow{hv} 2HCl$$ (in the light)

$$H_2 + I_2 \underset{}{\overset{t^0C}{\rightleftharpoons}} 2HI$$ (the reaction is reversible)

Factors affecting the rate of chemical reaction

The chemical reaction rate depends on:

2. The state of the reacting substances.
3. Environment the reaction is proceeding in.
4. The external conditions.
5. Concentration.

The dependence of the chemical reaction rate on temperature.

J. Van't Hoff formulated a empirical rule: when temperature rises to 10 K, the rate of most reactions increases by 2-4 times.

$$\gamma = K_{T+10}/K_T$$

where γ – the coefficient of the Van't Hoff;

K_T – the reaction rate constant at the initial temperatureT;

K_{T+10} – the reaction rate constant at a temperature of 10 K higher.

THE DEPENDENCE OF THE CHEMICAL REACTION RATE ON TEMPERATURE.

$$v_{t_2} = v_{t_1} \cdot \gamma^{\frac{t_2 - t_1}{10}}$$

Where **Vt_2** – *rate of a chemical reaction when the temperature is 10°C higher than the initial speed* ***Vt_1;***

γ – Van't Hoff's coefficient ;

t_2 – temperature 10°C higher than the initial temperature **t_1**

Mass action law

The mass action law: at a constant temperature chemical reaction rate is proportional to the product of reacting substances concentrations taken in the power of their stoichiometric coefficient.

$$xA + yB = zAB \qquad v = k \cdot C_A^x \cdot C_B^y$$

where K – Chemical reaction rate constant, C_A and C_B the molar concentrations of reacting substances, x, y, z - stoichiometric coefficients.

K=v, where $C_A = C_B = 1$ mole/L.

Mass action law for heterogeneous reactions

In case of a chemical reaction occurrence at the interface (gas-liquid, liquid-solid, solid-gas) the surface area of the interface should be taken into account .

$$xA_{sol.} + yB_{gas} = zAB \qquad \nu = S \cdot k \cdot c_A^x \cdot c_B^y$$

where К – Chemical reaction rate constant, S - surface area of the phase separation, C_A and C_B the molar concentrations of reacting substances, x, y, z - stoichiometric coefficients.

Kinetic chemical reactions classification according to the molecularity and order of reaction

Molecularity of reactions is determined by the number of molecules participating in the elementary act of interaction. Most common mono-, bi-and trimolecular reaction.

Decomposition reaction $CaCO_3 \rightleftharpoons CaO+CO_2$ (1)

The reaction of compound $H_2 + I_2 \longrightarrow 2HI$ (2)

Oxidation reaction $2NO + O_2 \longrightarrow 2NO_2$ (3)

Hydrolysis $C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$ (4)

Kinetic classification of chemical reactions

Order reaction is defined as the sum of the degrees of concentration in the kinetic equation.

For example:

1 $v=kC_{CaCO_3}$ $n=1$, 1st order

2 $v=kC_{H_2}C_{I_2}$ $n=2$, 2nd order

3 $v=kC^2_{NO}C_{O_2}$ $n=3$, 3rd order

4 $C_{H_2O}=const$, $v=kC_{C_{12}H_{22}O_{11}}$ - this is a first order reaction

The rate constant.

The rate constant has an expression and a dimension.

$$I\_order\_K = \frac{1}{t}\ln\frac{C_o}{C}\sec^{-1},$$

$$where\_t - time, C_o - init.\_concentration,$$

$$C - final\_concentration\_at\_the\_time\_t$$

$$II\_order\_K = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_o}\right)\frac{1 \bullet L}{\sec \bullet mole}$$

$$III\_order\_K = \frac{1}{t}\left(\frac{1}{2C^2} - \frac{1}{2C_o{}^2}\right)\frac{1}{\sec}\left(\frac{L}{mole}\right)^2$$

The period of half-transformation

In the kinetics the notion of the period of half-transformation $t_{1/2}$. is often used

The period of half-transformation is the time during which reacts half the concentration of initial substances.

$$I\_order\_K = \frac{\ln 2}{t_{1/2}} \sec^{-1}$$

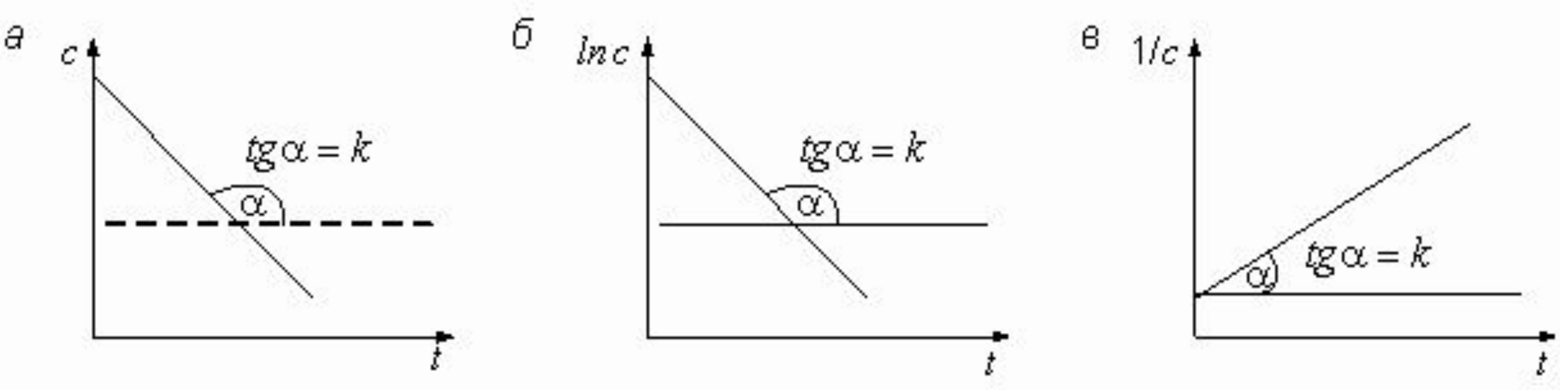
$$II\_order\_K = \frac{1}{t_{1/2} \cdot C_o} \cdot \frac{1}{\sec} \cdot \frac{L}{mole}$$

$$III\_order\_K = \frac{1 \cdot 3}{t_{1/2} \cdot C_o} \cdot \frac{1}{\sec} \cdot \left(\frac{L}{mole} \right)^2$$

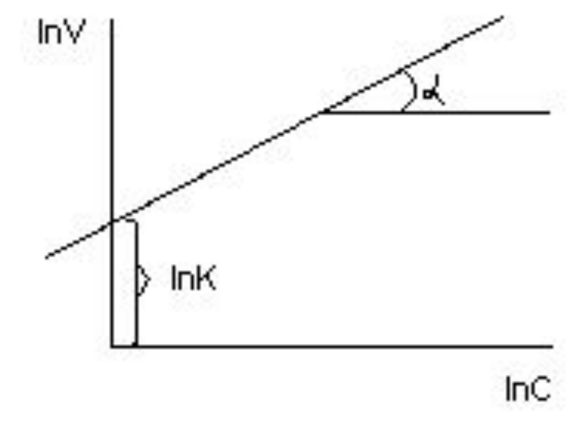
Methods for determining the order of reaction:

The substitution method.

The graphical method.



Differential method.



The activation energy.

A significant increase of the reaction rate as the temperature increases can be explained by the clash of active particles with a large reserve of energy. These include:

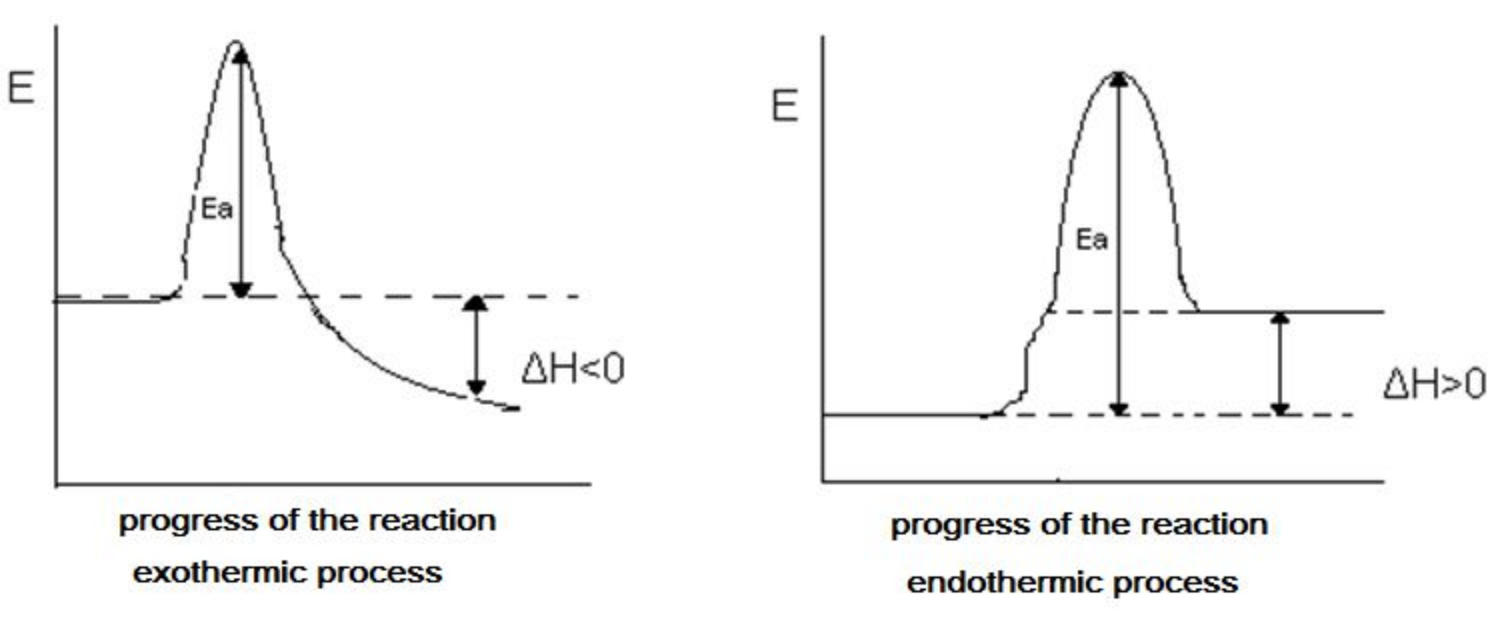
- *fastest molecules whose kinetic energy $E_c \geq 9{,}7$ kJ / mol.*
- *excited molecules.*

The energy required for the conversion of inactive particles in active is called the activation energy E_a kJ/mol.

Arrhenius Equation

$$K = A \cdot e^{-Ea/RT} \qquad \ln K = \ln A - \frac{Ea}{RT}$$

K – the reaction rate constant;
A – a constant value or the total number of collisions;
e – base of the natural logarithm;
R – gas constant;
T – temperature;
E_a – activation energy.



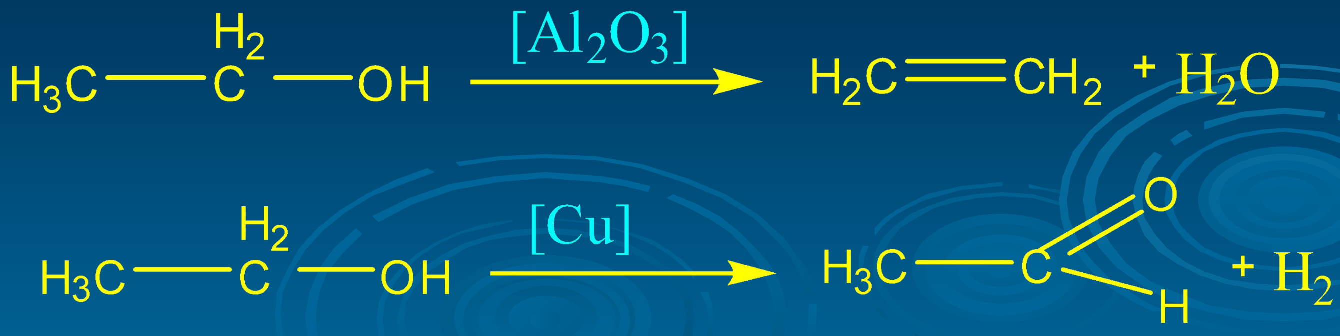
Catalytic reactions

Catalysis is the process of changing the rate of reaction by catalysts.

Reactions taking place with the participation of catalysts called catalytic.

A catalyst is a substance that changes the rate of a chemical reaction, but it is not spent.

Catalysis has specificity:



$$H_3C-CH_2-OH \xrightarrow{[Al_2O_3]} H_2C=CH_2 + H_2O$$

$$H_3C-CH_2-OH \xrightarrow{[Cu]} H_3C-CHO + H_2$$

Enzymes

Eduard Buchner,
1860–1917

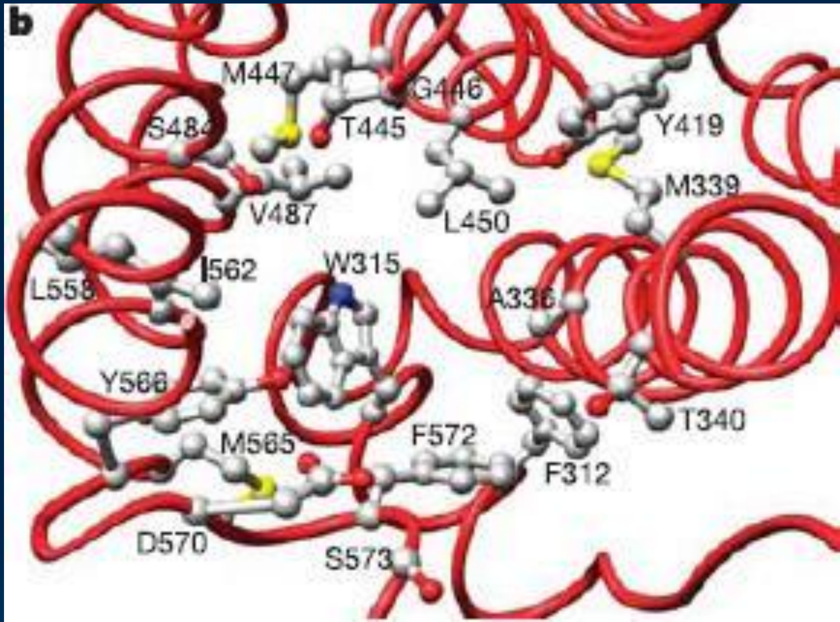
James Sumner,
1887–1955

J. B. S. Haldane,
1892–1964

Enzymes are protein molecules able to accelerate the course of biochemical reactions. Other than enzymes-proteins there are so-called ribozymes - RNA capable of catalysis.

The active center is a plot of an enzyme which is binding, and the transformation of molecules of substrate.

E - enzyme
P - product
S – substrate
I - inhibitor
[ES] – enzyme-substrate complex
[EP] – enzyme-product complex



$$E + S \rightleftharpoons ES \rightleftharpoons EP \rightleftharpoons E + P$$

Factors affecting the activity of the enzyme

The concentration of the substrate.

In 1913 Michaelis and Menten proposed equation

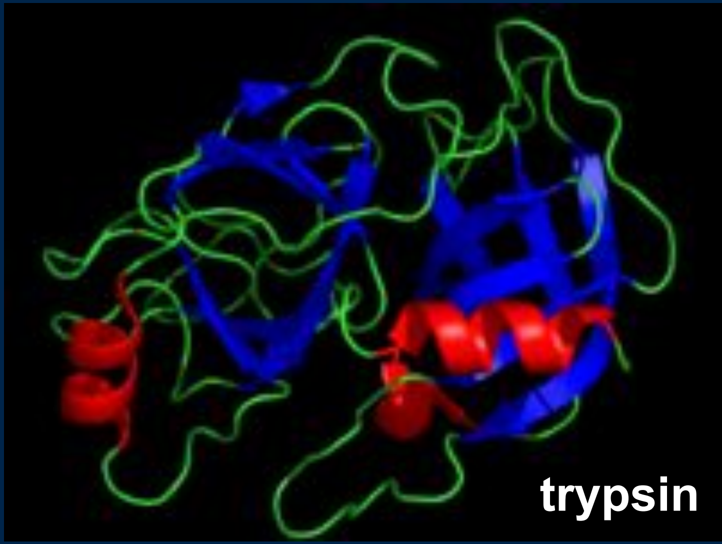
$$\upsilon = \upsilon_{max}[S]/Km+[S]$$

Km - Michaelis constant.

A limiting factor of the reaction is the formation of the enzyme-substrate complex.

Km= the substrate concentration at which the reaction rate equals to half of the rate to the maximum.

Specificity of enzymes:



- highly specific;
- law specific;
- nonspecific.

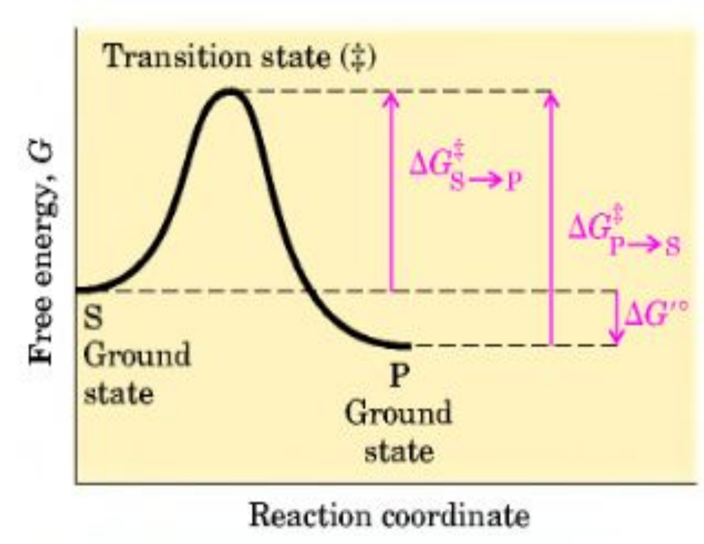
Most of the enzymes are highly specific, since they change only 1 substrate.

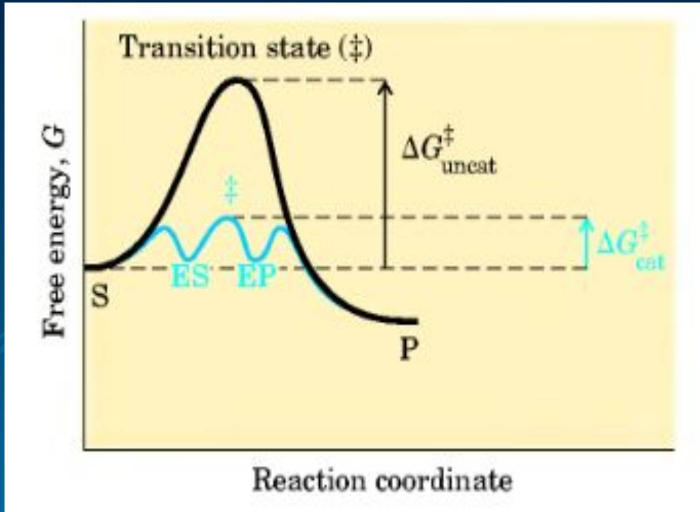
Low specific interact with a group of related substances.

Nonspecific change substances of different groups.

The mechanism of action of enzymes

Classic catalysts operate due to the energy of activation. Catalysts do not change Δ G they reduce the activation energy. The decrease of activation energy increases the number of molecules able to overcome the energy barrier.





The principle of irreversibility of chemical reactions

Irreversible reactions lead:
to the formation of gaseous substances:

$$Zn + 2H_2SO_4\ (k) \rightarrow ZnSO_4 + SO_2\uparrow + 2H_2O$$

sedimentation:

$$Ba(NO_3)_2 + Na_2SO_4 \rightarrow BaSO_4\downarrow + 2NaNO_3$$

weak electrolyte:

$Na_2S + 2HCl \rightarrow 2NaCl + H_2S$ (in solution)

Reversible chemical reactions. Equilibrium constant.

Reactions that proceed in opposite directions are called reversible.

$$H_2 + I_2 \underset{V_2}{\overset{V_1}{\rightleftarrows}} 2HI$$

$V_1 = K_1 C_{H_2} C_{I_2}$; $V_2 = K_2 C_{HI}^2$

At the moment of equilibrium $V_1 = V_2$, means $K_1 C_{H_2} C_{I_2} = K_2 C_{HI}^2$

Where $К_1 \backslash К_2 = C_{HI}^2 \backslash C_{H_2} C_{I_2} = Кp$

The equilibrium constant is equal to the ratio of the concentration of the reaction product to product concentrations of initial substances, taken in power of stoichiometric coefficient.

For equilibrium processes

$0 < Кp < \infty$

$К_p$ does not dependend on the concentration of substances. Depends on the nature and temperature.

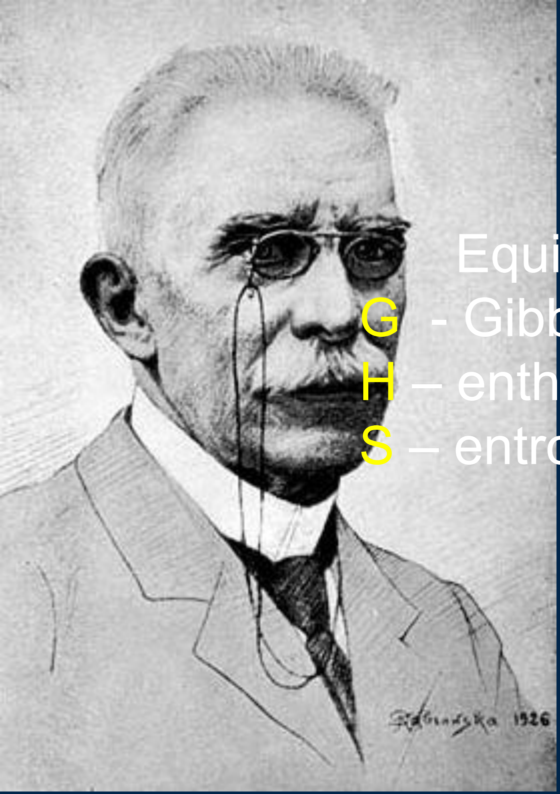
LE CHATELIER'S PRINCIPLE

Shift of the equilibrium based on the principle of Le Chatelier:

If the system is in a stable equilibrium, external influence upon changing any of the conditions determining the equilibrium position of the system will increase the directions of the process, which weakens the impact of exposure, and the equilibrium will shift in the same direction.

1. The increase in the concentration of initial substances shifts the balance in the direction of increasing the concentration of the reaction products. And Vice versa.
2. Pressure increase shifts the balance in the direction of reducing the volume of the system.
3. Temperature influence: temperature increase shifts the balance in the direction of the process that is accompanied by absorption the heat.

LE CHATELIER'S PRINCIPLE



$2CO + O_2 = 2CO_2$; $\Delta H<0$.

Equilibrium condition : $\Delta G = 0$; and $\Delta G=\Delta H-T\Delta S$.

G - Gibbs energy (j/mol),
H – enthalpy (j/mol),
S – entropy (j/mol * K)

The binding of oxygen by hemoglobin to form oxyhemoglobin occurs according to the equation:

$$Hb + O_2 \rightleftharpoons HbO_2$$

$$Kp = \frac{[HbO_2]}{[Hb][O_2]} = 1300$$

Increase $[O_2]$ leads to the binding O_2 and Hb and shift the equilibrium to the right, i.e. in favour of formation HbO_2 and Vice versa.

LE CHATELIER'S PRINCIPLE

Acid - base balance of the body is disturbed in violation of the balance between acid and base:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

If the reaction results in the formation of gas, insoluble or poorly soluble substance, which would leave the scope of the reaction, the balance shifts to the right.

$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$$

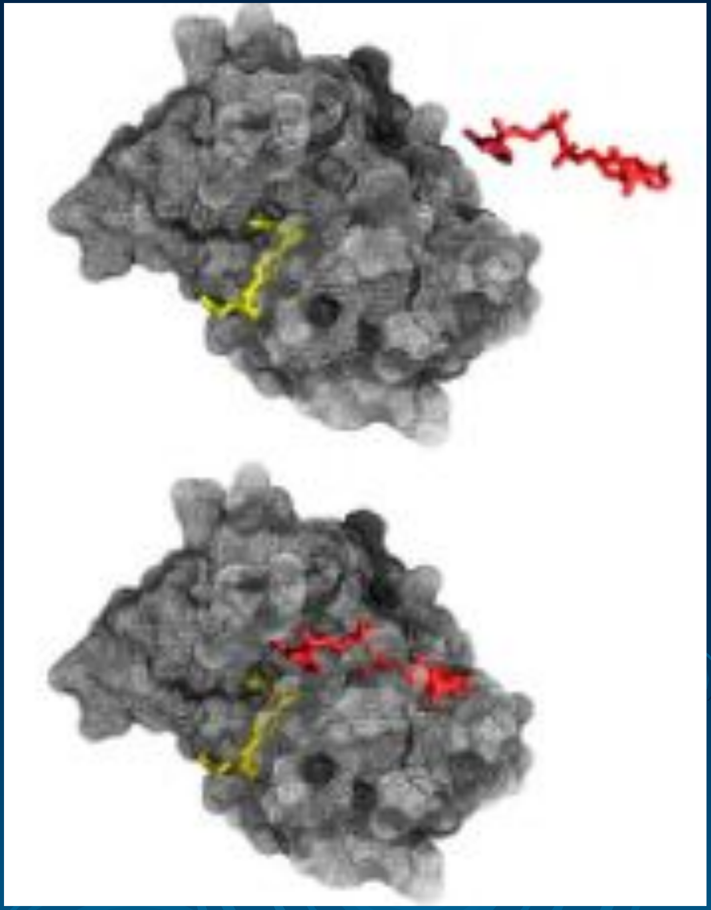
This reaction is used for preparation of radiopaque drug $BaSO_4$

Ability to use the principle of Le Chatelier's principle allows to predict changes in the body, caused by external influence.

The decrease of activation energy is achieved by:

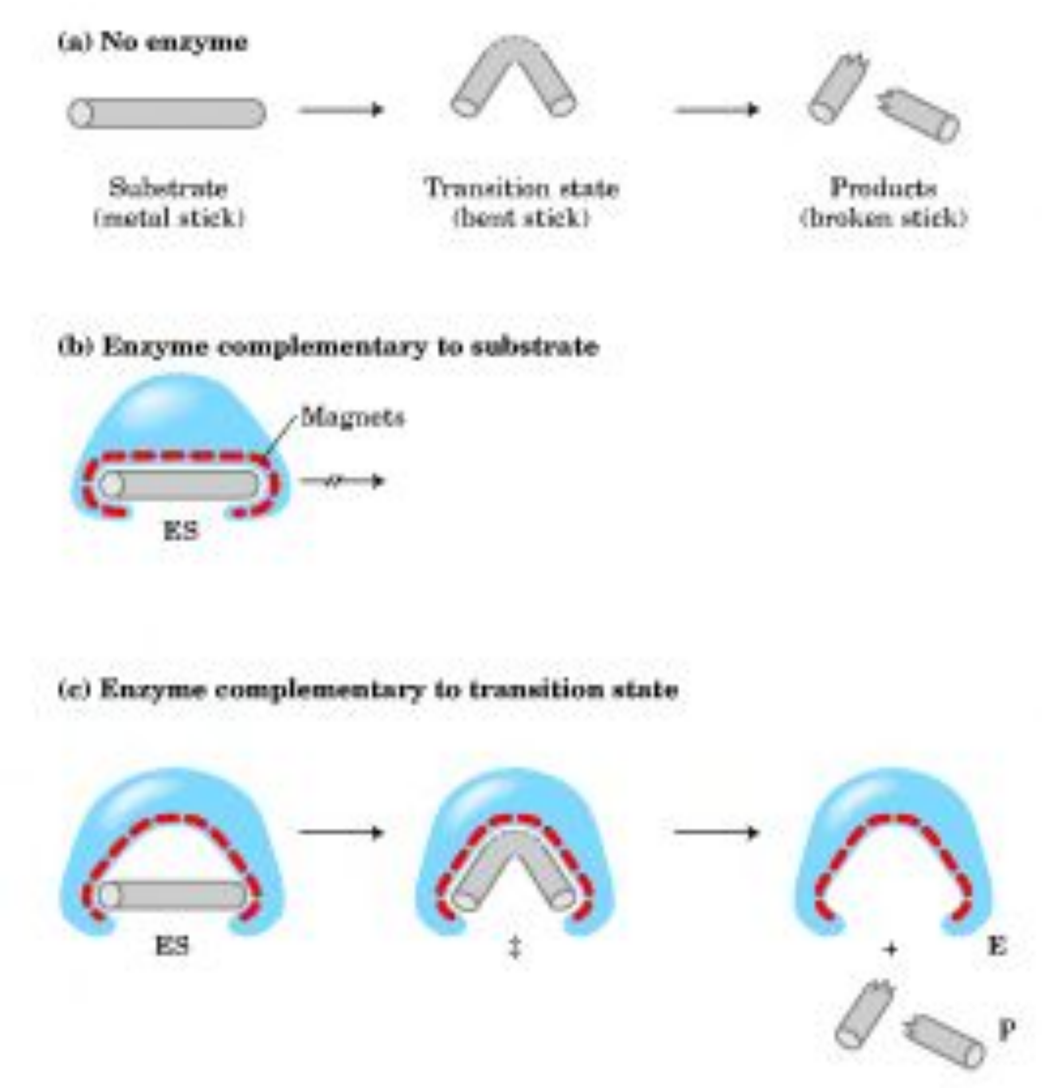
1. Orientation substrates.

2. Theory of steric interactions. Fischer suggested that the active center of spatially corresponds to the substrate molecule. Due to its spatial specificity of an enzyme and the substrate are oriented specifically.



3. The theory of induced correspondence.

Suggested by Koshland. After the formation of the enzyme-substrate complex, inside the enzyme molecule some conformation changes can be observed. They induce corresponding changes in the substrate molecule.



4. the formation of intermediate complexes.

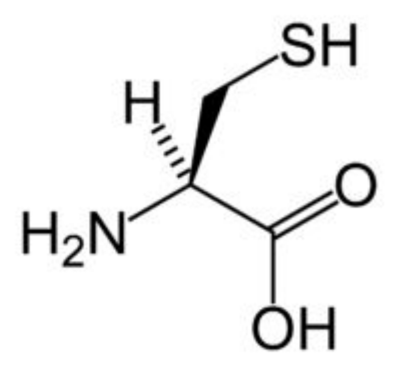
a) the acid-basic catalysis.

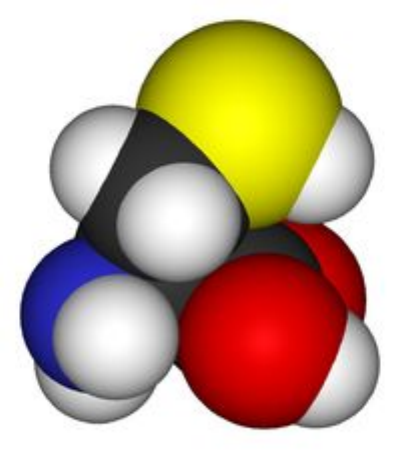
In the enzyme donors protons can be cysteine amino acid residues, glutamate, aspartate, lysine, gistidine. Acceptors of protons are the same groups but in the deprotonated form.

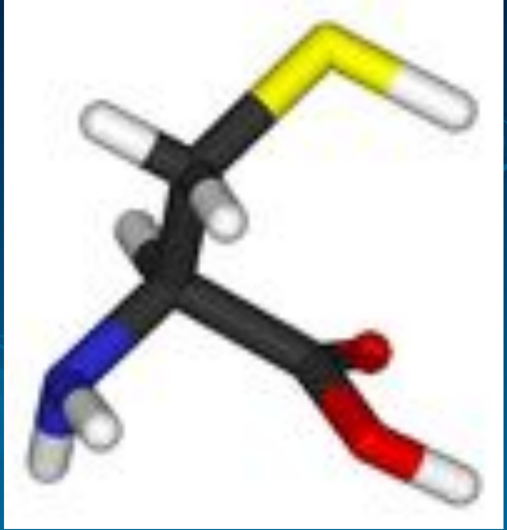
b) covalent catalysis.

During it the substrate or part of it formes stable covalent bonds with the enzyme molecule.

c) nucleophilic-electrophilic attack







PHOTOCHEMICAL REACTIONS

Photochemical reactions occur with the absorption of light energy

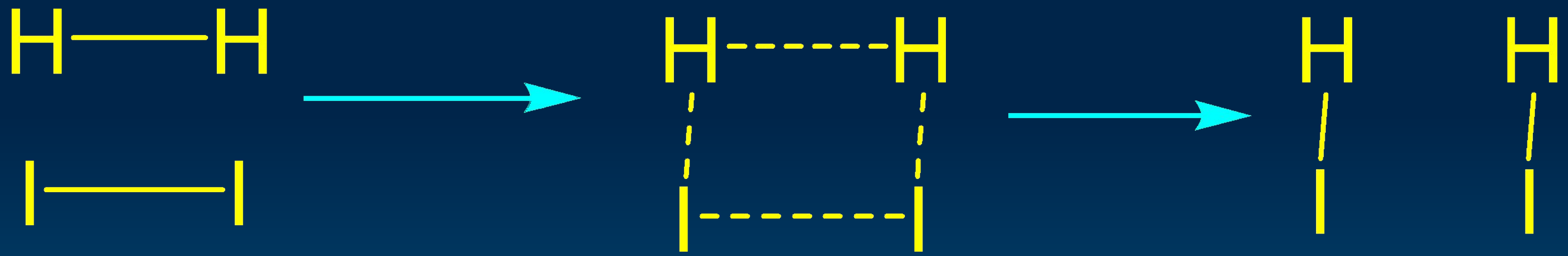
For example, photosynthesis of the glucose:

$$6CO_2 + 6H_2O \overset{hv}{\rightleftarrows} C_6H_{12}O_6 + 6O_2$$

Mechanisms of chemical reactions

Atoms, molecules, radicals, or ions may participate in reaction. It's simple, ion, and radical reaction.

Reactions occurring between the molecules are called simple : $H_2 + I_2 = 2HI$



$2NO + Cl_2 = 2NOCl$

Activation energy is 150-450 kJ/mol.

Mechanisms of chemical reactions

Chain reactions. Radical reactions proceed by a chain mechanism. Their peculiarity lies in the fact that a primary activation leads act to transform a huge number of molecules in the raw materials radicals. For example, the reaction

$$H_2 + Cl_2 = 2HCl$$

proceeds by a radical chain mechanism by heating or by lighting light. Due to the absorption of a photon (hv) Cl_2 molecule dissociates into free radicals - chlorine atoms:

$$Cl_2 + hv = Cl + {}^*Cl$$

Atom radical Cl * then reacts with the hydrogen molecule, forming a molecule of HCl and atom radical * N. Last interacts with a molecule of Cl_2, HCl and atom forms a radical Cl *, etc.

$$^*Cl + H_2 = HCl + {}^*H$$

$$^*H + Cl_2 = HCl + {}^*Cl \text{ and etc.}$$

On each absorbed quantum of light there is formed up to 100,000 molecules HCl