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КАФЕДРА ОБЩЕЙ ХИМИИ

**Элементы химической
термодинамики и кинетики**

Elements of Chemical Thermodynamics and Kinetics

Учебно-методическое пособие



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Preface

The students guide have been written on the basis of lectures delivered for foreign first year students of the Byelorussian State Medical University on General and Biophysical chemistry. The main emphasis will be on topics such as chemical thermodynamics and kinetics. They are fundamental to many disciplines other than chemistry. For example, the most general problems of chemical thermodynamics are necessary for understanding of energy characteristics of chemical and physico-chemical processes of vital activity of organism. On the other hand the problems of chemical kinetics are necessary for pharmokinetics and toxicology. These facts predisposed the laconic character of the guide and led to inevitable simplification of the material given.

Finally, we apologize for any typographical mistakes you may find in this guide. Any comments will be highly appreciated.

Chapter 1. Chemical Thermodynamics

In the living organisms, the chemical energy is transformed to other forms of energy. Bioenergetics studies the transformation of different kinds of energy in the living organisms. Chemical thermodynamics is the base of bioenergetics.

Thermodynamics is the science about mutual conversions of different kinds of energy and transmission of energy in the form of heat and work.

1.1. Problems of Chemical Thermodynamics

1. *Determination of the energy effects of the chemical and physico-chemical processes.*
2. *Determination of the possibility, direction and limits of spontaneous processes under given conditions.*

3. Determination of the conditions of equilibrium of the systems.

1.2. Terminology of Chemical Thermodynamics

It is necessary to define precisely certain concepts, terms and quantities used in thermodynamics since any ambiguity can lead to wrong conclusions.

A *thermodynamic system* is a body or group of interacting bodies which we consider apart from its surroundings. For example, a gas in a vessel, a cell, a plant, an organ, etc.

The following thermodynamic systems are known according to the character of interactions of its surroundings (fig. 1):

1. An *isolated system* is one which cannot exchange energy or matter with its surroundings. There are no such systems in the nature.

2. A *closed system* is one which can exchange energy but not a matter with its surroundings. For example an electric lamp.

3. An *opened system* is one which can change energy and matter with its surroundings. For example, a living organism.

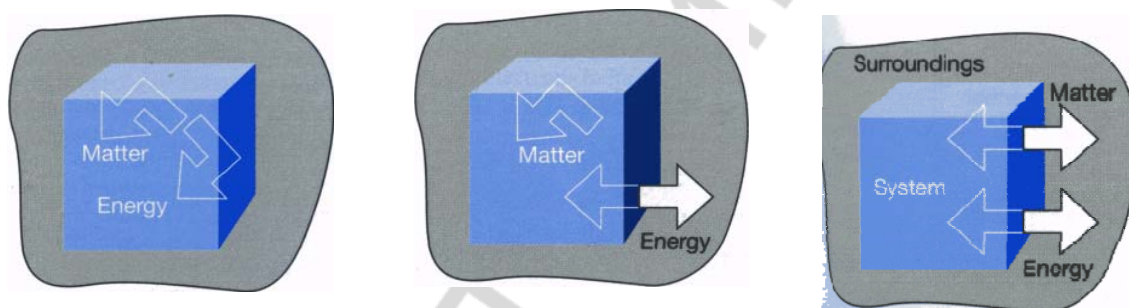


Fig. 1. Thermodynamic systems

A *homogeneous system* is one consisting of a single phase, no any boundary surfaces, all parts of the system have the same physical and chemical properties. For example, the mixture of gases, the solutions.

A *heterogeneous system* is one consisting of several phases, has boundary surfaces and different physical and chemical properties. For example, an ice is in water, liquid and vapour.

A *phase* is the part of the system with the same physical and chemical properties. For example, ice-water (an ice is the first phase, water is the second phase).

The thermodynamic quantities of the state of the system. The thermodynamic quantities characterize the state of the system. The *independent thermodynamic quantities* can be measured. They are: temperature, pressure, mass, volume and density.

Thermodynamic quantities whose value depends only on the state of the system are called *functions of state*. The change of such quantities in a process

depends only on the initial and final states of the system, it doesn't depend on the path by which the system is brought from one state to the other. For example, the internal energy depends on temperature, concentration, etc. It is impossible to determine the absolute value of functions of state, because they depend on the other thermodynamic quantities.

The functions of state are: U — the internal energy; H — the enthalpy; S — the entropy; G — the Gibbs free energy.

Thermodynamic processes. Any change in the state of system is the thermodynamic process. Two types of thermodynamic processes are distinguished.

A *reversible thermodynamic process* is defined as a process in which the system reverts to its initial state without having caused any changes in its surroundings. If changes do take place in the surroundings, then the process is *irreversible*.

It must be stressed that reversibility and irreversibility, as defined in thermodynamics, do not coincide with the concepts, as applied to chemical reactions in chemistry, where the term «reversible» frequently denotes that a reaction may proceed in either direction, although the return to the initial state leads to changes in the surroundings.

Processes which are carried out at constant temperature are called *isothermal* ($T = \text{const}$, $\Delta T = 0$).

If a reaction proceeds at constant volume ($V = \text{const}$, $\Delta V = 0$), the process is *isochoric*. Chemical reactions proceed more frequently at constant pressure. The process is *isobaric* ($p = \text{const}$, $\Delta p = 0$).

Adiabatic processes are those in which the system neither absorbs nor gives up heat on its surroundings.

1.3. Energy. Internal Energy

The quantitative measure of motion of matter is energy. Energy can exist in various forms, all of which are forms of motion of matter. The forms of motion of matter are various and therefore the forms of energy are various as well (mechanical, electric, chemical, etc.) Every form of motion of matter corresponds to its form of energy. The various forms of energy transform into each other. For example, transformation of chemical energy into other forms of energy in a living organism (mechanical, heat energy, electric, etc.).

The joule (J) is a unit of energy. $1 \text{ J} = 1 \text{ Nm}$ (Newton-meter). One calorie is equivalent to 4,184 joules.

The internal energy. One of the most important quantities in chemical thermodynamics is the internal energy U of the system. This quantity is a function of state.

The internal energy U of a substance (or system) is the total energy of the particles forming the substance. It consists of the kinetic and potential energies

of the particles. The kinetic energy is the energy of translational, vibrational and rotational motion of the particles (atoms, molecules, ions, electrons); the potential energy is due to the forces of attraction and repulsion acting between the particles (intra-and intermolecular interactions):

$$U = E_{kin} + E_{pot}.$$

The internal energy does not include the kinetic energy of motion of the system as a whole or its potential energy due to position. It is impossible at present to determine the absolute value of the internal energy of a system, but changes in internal energy can be determined for various processes, and this is enough for the fruitful application of this concept in thermodynamics.

$$\Delta U = U_2 - U_1,$$

where U_1 and U_2 are the internal energy of the system in the initial (1) and the final (2) state, respectively. The quantity ΔU is considered positive if the internal energy of the system increases as a result of the given process.

The internal energy only depends on the initial and final states of the system; it does not depend on the path by which the system is brought from one state to the other. The internal energy obviously depends both on the amount of the substance and on the environmental conditions. As all other things being the same, the internal energy is directly proportional to the amount of substance.

Energy can be transferred from one part of a system to another in the form of heat or work or simultaneously. *Heat and work are not functions of state, they are forms of energy transfer.*

1. *The heat (Q) is the form of energy transfer which is carried out as disordered motion of matter under the temperature's gradient.*

Such form of energy transfer occurs by the temperature's gradient only. If T_1 is greater than T_2 ($T_1 > T_2$) the energy transfer will take place. The process stops when T_1 equals T_2 (i. e. $T_1 = T_2$).

How does the energy transfer? Look at fig. 2.

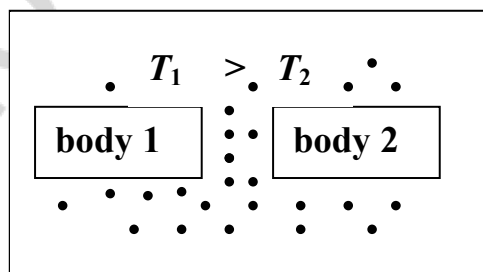


Fig. 2. The molecules move disorderly, collide with body 1, gain an excess of energy and then give to another molecules etc and at last to body 2

2. *Work* is one of the ways of transferring energy from one system (which performs work) to another system (on which work is performed). In the process the internal energy of the first system decreases, while that of the second system increases by an amount corresponding to the work performed (provided no heat has been transferred at the same time) (fig. 3).

The work (A) is the form of energy transfer which is carried out as ordered motion of matter. The work is connected with overcoming the force of friction and the movement of bodies in space.

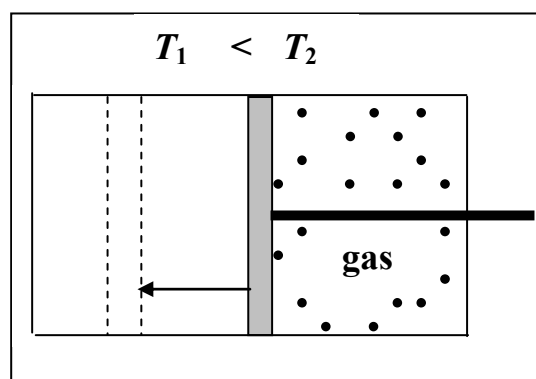


Fig. 3. The expansion of a gas makes piston to move

1.4. The First Law of Thermodynamics

The first law of thermodynamics is intimately related to the law of conservation of energy, which establishes the equivalence of the different forms of energy and the relation between the amount of heat absorbed or evolved in a process, the work performed or obtained, and the change in the internal energy of the system.

A number of consequences of this law are of great importance for physical chemistry and for the solution of various technological problems. By means of this law we can perform calculations of the energy balance, and in particular, the heat balance, and the heats of various processes. The first law of thermodynamics is a postulate; it cannot be proven by logical reasoning, but follows from the sum total of human experience. Its validity is demonstrated by the complete agreement of all its consequences with experience.

A great part in the formulation of the first law, as we know it today, was played by Hess, Joule and Meyer, Helm Holts and others.

The first law can be formulated in several ways, which are essentially equivalent to one another. One of its forms is as follows.

The heat energy (Q) flowing into a system can be used to change the internal energy of the system (ΔU) and allow the system to perform work (A) on its

surroundings. This statement can be written in equation form as $Q = \Delta U + A$, where A is the work of expansion.

The following highly useful formulation of the first law is a direct consequence of the proposition that the internal energy of an isolated system is constant «*in any process the change in the internal energy of a system $\Delta U = U_2 - U_1$ is equal to the heat Q absorbed by the system minus the work A done by the system*»:

$$\Delta U = Q - A.$$

It goes without saying, that all the quantities are to be expressed in the same units. This equation is the mathematical expression of the first law of thermodynamics. By means of it we can define the concept of internal energy thermodynamically as a quantity, the increase in which during a process is equal to the heat absorbed by the system plus the work done on the system by external forces.

The application of the first law of thermodynamics to various processes:

1. *An isochoric process.*

In the course of chemical reactions, work is mainly done against the force of the external pressure. This work depends on the change in the volume of a system. For an isochoric process $V = \text{const}$, $\Delta V = 0$, we have $A = 0$, $A = p\Delta V$, $Q_v = \Delta U + A$ and consequently *the mathematical expression for the first law of thermodynamics at the isochoric process is $Q_v = \Delta U$* , where Q_v is the heat absorbed by the system in conditions of a constant volume.

The heat effect of a reaction at constant volume and temperature corresponds to the change in the internal energy of the system during the reaction. Or: *for a chemical reaction proceeding without a change in the volume of the system, a change in the internal energy equals the heat effect of the reaction taken with the opposite sign.*

The quantity Q_v , like U , is a function of state of a system.

The last equation ($Q = \Delta U$) allows us to determine the change in the internal energy in processes. For instance, when a substance is heated at constant volume, the change in the internal energy is determined from the heat capacity of this substance: $Q_v = \Delta U = nC_v\Delta T$, where C_v is the molar heat capacity of the substance at constant volume, n is the number of moles of the substance, and ΔT is the difference between the final and initial temperatures.

Examples of reactions proceeding at constant volume are reactions in a closed vessel (an autoclave), between solids and liquids without the evolution of gases, and between gases if their amount does not change.

2. *An isobaric process.*

For isobaric processes we have $p = \text{const}$ and $\Delta p = 0$, $A = p\Delta V$.

In case of isobaric process $Q_p = \Delta U + p\Delta V$;

$Q_p = U_2 - U_1 + pV_2 - pV_1$, where Q_p is the heat absorbed by the system at constant pressure.

Then we write $Q_p = (U_2 + pV_2) - (U_1 + pV_1)$.

With a view to the sign conventions adopted in thermodynamics, the work is positive if it is done on a system ($\Delta V < 0$) and negative if a system does work against the forces of its surroundings ($\Delta V > 0$).

The function $U + pV$ designated by H is called the enthalpy. The enthalpy, like the internal energy, is a function of state. The enthalpy has the dimension of energy. We obtain $Q_p = H_2 - H_1 = \Delta H$; $Q_p = \Delta H$.

The heat effect of a reaction at constant pressure and temperature corresponds to the change in the enthalpy of the system during the reaction.

The quantity Q_p , like Q_v , is a function of state of a system. The enthalpy characterizes energy content of the system.

The enthalpy, like the internal energy, characterizes the energy state of a substance, but includes the energy spent to overcome the external pressure, i. e. to do the work of expansion. Like the internal energy, the enthalpy is determined by the state of a system and does not depend on how this state was reached. For gases, the difference between ΔU and ΔH in the course of a process may be considerable. For systems containing no gases, the changes in the internal energy and enthalpy attending a process are close to each other. The explanation is that the changes in the volume (ΔV) in processes occurring with substances in condensed (i.e. in the solid or liquid) states are usually very small, and the quantity $p\Delta V$ is small in comparison with ΔH .

The equation $Q_p = \Delta H$ allows us to determine the change in the enthalpy in different processes. Such determinations are similar to those of the internal energy, the only difference being that all the measurements must be conducted in conditions of a constant pressure. Thus, when a substance is heated, the change in its enthalpy is determined from the heat capacity of this substance at constant pressure. $\Delta H = Q_p = nC_p\Delta T$, where n is the number of moles of the substance, and C_p is its molar heat capacity at constant pressure.

3. An isothermal process.

$T = \text{const}$ and then $\Delta U = 0$, and $Q_T = A$, i. e. heat transforms into the work of expansion $A = p\Delta V$.

4. An adiabatic process.

An adiabatic process is one in which the system doesn't change heat with its surroundings, the work is performed according decreasing of the internal energy of the system i. e. $Q = 0$, $Q = \Delta U + A$, $A = -\Delta U$.

1.5. Thermochemistry

Thermochemistry is the branch of chemical thermodynamics devoted to a quantitative study of the energy effects of chemical and physico-chemical processes.

The heat effect of a reaction is the amount of heat evolved or absorbed in a reaction. Reactions proceeding with the liberation (release) of energy are called *exothermic*, reactions in which energy is absorbed, *endothermic*.

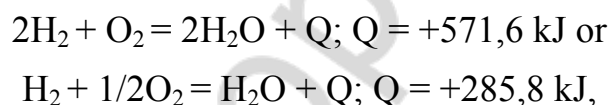
The magnitude of the heat effect depends on the nature of the reactants (initial substances) and the reaction products, their state of aggregation and temperature.

To be able to compare the heat effect of various reactions, one must indicate exactly the conditions under which these reactions occur, and also the physical state of each reaction component. Thermodynamic quantities are generally determined at *standard temperature and pressure (STP)*, namely, at $T = 298\text{ K}$ (more exactly, $298,15\text{ K}$) and $p = 101\text{ kPa}$ (more exactly, $101,325\text{ kPa}$).

The heat effect of a reaction is measured at a constant temperature (298 K) and 101,325 kPa (1 atm) pressure for the formation of one mole of the product is called the standard heat effect of a reaction.

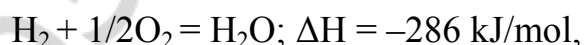
Heat effect can be included in the equations of reactions. Chemical equations in which the amount of liberated or absorbed heat is indicated are known as *thermochemical equations*. The physical state of the reactant and products are indicated. The symbols of the elements and the formulas of substances indicate the amount of a substance, therefore the coefficients in thermochemical equations may be either integers or fractions.

There are two forms of writing thermochemical equations. The first form of writing is:



where Q is the thermochemical heat effect of reaction which characterizes the energy change in the surroundings. If energy (E) flows from a system to the surroundings this process is called *exothermic* and $Q > 0$. If energy (E) flows into the system from its surroundings this process is called *endothermic* and $Q < 0$.

Another way to write this equation is:



where ΔH is the thermodynamic heat effect of the reaction which reflects the energy changes in a reaction system. When $\Delta H < 0$, a reaction is *exothermic* and energy decreases in a system. When $\Delta H > 0$, a reaction is *endothermic* and energy increases in a system. In any case $Q = -\Delta H$.

1.6. Hess's Law

The fundamental principle on which all thermochemical calculations are based was established in 1840 by the Russian chemist, academician G. Hess.

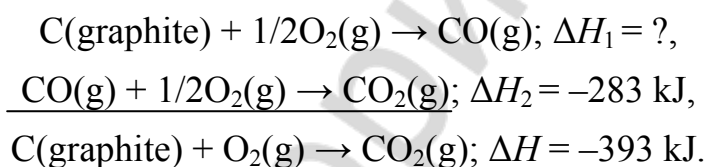
This principle is known as Hess's law and is a particular case of the law of energy conservation. It can be formulated as follows:

«The isochoric and isobaric heat effect of a reaction depends only on the initial and final state of substances and does not depend on the intermediate stages of the process».

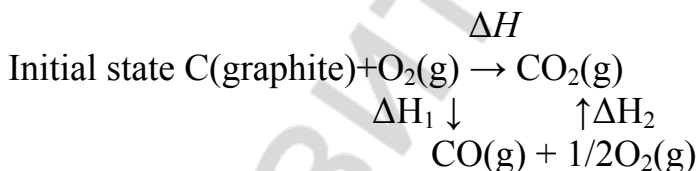
Hess's law allows us to calculate the heat effects of reactions when for some reason or other they cannot be measured directly. Let us consider as an example of such calculations the determination of the heat of formation of carbon monoxide from graphite and oxygen. It is very difficult to measure the heat effect of the reaction $C(\text{graphite}) + 1/2O_2(g) = CO(g)$, because upon the combustion of graphite in a limited amount of oxygen, what is obtained, is not only carbon monoxide, but its mixture with carbon dioxide. But the heat of formation of CO can be computed if we know its heat of combustion (283 kJ/mol) and the heat of formation of carbon dioxide (393 kJ/mol).

The combustion of graphite is expressed by the thermochemical equation $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta H = -393 \text{ kJ}$.

To calculate the heat of formation of CO, we shall write this reaction as two stages and summarize the thermochemical equations corresponding to these stages:



The above transformations can be depicted schematically as follows:



By Hess's law, $\Delta H = \Delta H_1 - \Delta H_2$. This enables us to find the value of ΔH_1 , which doesn't lend itself to experimental measurement, namely, $\Delta H_1 = \Delta H - \Delta H_2 = -393 - (-283) = -110 \text{ kJ}$.

The heat effect of oxidation of glucose in the living organism and in the bomb calorimeter is the same!

The thermodynamical substantiation of Hess's law. Hess's law was established before the first law of thermodynamics. So Hess's law is a corollary of the first law of thermodynamics.

According to the first law of thermodynamics $Q_V = \Delta U$. ΔU doesn't depend on the path by which the system is brought from one state to the other. ΔU is a function of state. In this case Q_V doesn't depend on intermediate stages of proceeding of process as well.

$Q_p = \Delta H$, but ΔH doesn't depend on intermediate stages of proceeding of process, and in this case Q_p doesn't depend on intermediate stages of proceeding either.

$Q_T = A$, but work is not a function of state and it is a function of process.

Hence, Hess's law is strictly valid only for constant-volume processes (the isochoric processes) or for constant-pressure processes (isobaric processes). For these processes it is easily deduced from the first law of thermodynamics.

The corollaries of Hess's law. The physical state in which a pure substance is the most stable at $p = 101$ kPa and a definite temperature (most often — 298 K) is assumed to be the standard state of this substance.

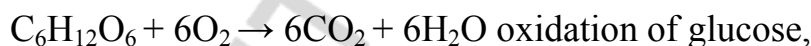
The standard enthalpy of formation of substance (ΔH_f°) is defined as the heat of the formation of one mole of a compound from its elements at standard conditions ($T = 298$ K, $p = 101$ kPa). Standard enthalpies of formation for the elements are defined as zero.

Standard enthalpies of combustion of substance (ΔH_{com}°) is defined as the heat effect of oxidation of one mole of a compound by oxygen to the higher oxides. Standard enthalpies of combustion of the higher oxides and oxygen are defined as zero.

It follows from Hess's law that:

1. *The enthalpy of formation of substance is equal to the enthalpy of decomposition of substance but opposite in sign, i. e. $\Delta H_f = -\Delta H_{decomp}$; (Law of Lavoisier and Laplace).*

2. *The heat effect of a reaction equals the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants taking into account the proper stoichiometric coefficients:*



$$\Delta H_{rxn}^\circ = [6\Delta H_f^\circ(\text{CO}_2) + 6\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + \Delta H_f^\circ(\text{O}_2)] = -2800 \text{ kJ,}$$

$$\Delta H_f^\circ(\text{O}_2) = 0,$$

$$\Delta H_{rxn}^\circ = \sum(m\Delta H_f^\circ) \text{ prod.} - \sum(n\Delta H_f^\circ) \text{ react.},$$

where m and n are the coefficients in the equation of the reaction.

3. *The heat effect of a reaction equals the sum of the standard enthalpies of combustion of the reactants minus the sum of the standard enthalpies of combustion of the products taking into account the stoichiometric coefficients:*

$$\Delta H_{rxn}^\circ = \sum(m\Delta H_{com}^\circ) \text{ react.} - \sum(n\Delta H_{com}^\circ) \text{ prod.}$$

Subscript «rxn» is an abbreviation for «reaction».

1.7. Thermochemical Calculations and Their Using for Characteristics of Biochemical Processes

The values of the standard enthalpies is in the reference books. These values are used for the calculations.

Example. Calculate the heat effect of the reaction of oxidation of glucose.



$$\Delta H_f^\circ[\text{CO}_2(\text{g})] = -393,5 \text{ kJ/mol};$$

$$\Delta H_f^\circ[\text{H}_2\text{O}(\text{e})] = -285,8 \text{ kJ/mol}.$$

Solution:

$$\begin{aligned} \Delta H_{rxn}^\circ &= (6\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] + 6\Delta H_f^\circ[\text{CO}_2(\text{g})] - \Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})]) = \\ &= [6(-285,8) + 6(-393,5) - (-1260)] = -2815,8 \text{ kJ/mol}. \end{aligned}$$

It is known, the oxidation of one mole of glucose is attended by evolving of 2800 kJ of energy in the process of vital activity of organism. The $\approx 80\%$ of this energy distributes into the surroundings in the form of heat, the $\approx 20\%$ of this energy is consumed for work (electrical, chemical, etc).

Thermochemistry is a theoretical base for a dietology. The thermochemical properties of foods are discussed in terms of their *specific enthalpy*, the magnitude of the enthalpy of combustion per gram of matter. The specific enthalpy of carbohydrates, which are the main source of energy for a human body, is about 6,7 kJ/g.

Specific enthalpy of lipids is much greater, at around 37,6 kJ/g. Lipids are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply.

Proteins are also used as a source of energy, but their components, the amino acids, are often too valuable to squander in this way, and are used to contract other proteins instead. When proteins are oxidized to urea, the equivalent specific enthalpy is comparable to that of carbohydrates (16,7 kJ/g).

Various foods have different compositions and hence different energy contents. Many labels on food packages show the calorie content of the food. The calorie (cal) is a non-SI unit of energy where 1 cal = 4,184 J (1 kcal = 4,184 kJ).

Daily Requirements in Energy depend upon muscle activity of a person:

1. Easy muscle work — 2500 kcal.
2. Average muscle work (students, doctors and some others) — 3500 kcal.
3. Hard muscle work — 4500 kcal.
4. Especially hard muscle work (sportsmen) — 7000 kcal.

Fuel values of food products

Food product	Content, %				Heat content, kJ/kg
	proteins	lipids	carbohydrates	H ₂ O	
Bread	6,3	1,3	46,1	43,9	9500
Noodle	11,0	0,9	74,2	13,6	14 980
Sugar	–	–	99,9	0,1	17 150
Butter	0,5	83,0	0,5	16,0	32 470
Beaf	18	10,5	–	71,3	7150
Potatoes	2,0	–	21,0	76	3930
Apples	0,4	–	11,3	87	2130

High muscle activity increases energy requirements by 30–50 %. They are also increased by serious diseases of patients. Thus rheumatoid attrite gives increase in energy requirements up to 10 %. High mental activity doesn't require increase in energy. Brain constantly oxidizes 5–6 g of glucose.

Increase in energy of food products and decrease in physical activity is responsible to obesity. Obesity is a non inflectional Epidemic of the 21 century. 300 millions people suffer from obesity in the world. In high developed countries their number is 30 % of the total population. Obesity increases the risk of heart and oncological diseases, diabetes mellitus.

1.8. The Second Law of Thermodynamics

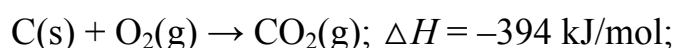
The multitude of different processes which take place in the world about us — in nature, technology, ect. — can be divided in two groups: *spontaneous and non-spontaneous processes*.

1. *The physical and chemical processes that occur without the outside energy are called spontaneous processes.*

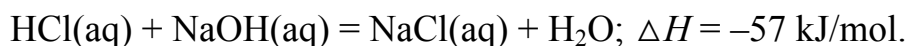
Examples of the spontaneous processes are: the fall of a sphere, the mixing of gases, the neutralization of a strong acid by a strong base, any of the reactions occurring during the work of an electrochemical cell, the combustion of fuel, the detonation of an explosive, the rusting of iron, the transformation of a substance from the glassy to the crystalline state, etc.

Majority of the spontaneous processes are exothermic reactions because there is decrease in energy. Examples of the spontaneous exothermic reactions:

a) burning of a substance:



b) neutralization of an acid with a base:



However, many spontaneous reactions may be endothermic. For example, dissolving NH_4NO_3 in water.

2. *The physical and chemical processes that occur with the outside energy are called non-spontaneous processes.*

In non-spontaneous processes work must be done on the system in an amount directly proportional to the change which is brought about.

Examples of non-spontaneous processes are: a separation of a mixture of gases, the motion of a sphere on an inclined plane upwards, the dissociation of water by an electric current, etc.

Changes that are spontaneous in one direction are non-spontaneous in the opposite direction.

The first law, as we have seen, states that the internal energy of an isolated system is constant, and that transformations between different forms of energy take place in equivalent amounts. This can also be expressed in the form of a relation between the change in the internal energy of a system, the amount of heat supplied to it, and the work performed. The first law, however, says nothing about the character, permissibility or direction of the processes by which the various conversions of energy are brought about.

The second law on the other hand, specifies what processes in the system of interest at given temperature, pressure, concentrations, etc., can occur spontaneously (i. e., without work being done on the system), what amount of work can be obtained from such processes, and what is the limit of the spontaneous process, i. e., to what state of equilibrium the system tends under the given conditions.

The second law allows us to indicate the external conditions necessary for the process of interest to proceed in the desired direction and to the required extent. For processes in which work must be done we can determine by means of the second law the amount of work required for the process to be carried out and the dependence of this quantity on the external conditions.

All this is of very great importance both for theoretical investigations in physical chemistry, and for the solution of various practical problems.

The second law of thermodynamics has a more limited field of application than the first law. It is of a statistical nature and is therefore applicable only to systems composed of a large number of particles, i.e. to systems whose behavior can be described by the laws of statistics.

The changes in energy are not the only criterion for deciding the spontaneity of a reaction. The spontaneous processes lead to an equilibrium in a system as the final result. The quantitative measure of approach of the system to the equilibrium is *entropy* (S).

This function is introduced by the second law of thermodynamics.

Entropy is a measure of the degree of disorder of a system. When disorder increases, entropy also increases. The entropy, like the enthalpy and internal energy, is a function of state of a system, hence the change in the entropy ΔS dur-

ing the transformation of a system is determined only by the initial and final states of the system, its temperature and pressure and does not depend on the path of the process.

For isolated systems, a change in the entropy is a criterion determining the direction of a process. *By the second law of thermodynamics in isolated systems the entropy of a spontaneous process increases, i. e. $\Delta S > 0$.*

In a closed system, the entropy may either increase or decrease during a process. It increases when a system passes from a more ordered state into a less ordered one.

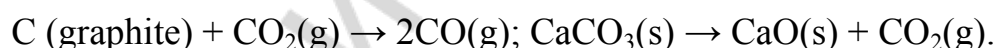
The reverse transition of a system causes its entropy to diminish. *When the entropy is maximum the system is in condition of complete thermodynamic equilibrium ($\Delta S = 0$).*

The processes for which $\Delta S > 0$ include the expansion of gases, phase transitions during which a substance transforms from the solid to the liquid and gaseous states, and the dissolution of crystalline substances. The processes for which $\Delta S < 0$ include the compression of gases and the condensation and crystallization of substances.

Gaseous state is the most disordered and so has the highest entropy. Liquid state is less ordered and so has less entropy than the gaseous state. Solid state is the most ordered and so has the lowest entropy. S (solid) $<$ S (liquid) $<$ S (gas).

The second law of thermodynamics will be expressed by the following expressions: $\Delta S > 0$, that S is positive for an irreversible spontaneous change; $\Delta S = 0$, that S is zero for a reversible change.

In a chemical reaction, the entropy grows if the volume of the system increases. Examples are the reactions:



A decrease in the volume in a reaction is attended by a decrease in the entropy, e. g. $2\text{C (graphite)} + 3\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$.

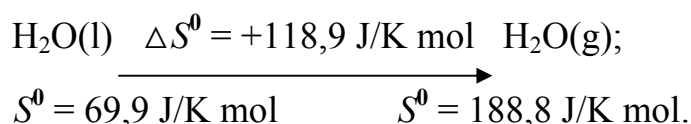
Unlike H and U , we can determine the absolute values of the entropy for all pure substances at any temperatures. By the third law of thermodynamics, the entropy of pure substances existing in the form of perfect crystals is zero at 0 K. In other words, at absolute zero, complete order sets in in a perfect crystal.

The *standard entropy* of pure substances is determined for one mole of a substance at $p = 101,325$ kPa and a definite temperature, generally 298 K. It is designated by S^0_{298} or S^0 . The unit of the entropy is J/mol·K.

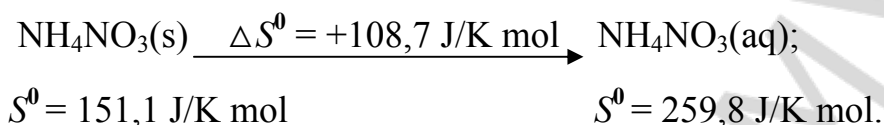
The standard entropy of simple substances does not equal zero.

The greater the disorder or randomness in a system, the larger the entropy.

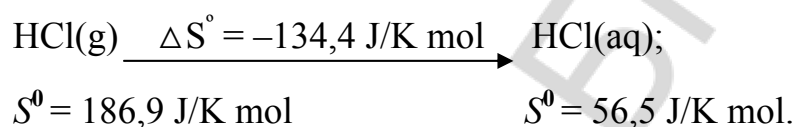
1. The entropy of a substance increases as it changes from solid to liquid to gas:



2. When pure solids or liquids dissolve in a solvent, the entropy of the substance increases:



3. When a gas dissolves in a solvent, its entropy declines:



A gas is clearly the most disordered state. When the substance dissolves, there are intermolecular interactions that impose some order, and the entropy declines.

4. Entropy generally increases with increasing molecular complexity.

There are several aspects to the relation between molecular complexity and entropy. For example, the standard entropy increases as the number of ions per formula unit in an ionic solid increases.

	KCl(s)	CaCl ₂ (s)	GaCl ₃ (s)
S° (J/K mol)	83	115	142

Similarly, entropy increases as the number of atoms increases in a related series of molecules.

In the following series of straight-chain hydrocarbons (all C atoms are bound into a non branching chain), notice that the entropy increases by about 40 J/K mol every time another $-\text{CH}_2-$ group is added to the chain.

		S° (J/K mol) for gaseous compound
Methane	CH ₄	186,3
Ethane	C ₂ H ₆	229,6
Propane	C ₃ H ₈	269,9
Butane	C ₄ H ₁₀	310,0
Octane	C ₈ H ₁₈	463,6

A corollary to this is that entropy increases when going from a three-dimensional network solid to one that is only two dimensional. The best examples are of course diamond and graphite, whose very low entropies reflect the high degree of order.

	S^0 J/K mol
Diamond	2,38
Graphite	5,74
Quarts(SiO_2)	41,8

In general, elements that have a high degree of covalent bonding in the solid state (B, C, P, S) have relatively low standard entropies. Metals have values ranging from about 10 J/K mol to 80 J/K mol, while the gaseous elements have the highest values of all.

Since the entropy is a function of state, the change in the entropy ΔS attending a chemical reaction equals the difference between the values of the absolute entropies of the products and reactants at the temperature and pressure of the reaction. For a chemical reaction at standard temperature and pressure (STP) we have:

$$\Delta S^0_{rxn} = \sum m S^0 \text{ prod.} - \sum n S^0 \text{ react.},$$

where m and n are the number of moles of products or reactants, respectively.

1.9. THE STATISTICAL INTERPRETATION OF ENTROPY

The statistical interpretation of entropy (relies on) is based on the kinetic theory of gases.

Consider a system containing about five molecules. Every molecule has its own number. Take photograph of this system and have a photo. Then, take another photograph of this system and have another photo, etc. After all we conclude that a macrostate is the state of substance characterized by definite values of its macroscopic properties (temperature, pressure, volume, etc.); a microstate is the state of substance characterized by a definite state of each particle (molecule, atom). The same macrostate corresponds to a great number of various microstates. The number of microstates that form given macrostate is called *the thermodynamic probability* of the given state of the system (W).

If $W = 1000$ it means that one macrostate corresponds to 1000 microstates. (The thermodynamic probability should not be confused with mathematical probability which is not greater than one).

There is a relation between entropy and thermodynamical probability of the system (*Boltzmann's equation*): $S = k \ln W$, where k is a constant in energy or is Boltzmann's constant $k = \frac{R}{Na}$, where R is the molar gas constant equal to

8,314 J/mol K; Na is Avogadro's number equal to $6,02 \cdot 10^{23} \text{ mol}^{-1}$. $k = 1,38 \cdot 10^{-23} \text{ J/K}$.

Greater the thermodynamic probability of the given system, greater will be entropy.

1.10. THE THERMODYNAMICAL INTERPRETATION OF ENTROPY

If the statistical interpretation of entropy is given by L. Boltzmann, the thermodynamical interpretation of one is given by Clausius.

We know the entropy of a pure perfectly ordered crystalline substance is zero at the absolute zero of temperature ($S = 0$). In this case one macrostate corresponds to one microstate ($W = 1$), that is $S = 0$ and a system is in equilibrium ($\Delta S = 0$).

With elevation of the temperature the entropy increases, the thermodynamic probability increases but the order decreases in the system. So the entropy of a system depends on quantity of energy (Q) put into a system and temperature (T) at which the process is carried out. The change in entropy is related to the heat absorbed by the equation: $\Delta S_{\text{sys}} \geq Q_{\text{sys}}/T$. It is a mathematical expression of the second law of thermodynamics.

For processes with the system at equilibrium:

$$\Delta S_{\text{sys}} = Q_{\text{sys}}/T. \quad (1)$$

According to equation (1) in reversible isothermal processes the entropy change is equal to the heat of the process divided by the absolute temperature.

For a spontaneous process:

$$\Delta S_{\text{sys}} > Q_{\text{sys}}/T. \quad (2)$$

This equation makes an important distinction between equilibrium and non-equilibrium systems; spontaneously changing systems experience greater disorder (2) than they would if the change were made under equilibrium conditions (1).

Proteins are formed in the living organisms from amino acids. The process is attended with the decreasing of entropy and consequently the proteins are higher ordered systems.

Synthesis of DNA, RNA proceeds with the decreasing of entropy as well. They are non-spontaneous processes. These processes are needed in energy.

The living organism is an open system which changes energy and matter with its surroundings.

We must consider the living organism as an open system with its surroundings. In this case $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$. It is impossible to apply the second law of thermodynamics for living organism without biological processes as well.

1.11. THE GIBBS FREE ENERGY

In order to know about direction and limit of the processes in opened and closed systems it is necessary to take account of change in entropy of surroundings. It is very complex and sometimes impossible task.

Besides the change in the enthalpy in the course of a chemical reaction is not a criterion of its direction. Both exothermic and endothermic reactions may proceed spontaneously, although the latter are fewer in number under ordinary conditions.

Consequently the possibility of processes occurring in closed and opened systems at constant temperature and pressure is determined by the change in a thermodynamic function of state called the *Gibbs energy* ΔG , which is related to the enthalpy and entropy by the equation: $G = H - TS$, where T is the absolute temperature.

Synonyms are the isobaric — isothermal potential, isobaric potential, and the free energy at constant pressure.

The change in the Gibbs energy shows how the direction of a chemical reaction is affected by two competing trends simultaneously acting in a system, namely (1) the trend to a minimum energy, and (2) the trend to maximum entropy. At constant temperature and pressure, the change in the Gibbs energy is $\Delta G = \Delta H - T\Delta S$.

The notion about the Gibbs energy was introduced on the basis of equations of the first law and second law of thermodynamics.

The equation for the first law of thermodynamics is $Q = \Delta H + A$ (1), the equation for the second law of thermodynamics is $\Delta S = Q/T$, or $Q = T\Delta S$ (2).

Inserting in the expression (1) the value $Q = T\Delta S$ from (2) we obtain:

$$T\Delta S = \Delta U + A. \quad (3)$$

The system can perform not only the work of expansion ($p\Delta V$) but perform another forms of work (electric, chemical, osmotic, etc.).

Write the maximum work of process (A_{max}):

$$-A_{max} = p\Delta V + A_u, \quad (4)$$

where A_u is the maximum useful work.

Comparing equations (3) and (4) we obtain:

$$\begin{aligned} T\Delta S &= \Delta H + p\Delta V + A_u, \\ -A_u &= \Delta U + p\Delta V - T\Delta S, \\ -A_u &= U_2 - U_1 + pV_2 - pV_1 - TS_2 + TS_1, \\ -A_u &= \underbrace{(U_2 + pV_2 - TS_2)} - \underbrace{(U_1 + pV_1 - TS_1)}, \end{aligned}$$

$$\begin{aligned}
 & \qquad \qquad H_2 \qquad \qquad \qquad H_1 \\
 -A_u &= (H_2 - TS_2) - (H_1 - TS_1); \mathbf{H - TS = G}, \\
 -A_u &= G_2 - G_1 = \Delta G, \\
 -A_u &= \Delta G.
 \end{aligned}$$

In the reversible and isothermal conducting of a process, ΔG is equal in magnitude, but opposite in sign, to the maximum useful work that the system does in the given process.

By useful work is meant all the work done in the course of a process less the work of expansion $p\Delta V$.

It follows from equation $A_u = -\Delta G$ that if a system performs work spontaneously ($A > 0$), then $\Delta G < 0$. In this case a criterion of a spontaneous process is:

$$A > 0 \text{ or } \Delta G < 0.$$

If the system doesn't perform work then $A = 0$ and $\Delta G = 0$. It is a criterion of equilibrium state.

The unit of the Gibbs free energy is J/mol.

The enthalpy and entropy factors and direction of a process.

$\Delta G = \Delta H - T\Delta S$. The sign and the magnitude of ΔG are determined by two factors: entropy ($T\Delta S$) and enthalpy (ΔH).

The enthalpy factor defines the tendency of a system to its minimum of energy.

The entropy factor defines the tendency of a system to its disorder.

The Gibbs free energy is an integral function of state of a system.

Depending on the temperature, the influence of one of these factors on the value and sign of ΔG and consequently on the direction of a process may be determining the table 2.

Table shows the possibility (or impossibility) of the spontaneous proceeding of a reaction with different combinations of the signs of ΔH and ΔS .

1. If $\Delta H < 0$ for a reaction (an exothermic reaction), and $\Delta S > 0$, it follows from the equation $\Delta G = \Delta H - T\Delta S$ that at all temperatures $\Delta G < 0$. This signifies that the reaction can proceed spontaneously at any temperatures.

The exothermic reactions attended by an increase in the entropy can proceed spontaneously. ($\Delta H < 0$, $\Delta S > 0$, $\Delta G < 0$).

Directions of reactions with different signs of ΔH and ΔS

Sing of change in function			Possibility (impossibility) of spontaneous proceeding of reactions
ΔH	ΔS	ΔG	
-	+	-	Possible at any temperature
+	-	+	Impossible at any temperature
-	-	\pm	Possible at sufficiently low temperature
+	+	\pm	Possible at sufficiently high temperature

2. If $\Delta H > 0$ (endothermic reaction) and $\Delta S < 0$ it follows from the equation $\Delta G = \Delta H - T\Delta S$ that $\Delta G > 0$. *The endothermic reactions attended by a decrease in the entropy and the process can't proceed spontaneously:* (at an ordinary temperature and atmospheric pressure). ($\Delta H > 0$, $\Delta S < 0$, $\Delta G > 0$).

3. If $\Delta H < 0$ and $\Delta S < 0$ or $\Delta H > 0$ and $\Delta S > 0$. In this case value of ΔG depends on absolute values of ΔH and $T\Delta S$: if $|T\Delta S| \gg |\Delta H|$ then $\Delta G < 0$; if $|T\Delta S| \ll |\Delta H|$ then $\Delta G > 0$.

If $\Delta H < 0$ and $\Delta S < 0$, the reaction is possible ($\Delta G < 0$) provided that the term ΔH in the equation for the Gibbs energy is greater in magnitude than the term $T\Delta S$; since the magnitude of the term $T\Delta S$ increases with a growth in the factor T , this condition will be observed at sufficiently low temperatures.

In other words, at low temperatures, the spontaneous proceeding of exothermic reactions is most probable even if the entropy of the system diminishes.

At high temperatures, as can be seen from the table, reactions attended by a growth in the entropy are most probable, including endothermic reactions.

We must add that a negative value of ΔG for a reaction points only to the possibility of its occurring. Actually, the reaction may not be observed. The matter is that its rate may be low; hence, notwithstanding observance of the condition $\Delta G < 0$, the reaction will virtually not proceed. In these cases, an appropriate catalyst must be found to increase the rate of the reaction. Such cases are especially frequent at low temperatures.

4. If $\Delta H = T\Delta S$, then $\Delta G = 0$ and the equilibrium sets in (is settled) in the system.

Calculation of ΔG^0 in chemical reactions:

1. *The standard free energy of formation ΔG_f^0 is the change of free energy during the formation of a substance in its standard state from the elements*

in their standard states. The standard free energies of formation of elements in their standard states are zero. The free energy change for a reaction can be found from values of ΔG_f^0 by general equation.

$\Delta G_{rxn}^0 = \sum m \Delta G_f^0 \text{ prod.} - \sum n \Delta G_f^0 \text{ react.}$, where m and n are the numbers of moles of a given product or reactant, respectively. But the reactions don't proceed at standard conditions (the concentration can not be 1 mol/liter).

2. For the reaction $A + B = C + D$ in real conditions calculation of ΔG can be performed according to the equation: $\Delta G_{rxn} = \Delta G^0 + RT \ln[C][D]/[A][B]$, where $[C]$, $[D]$, $[A]$ and $[B]$ are the concentrations of the substances; ΔG^0 is the standard change in the Gibbs energy of the reaction, R is the molar gas constant ($R = 8,314 \text{ Jmol/K}$); T is the temperature, K.

3. Alternatively, you can calculate the enthalpy and entropy changes for the reaction ΔH_{rxn}^0 and ΔS_{rxn}^0 and combine them using the Gibbs equation:

$$\Delta G_{rxn}^0 = \Delta H_{rxn}^0 - T \Delta S_{rxn}^0,$$

$$\Delta H_{rxn}^0 = \sum \Delta H^0 \text{ prod.} - \sum \Delta H^0 \text{ react.},$$

$$\Delta S_{rxn}^0 = \sum S^0 \text{ prod.} - \sum S^0 \text{ react.};$$

a) $\Delta G^0 < 0$ (is less than zero), a process is spontaneous at standard conditions;

b) $\Delta G^0 > 0$ (is greater than zero), a process is not spontaneous at standard conditions;

c) $\Delta G^0 = 0$, the process is at equilibrium.

1.13. BIOENERGETICS. ENDERGONIC AND EXERGONIC REACTIONS

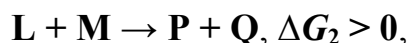
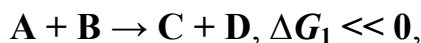
Bioenergetics is thermodynamics of biological systems. It deals with the energy, heat and work exchange in plants, animals and human bodies. A human body is an open stationary system. Its main source of energy is chemical energy of food products (99 %). Carbohydrates are responsible for 55–60 %, lipids — 20–25 %, and proteins — 15–20 %.

In general efficiency of food chemical energy conversion in a human body is approximately 20–25 %. Thus waste energy dissipated into surroundings is 75–80 %. 20 liters of water can be boiled if focused daily waste energy of one person. Biochemical reactions are chemical reactions which proceed in vivo. They are:

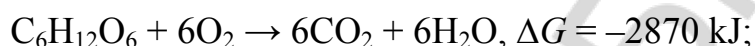
1. *Exergonic (spontaneous) $\Delta G < 0$.*
2. *Endergonic (nonspontaneous) $\Delta G > 0$.*

Many biochemical reactions are endergonic, but in some cases they can be carried out to an appreciable extent by coupling them with an exergonic reaction.

A coupled (conjugated) reaction is a process in which an endergonic reaction is made to proceed by coupling it to an exergonic reaction. Biologically coupled reactions are usually mediated with the aid of enzymes. A scheme of a coupled reaction can be represented as follows:



Carbohydrates and lipids metabolism involves highly spontaneous oxidation reactions:



Some of this energy is released as heat that maintains constant body temperature. Another portion is stored in high-energy molecules that a body uses as «power sources» for numerous reactions that occur within cells. The most important of these energy transport molecules is adenosine tri-phosphate (ATP) (fig. 4).

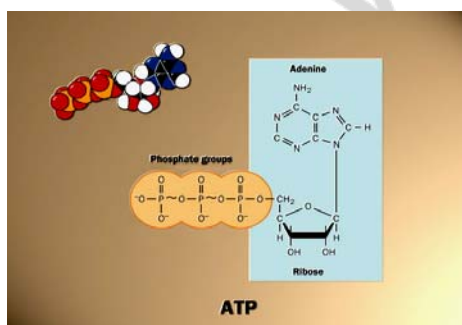
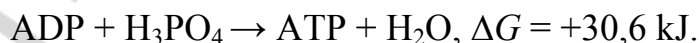


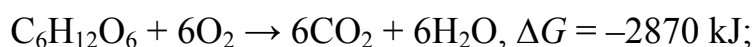
Fig. 4. The structure of ATP

Adenosine triphosphate (ATP) is a high-energy triphosphate ester used in living systems to provide chemical energy for etabolic needs.

Synthesis of ATP molecules from ADP and phosphoric acid is nonspontaneous under physiological conditions:



In cells ATP production is coupled with glucose oxidation. One molecule of glucose can convert as many as 36 ADP molecules into ATP molecules as it is oxidized to CO_2 and water:



$$\Delta G_{\text{overall}} = -2870 + 1100 = -1770 \text{ kJ.}$$

Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is «wasted». Efficiency of a process is: $1100/2870 = 0,38$ or 38 %.

Thus cells harness 38 % of the chemical energy stored in glucose to drive the biochemical machinery of metabolism. The remaining 62 % of energy is dissipated as heat.

1.14. THERMODYNAMICS OF THE CHEMICAL EQUILIBRIUM

All chemical reactions can be divided into two groups: *irreversible* and *reversible* reactions. *Irreversible reactions proceed to the end* — until one of the reactants is completely used up. Irreversible reactions are characterized by the formation of an insoluble substance, the formation of a gas, the formation of a weak electrolyte (H_2O).

A reversible reaction is the reaction which can proceed either in the forward or in the reverse direction. Reversible reactions are characterized by the symbol \rightleftharpoons between the reactants and products. When the rates of the forward (V_f) and reverse (V_r) reactions become the same, *chemical equilibrium sets in*, i. e. $V_f = V_r$. As soon as equilibrium has been reached, the concentrations of the substances (both the reactants and the products) remain unchanged provided the conditions are not altered. These concentrations are called *equilibrium concentrations*.

Chemical equilibrium is characterized quantitatively by a quantity known as the chemical equilibrium constant. *The chemical equilibrium constant is the ratio of the product of product equilibrium concentrations to the product of reactant equilibrium concentrations.* For example, for the reaction $\mathbf{aA + bB \rightleftharpoons cC + dD}$ the chemical equilibrium constant is:

$$K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}.$$

Concentrations of solids are assumed to be 1 and they can be left out of the concentration ratio without altering the value of K.

The numerical value of the equilibrium constant in the first approximation characterizes the yield of the given reaction (the yield of a reaction is defined as the ratio of the amount of a substance produced to its amount that would have been produced if the reaction proceeded to the end). For example, *when $K \gg 1$, the yield of a reaction is high*, because $[\text{C}]^c [\text{D}]^d \gg [\text{A}]^a [\text{B}]^b$ i. e. at equilibrium, the concentrations of the products are much greater than those of the reactants, and this is exactly what signifies that the yield of the reaction is high. *When $K \ll 1$ the yield of the reaction is low.*

The magnitude of the equilibrium constant depends on the nature of the reacting substances and on the temperature. It does not depend on the presence of catalysts. A catalyst does not affect the magnitude of the equilibrium constant and, consequently, cannot either increase or lower the yield of the reaction. It can only accelerate or retard the setting in of equilibrium.

The equilibrium constant determines the extent of a process by the instant of reaching the equilibrium state. The larger this quantity, the greater is the degree of conversion of the reactants into the products.

The ways of designation of the equilibrium constant:

1. For solutions of non-electrolytes and sufficiently dilute solutions of electrolytes the equilibrium constant K_c is used (the equilibrium concentrations are expressed in mol/liter in liquid phase):

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}.$$

2. For strong electrolytes the activity (a) is used:

$$K_a = \frac{a^c(C) \cdot a^d(D)}{a^a(A) \cdot a^b(B)}.$$

3. Chemical equilibrium between gases at low pressures is expressed in terms of the partial pressures p_i of the reactants and products:



$$K_p = \frac{p^2(\text{HI})}{p(\text{H}_2) \cdot p(\text{I}_2)}.$$

A relationship between K_c and K_p is given by an equation:

$$K_c = K_p \cdot RT^{(a + b - c - d)}.$$

1.15. THE EQUATION OF THE ISOTHERM OF A CHEMICAL REACTION

$A + B \rightleftharpoons C + D$. The reaction takes place at constant temperature and constant pressure.

The change in the Gibbs energy of this reaction in real conditions is:

$$\Delta G = \Delta G^\circ + RT \cdot \ln \frac{[C][D]}{[A][B]}. \quad (5)$$

The value of the change in the Gibbs energy in a reaction depends on the temperature and also on the nature and concentrations of the reactants and products.

For the state of chemical equilibrium $\Delta G = 0$, then we obtain from (5):

$$0 = \Delta G^\circ + RT \cdot \ln \frac{[C][D]}{[A][B]}, \text{ but } \ln \frac{[C][D]}{[A][B]} = \ln K_c \text{ and } \Delta G^\circ = -RT \cdot \ln K_c. \quad (6)$$

We can write this equation (6) as $\ln K_c = -\Delta G^\circ/RT$ or in exponential form:

$$K_c = e^{-\Delta G^\circ/RT}, \quad (7)$$

where e is the base of natural logarithms ($e = 2,718\dots$).

From equation (7) we can deduce, that K_c depends on the temperature and the nature of the reactants (entropy and enthalpy factors).

With elevation of the temperature the equilibrium constant increases too.

The $\ln K_c$ determines the extent of a proceeding of a reaction.

K_c is the equilibrium constant expressed in terms of concentrations of the components A, B, C and D in equilibrium.

If we introduce the value 2,303 (the number 2,303 is coefficient of transition from natural logarithm to common one) and the value of the molar gas constant $R = 8,31 \text{ J/mol K}$ into the above equation (6), we get:

$$\Delta G^\circ = -2,303 \cdot 8,31 \cdot T \log K_c = -19,1 \log K_c \text{ (J/mol)}$$

$$\text{or } \Delta G^\circ = -0,0119 \cdot T \log K_c \text{ (kJ/mol)}.$$

Introduce the equation (6) $\Delta G^\circ = -RT \ln K_c$ into the equation (5)

$$\Delta G = \Delta G^\circ + RT \cdot \ln \frac{[C][D]}{[A][B]}$$

We get $\Delta G = -RT \cdot \ln K_c + RT \cdot \ln \frac{[C][D]}{[A][B]}$, where [A], [B], [C], [D] are not equilibrium concentrations. It is the equation of the isotherm of a chemical reaction, where $\ln \frac{[C][D]}{[A][B]}$ is the concentration term; $\ln K_c$ is the constant term.

The sign of ΔG depends on the real concentrations of the reactants and products for given time (for a moment).

The analysis of the equation:

1. $\ln \frac{[C][D]}{[A][B]} < \ln K_c$ and $\Delta G < 0$.

A spontaneous chemical reaction occurs from left to right. If we change the concentrations we can affect the direction of the spontaneous proceeding of the reaction.

$$2. \ln \frac{[C][D]}{[A][B]} < \ln K_c \text{ and } \Delta G > 0.$$

A spontaneous chemical reaction doesn't occur from left to right, but the reaction is spontaneous from right to left.

$$3. \ln \frac{[C][D]}{[A][B]} = \ln K_c \text{ and } \Delta G = 0.$$

The system is in an equilibrium.

The equation $\Delta G^\circ = -19,1 \lg K_c$ makes it possible to calculate the equilibrium constant, if we know ΔG° and, conversely, to determine ΔG° for a reaction using the experimentally found value of the equilibrium constant. It must be stressed in this connection that the sign of ΔG° indicates the possibility or impossibility of a reaction proceeding only in standard conditions, when all the reactants and products are in standard states.

In the general case, however, the possibility (or impossibility) of a reaction is determined by the sign of ΔG , and not of ΔG° .

The equilibrium constant's dependence on the enthalpy and entropy factors indicates that it also depends on the nature of the reactants.

1.16. THE EQUATION OF THE ISOBAR OF A CHEMICAL REACTION

$p = \text{const}$, in the integral form we have the equation:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (8)$$

where K_1 and K_2 are equilibrium constants at the different temperatures T_1 and T_2 ; ΔH is change in enthalpy; R is the molar gas constant.

This equation relates the equilibrium constant, the enthalpy change and the temperature, i. e. its relates the kinetics and thermodynamics.

The equation is in the differential form:

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}. \quad (9)$$

These equations (8 and 9) establish a relation between the change in the equilibrium constant with temperature and the heat of the reaction. They are valid for processes which take place at constant pressure, and are called *the equations of the reaction isobar*.

For constant-volume processes a similar equation can be obtained:

$$\frac{d \ln K_c}{dT} = \frac{\Delta U}{RT^2} \quad (10)$$

This equation relates the change in the equilibrium constant with temperature to the heat of the reaction and is called *the equation of the reaction isochore*. ΔU is the change in internal energy.

The analysis of the equation of the Isobar of a chemical reaction:

1. $\Delta H < 0$ exothermic reaction.

When heat is evolved in the chemical reaction i. e. $\Delta H < 0$ and $\frac{\Delta H}{RT^2} < 0$ as well, then from equation (9) we conclude that $\frac{d \ln K_p}{dT} < 0$. This denotes that the equilibrium constant decreases with rise in temperature (the numerator decreases) and equilibrium is displaced towards the left. In other words, with rise in temperature equilibrium is displaced in the direction of the endothermic process.

With lowering in temperature the equilibrium constant increases ($dT < 0$) and equilibrium is displaced towards the right.

2. $\Delta H > 0$ endothermic reaction.

When heat is absorbed in the chemical reaction, i. e. $\Delta H > 0$ and $\frac{\Delta H}{RT^2} > 0$ as well, then from equation (9) we conclude that $\frac{d \ln K_p}{dT} > 0$. This denotes that the equilibrium constant increases with rise in temperature and with lowering in temperature the equilibrium constant decreases.

The equations (9) and (10) of the reaction isobar and isochore describe the change in the equilibrium constant with temperature. They express this dependence in differential form. For practical computations of equilibrium at different temperatures it is usually necessary to integrate these expressions.

1.17. LE CHATELIER PRINCIPLE

A change in the conditions (temperature, pressure, concentration) under which a system is in a state of chemical equilibrium disturbs equilibrium be-

cause of the different changes in the rates of the forward and reverse reactions ($V_f \neq V_r$). With time, new chemical equilibrium sets in in the system ($V_f = V_r$) that corresponds to the new conditions. The transition from one equilibrium state to another is called a *shift of equilibrium*.

The direction of a shift of chemical equilibrium as a result of a change in the external conditions is determined by *Le Chatelier's principle*: «*if any change of conditions is imposed on a system in equilibrium, equilibrium will shift in the direction of the process that counteracts the imposed change*».

For instance:

- *elevation of the temperature* leads to the shifting of equilibrium in the direction of the reaction attended by the absorption of heat, i. e. by cooling of the system;

- *an increase in the pressure* causes equilibrium shift in the direction of a decrease in the total number of moles of gaseous substances, i. e. in the direction leading to lowering of the pressure;

- *the removal from a system of one of the products* results in equilibrium being displaced in the direction of the forward reaction;

- *diminishing of the concentration of one of the reactants* leads to shifting of equilibrium in the direction of the reverse reaction.

Chapter 2. Chemical Kinetics

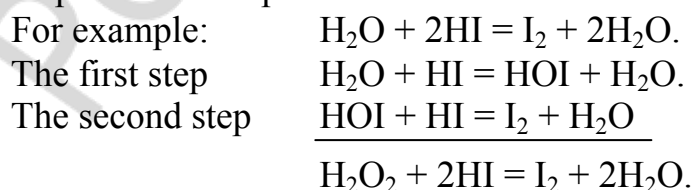
Chemical kinetics is the science about rates and mechanisms of chemical reactions. Tasks of chemical kinetics:

1. The establishment of factors affecting rates of chemical reactions.
2. The establishment of mechanism of chemical reactions.

2.1. BASIC CONCEPTS OF CHEMICAL KINETICS, SIMPLE AND COMPLEX REACTIONS

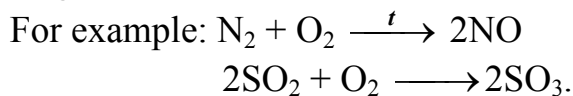
Simple reaction — simple reactions have one step and their stoichiometric equations exactly express the real process. For example: $H_2 + I_2 = 2HI$.

Complex reactions have several steps and their stoichiometric equations don't express the real process which consists from several steps.

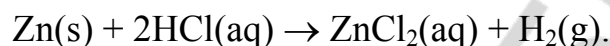


Most reactions are complex. The mechanism of every chemical reaction is determined by the sum of steps. Every individual step of mechanism of chemical reaction is called a simple reaction.

Homogeneous and heterogeneous reactions. Homogeneous reaction refers to reaction occurring amongst species present in the same phase, or in liquid and gaseous solutions.



When different phases occur, for example between two immiscible liquids or a solid and a liquid, the reaction is referred to as heterogeneous. The reaction can occur only at the surface of contact of the two phases:



2.2. RATES OF REACTIONS

Chemical reactions proceed at different rates. The reaction of neutralization between aqueous acids and bases occurs almost instantaneously, while the rusting of iron is slow.

The rates of chemical processes in vivo differ greatly. The time of the total renewal of bone tissue is 4–7 years, the time of a half proteins renewal — 70 days, chemical reactions responsible for neural activity run instantly.

The rate of chemical reaction is a basic concept in chemical kinetics.

The rate of a reaction can be measured by the change of molar concentration of one of the reactants or products per unit time.

The rate of chemical reaction can be calculated from the formula:

$$V = \frac{\Delta C}{\Delta t},$$

where ΔC is the change of concentration in mole /liter; Δt is the change of time in sec, min, hour. $[V] = \left[\frac{\text{mol}}{\text{liter} \cdot \text{sec}} \right] \text{ or } \left[\frac{\text{mol}}{\text{liter} \cdot \text{min}} \right]$.

This is an average rate of chemical reaction, i. e. the rate in the period of time from t_0 till t . The average rate is designated as \bar{V} . In practice the instantaneous rate is used. The instantaneous rate is the rate at the given moment of time (R).

The smaller the period of time Δt the nearer the average rate (\bar{V}) to the instantaneous rate (R), i.e. the average rate \bar{V} in the period of time from t_0 till t aspires t_0 the instantaneous rate of chemical reaction provided t leads to t_0 (provided $t \rightarrow t_0$) or mathematically:

$$R = \lim_{t \rightarrow t_0} \bar{V} = \lim_{t \rightarrow t_0} \left(\frac{\Delta C}{\Delta t} \right).$$

The instantaneous rate i.e. the rate at instant t_0 will be the limit of the average rate $\frac{\Delta C}{\Delta t}$ as t tends towards t_0 . The ratio $\frac{\Delta C}{\Delta t}$ can go on to the infinitesimals and give derivative $\frac{dC}{dt}$, i. e. $R = \pm \frac{dC}{dt}$.

In the way the derivative from concentration (C) to time (t) characterizes the instantaneous rate (real rate) of chemical reaction.

Measurement of rate of a chemical reaction. Rate of reaction is always to be determined experimentally and cannot be predicted theoretically.

1. Direct methods.

The concentration of reactants or products is determined depending on time (dependent on). By plotting C against t a graph of the type shown in the figures 5, 6 is obtained. This graphs are called a Rate Curve.

Knowing the Rate Curve for any substance it is easy to calculate the rate of decomposition or formation of the substance by measuring slope as shown in figures 5, 6. The slope of the Rate Curve characterizes the real rate at the given moment, i.e. the tangent α of slope numerically equals the real rate. Mathematically: $\text{tg}\alpha \approx \frac{\Delta C}{\Delta t} \approx \bar{V}$ (average rate). Tangent of α approximately equals the ratio

of ΔC to Δt and equals the average rate, or in differential form: $\text{tg}\alpha = \frac{dC}{dt} = R$. α

is the angle of slope of Rate Curve.

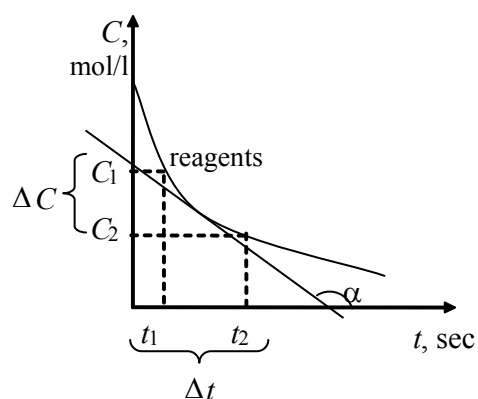
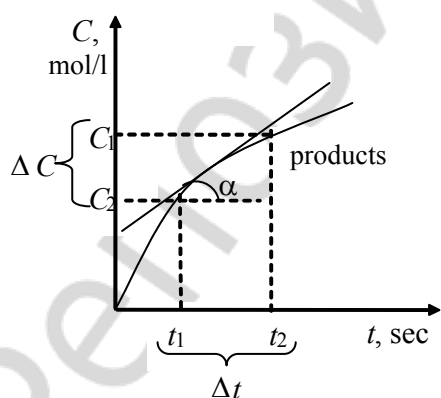


Fig. 5. The concentration increases Fig. 6. The concentration decreases

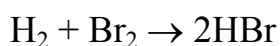
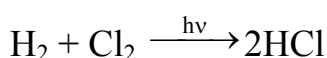
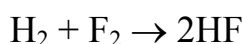
2. Indirect methods.

During a chemical reaction the concentrations of the reactants present change with time, and hence the properties of the reaction mixture are apt to change. The rate of the reaction is determined by measuring a changing property, such as intensity of color, partial pressure of one component, refractive index, pH (negative common logarithm of H^+ concentrations), conductivity et al.

2.3. FACTORS INFLUENCING THE RATE OF A REACTION

Experimentally, the reaction rate is found to be affected by the following factors:

1. *Nature of reactants.*



2. *Effect of temperature.*

3. *Effect of concentration.*

Experiment shows that the rate of a given reaction may be increasing the concentration of one or of all the reactants.

E. g. A very dilute aqueous hydrochloric acid solution reacts with zinc more slowly than a more concentrated solution of the acid. However, the quantitative influence of the concentration and how the reaction rate changes can be found only by experiment.

4. *Effect of pressure (gaseous systems).*

5. *The form of vessel.*

6. *Catalysts.*

The effect of concentration on the rate of chemical reaction. The effect of concentration on the rate of chemical reaction is expressed by basic postulate of chemical kinetics.

The rate of a chemical reaction (instantaneous) at a constant temperature is directly proportional to the product of the concentrations of the reactants to powers is expressed with small numbers.

Thus, for the reaction $mA + nB \rightleftharpoons C + D$ we have $V = k[A]^m[B]^n$, where V is the rate; k is the rate constant; and $[A]$ and $[B]$ are the concentrations of the reactants A and B; m , n are small numbers. The equation reflecting the function connection between the rate of the reaction and concentration of the reactants is called kinetic equation where k is the rate constant:

$$V = \pm \frac{dC}{dt} = k[A]^m[B]^n.$$

Concentrations of solids are assumed to be 1 (constant) and they can be left out of kinetic equation.

Physical sense of k:

k is a such rate of the reaction when concentration of the reactants equal 1 mol/liter or product of this concentrations equal one, i. e. $\frac{dC}{dt} = k$ at $[A] = [B] = 1$ mol/liter.

Sometimes k is called the specific rate.

Chemical sense of k: the rate constant of the chemical reaction is quantitative measure of reaction ability of molecules.

The more k the more rate of the reaction.

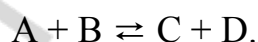
The rate constant doesn't depend on concentration of the reactants but depends on temperature.

Write equation: $V = k[A]^m[B]^n$, where m is the order with respect to reactant A, while n is the order with respect to reactant B. The sum ($m + n$) is called the common (total) order of the reaction.

The order of the reaction is the formal magnitude and depends upon the concentration, the temperature, the catalyst. The order of the reaction can be positive, negative, whole or fractional numbers, nought.

The order of the reaction is determined by experimentally and it is not necessarily related to the equation written for the reaction. The order of the reaction cannot be predicted before.

Consider the balanced reaction between A and B to give C and D:



Assume that the reaction takes place in a container with a constant volume and of a constant temperature.

Take the substance A in excess and its concentration remains constant. Then we study the rate of the reaction to reactant B, changing its concentration.

$[B] \rightarrow V$ then the order of the reaction:

$2[B] \rightarrow 4V$ with respect to reactant B:

$3[B] \rightarrow 9V$ is n , id est $2n = 2$.

If we take the substance B in excess its concentration remains constant. Then we study the rate of the reaction to reactant A, changing its concentration.

$[A] \rightarrow V$ then the order of the reaction:

$2[A] \rightarrow 2V$ with respect to reactant A:

$3[A] \rightarrow 3V$ is m , id est $1m = 1$.

2.4. CLASSIFICATION OF THE REACTIONS IN ORDER

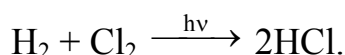
1. Zero order reactions.

Here the rate doesn't depend on the concentration. The rate is constant.

Kinetic equation is $V = -\frac{dC}{dt} = k_0$, where k_0 is the rate constant, the units of k_0 are: $[k_0] = [C][t^{-1}] = [\text{mol} \cdot \text{liter}^{-1} \cdot \text{sec}^{-1}]$, where C is concentration in mol/liter, t is time in seconds.

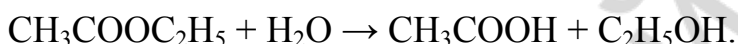
Examples:

1. Photochemical reactions:



The rate of the reaction depends upon quantum's of light.

2. Hydrolysis of an ester:



The ester is taken in excess and its concentration will be constant because expense of the ester is constantly filled in from the ester layer. In this way the concentration of the aqueous layer will remain constant and the rate will not vary, $V = \text{const}$.

3. Decomposition of some compounds on the surface of different substances when the rate of decay doesn't depend on its concentration in volume.

2. First order Reactions.

Here the rate depends on the concentration. Kinetic equation is $V = -\frac{dC}{dt} = k_1 C^1$,

where k_1 is the rate constant. The unit of k_1 is sec^{-1} . $[k_1] = [\text{sec}^{-1}]$. On separating

the variables in equation $-\frac{dC}{dt} = k_1 C$; $-\frac{dC}{C} = k_1 dt$ and integrating, we obtain

$\ln C = -k_1 t + \text{const}_1$. Designating the initial concentration (of $t = 0$) by C_0 , we determine the constant of integration $\text{const}_1 = \ln C_0$, whence $\ln C = -k_1 t + \ln C_0 \Rightarrow$

$\ln C - \ln C_0 = -k_1 t \Rightarrow \ln \frac{C}{C_0} = -k_1 t$; $k_1 = \frac{1}{t} \ln \frac{C_0}{C}$ or in common logarithm $k_1 =$

$\frac{2,303}{t} \lg \frac{C_0}{C}$, where t is time; C_0 is the initial concentration; C is the concentration at t .

Examples:

1. Hydrolysis sucrose: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$.

2. Decomposition of N_2O_5 : $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$.

3. Decay of radioactive elements.

3. Second order reactions.

Kinetic equation is $V = -\frac{dC}{dt} = k_2C^2$ or $V = -\frac{dC}{dt} = k_2C_1C_2$, where k_2 is the rate constant.

The units of k_2 are therefore $\text{sec}^{-1}(\text{concentration}^{-1})$:

$$[k_2] = [\text{sec}^{-1}(\text{concentration}^{-1})] = [\text{liter} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}].$$

It should be noted that the rate constant for a second order reaction depends on the units of concentration used.

On separating the variables in equation $-\frac{dC}{dt} = k_2C^2$; $-\frac{dC}{C^2} = k_2dt$ and integrating, we obtain $\frac{1}{C} = k_2t + \text{const}_2$. The constant of integration may be determined if the concentration C is known for a given time t . For instance if the initial concentration at $t = 0$ is known, then $\text{const}_2 = \frac{1}{C_0}$, whence $\frac{1}{C} - \frac{1}{C_0} =$

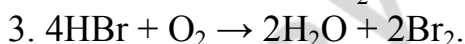
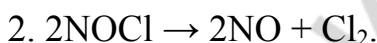
$$k_2t, \text{ or } k_2 = \frac{1}{t} \cdot \frac{C_0 - C}{C_0 \cdot C}.$$

Examples:

1. Most well known second order reactions take place in solution:



The «saponification» of an ester differs from first order aqueous hydrolysis in that the two reactants are present in approximately equal concentration, and both these concentrations affect the rate of reaction.



The units of rates of different order reactions are equal and therefore we can compare them.

The reaction rate constants have different units and we cannot compare them. It may be compared the rate constants of chemical reactions if orders of reactions are equal.

2.5. HALF-LIFE OF A REACTION

The time in which half of the reactant is consumed is called the half-life of a reaction. It is the time in which the concentration of a reactant is reduced to one half of its initial concentration and is written as $t_{1/2}$.

1. Putting $t_{1/2}$ and $C = \frac{C_0}{2}$ into equation for the first order reaction we obtain:

$$k_1 = \frac{2,303}{t} \lg \frac{C_0}{C} = \frac{2,303}{t_{1/2}} \lg \frac{C_0}{1/2 C_0} = \frac{2,303}{t_{1/2}} \lg 2 = \frac{2,303 \cdot 0,3010}{t_{1/2}} \Rightarrow t_{1/2} = \frac{0,693}{k_1}.$$

This equation shows that half-life for a first order reaction is independent of the initial concentration.

2. For a second order reaction the half-life is:

$$k_2 = \frac{1}{t_{1/2}} \cdot \frac{C_0 - 1/2 C_0}{C_0 \cdot 1/2 C_0} = \frac{1}{t_{1/2} \cdot C_0},$$

whence $t_{1/2} = \frac{1}{k_2 C_0}$. This equation shows that half-life for a second order reaction depends on the initial concentration of the reactant.

The more $t_{1/2}$ the more substance is in the organism. This concept is important for toxicology and pharmacology.

For simple reactions powers in kinetic equations are the corresponding stoichiometric coefficients in chemical equation $aA + bB \rightarrow cC + dD$ and $\frac{dC}{dt} = k[A]^a[B]^b$.

This regularity is in accordance with the Law of mass action which is formulated by Guldberg and Waage (1867).

The Law of mass action is a particular case of base postulate of chemical kinetics and is only applied for simple reactions.

The Law of mass action states that for a homogeneous system at constant temperature *the rate of simple reaction is directly proportional to the active masses of reactants in powers are the corresponding stoichiometric coefficients in chemical equation.*

2.6. MOLECULARITY

It is defined as the number of molecules colliding and leading to chemical transformations. Molecularity characterizes the simple reaction, i. e. elementary act of the reaction (individual steps by which a reaction proceeds).

Molecularity has a definite physical sense.

Classification of molecularity:

1. Unimolecular reactions.

To unimolecular reactions belong some molecular decompositions and intramolecular rearrangements. Thus, the gas reaction $I_2 = 2I$ is unimolecular; $CH_3NH_2 \rightarrow HCN + 2H_2$; $CaCO_3 \rightarrow CaO + CO_2$.

For simple unimolecular reactions $V = kC$, where C is the concentration of the initial substance.

2. Bimolecular reactions.

Bimolecular reactions are those resulting from collision of two molecules of the same or different species: $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$; $\text{I}_2 + \text{H}_2 \rightarrow 2\text{HI}$.

$V = kC_1C_2$, where C_1 and C_2 are the concentrations of the reactants.

3. Trimolecular reactions.

To trimolecular reactions belong those which require a collision between three molecules (of the same or different species) in order to take place. In the general case the equation for the rate of simple trimolecular reactions assumes the form $V = kC_1C_2C_3$; an example of such a reaction is $2\text{NO} + \text{H}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$.

Theoretically higher molecularities are possible, but actually the simultaneous collision of three molecules is already highly improbable and trimolecular reactions are encountered rarely. Practically no reactions of a higher molecularity are known.

Molecularity is always a whole number and never greater than three. A molecularity of four is not known because collision of four particles in a single step is not favorable.

When the equation of the reaction indicates that a large number of molecules participate, this usually means that the process must proceed in a more complicated manner, namely through two or more consecutive stages of which each is due to collision between two, or, rarely, three molecules.

For example, $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$. It is a complex reaction.

For simple reactions the order of reaction and molecularity coincides. For complex reactions the order of reaction and molecularity doesn't coincide more off.

Let's take another reaction: $\text{H}_2\text{O}_2 + 2\text{HI} \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$.

The oxidation of iodide ions to iodine by hydrogen peroxide solution is known to proceed via the following mechanism:

First step $\text{H}_2\text{O}_2 + \text{HI} \rightarrow \text{HOI} + \text{H}_2\text{O}$ slow.

Second step $\text{HIO} + \text{HI} \rightarrow \text{I}_2 + \text{H}_2\text{O}$ fast.

General rate of this reaction is determined by the slowest step, which is called the rate controlling or rate determining step.

The *seeming molecularity* of this reaction is three. This reaction is complex; the order of this reaction is two. It is known, if molecularity and the order don't coincide, it means:

- 1) the reaction is complex;
- 2) the rate of this reaction is limited by rate determining step.

2.7. THE EFFECT OF TEMPERATURE ON THE RATE OF CHEMICAL REACTION

Besides the concentrations of the reactants, the reaction rate must be influenced by the temperature, since raising the temperature increases the velocity of motion of the molecules, thus increasing the number of collisions. This depend-

ence between the temperature and the reaction rate was first analyzed by Vant-Hoff (1887).

Vant Hoff's Rule: *each 10-degree rise in temperature approximately will speed up the reaction by 2–4 times.*

At temperature T the reaction rate is V_T at temperature $T + 10$ the reaction rate is V_{T+10} then $V_{T+10}/V_T = \gamma$, where γ is *Vant Hoff's coefficient*.

From that equation we have: $V_{T+10} = V_T \cdot \gamma$ or in general $V_T = V_0 \gamma^{\Delta T/10}$.

The number characterizing the acceleration of a reaction due to raising the temperature 10°C is often called the temperature coefficient of the reaction or Vant Hoff's coefficient. For most reactions the values of these coefficients under ordinary conditions lie between 2 and 4. As the temperature is raised, the coefficients decrease and gradually approach unity.

The γ shows how many times does the reaction rate increase for a rise in temperature of 10°C . But this dependence is very rough.

2.8. COLLISION THEORY

The collision theory gives more exact dependence (function) between temperature and the rate of reaction.

This theory is connected with Arrhenius (1889).

The rate of homogeneous reactions depends on a number of collisions of the reacting particles per unit time. The number of collisions, in turn, is directly proportional to the concentration of the reactants.

The collision theory is built on a number of assumptions:

1. A chemical reaction takes place when collisions take place between the reacting particles: atoms, molecules or ions.
2. No each collision between reactants is effective; effective in the sense that a reaction occurs.

According to the collision theory that only those collisions which involve more than a certain amount of energy, result in the formation of products. Obviously, not all collisions between reactants can lead to a reaction (fig. 7).

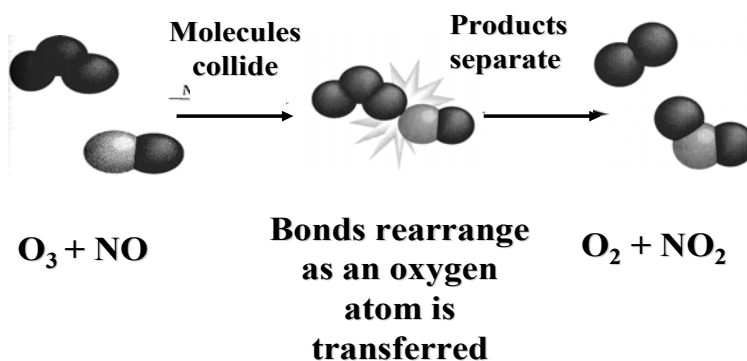


Fig. 7. The reaction between ozone and NO is believed to occur by a mechanism that consists of the single bimolecular step shown here in a molecular view

Energetic diagram (fig. 8) shows a rate of chemical reaction (elementary step of the reaction).

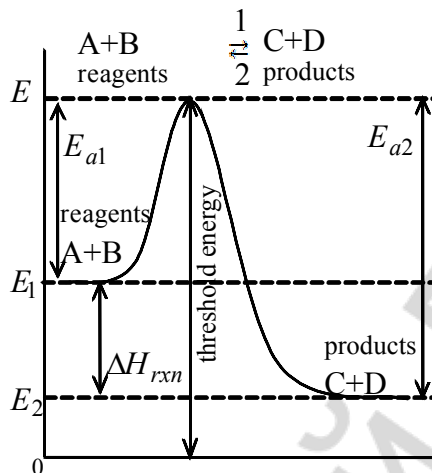


Fig. 8. Energetic diagram

E — the minimum energy which the reactants or products must have before they can react by collision. It is called *threshold energy (energy barrier)*.

E_1 — the average energy which the reactants have before they can react in the forward direction.

E_2 — the average energy which the products have before they can react in the reverse direction.

E_a — the minimum energy, which needed to add to average energy of molecules to be collisions effective, is called the *activation energy*. It is a part of threshold energy. If the activation energy is high the rate of the reaction is low. Conversely, a low activation energy means a high reaction rate.

E_{a1} — the activation energy of forward reaction (1).

E_{a2} — the activation energy of reverse reaction (2). $E_{a1} < E_{a2}$.

ΔH_{rxn} — is the heat effect of a reaction. According to the graph of fig. 6, ΔH of forward reaction (1) is negative ($\Delta H < 0$). In other words this reaction is exothermic ($E_1 > E_2$). ΔH of reverse reaction (2) is positive ($\Delta H > 0$), i. e. an endothermic reaction ($E_2 < E_1$).

Reaction coordinate is a function of distance between atoms.

The term «reaction coordinate» refers to the relative distance between particles involved in the reaction. An average kinetic energy doesn't enough for overcoming of threshold energy.

Normally, only a small fraction of the reacting molecules have enough kinetic energy to exceed the activation energy. The higher the temperature the

greater the kinetic energy of reacting molecules and the larger is a fraction of active molecules in a mixture. Thus increase in temperature accelerates most chemical reactions.

According with Arrhenius the fraction of active collisions from total numbers of collisions is denoted as α and equals $\alpha = e^{-E_a/RT} = Z/Z_0$, where e is the base of natural logarithm; Z_0 is the total number of collisions; Z is the number of active collisions; E_a is the energy of activation [$\text{J}\cdot\text{mol}^{-1}$]; R is the molar gas constant equal to $8,314 \text{ J/mol K}$; T is absolute temperature.

From expression Z (the number of active collisions) can be obtained $Z = Z_0 e^{-E_a/RT}$, where $\alpha = e^{-E_a/RT}$.

If a large-sized molecules react (proteins) it should be taken into account the steric factor P . It is known that collisions even between active molecules do not always result in a reaction. The molecules must have a definite orientation. The proteins have active groups and macromolecules of proteins must have a definite (proper) to collide their active groups.

The steric factor P takes into account a definite orientation or a favorable spatial collision. The factor P is proportional to the ratio of the number of ways of the mutual orientation of the molecules favorable for proceeding of a reaction to the total number of possible ways of orientation: the greater this ratio the more rapidly will a reaction proceed. The steric factor P is usually much smaller than unity; it has an especially great influence on the rate of reactions proceeding with the participation of complex molecules (for example proteins), when the total number of various possible orientations is very great, and the number of favorable orientations are very limited:

$$Z = Z_0 \cdot P \cdot e^{-E_a/RT}$$

Arrhenius suggested the equation: $k = A \cdot \alpha$, $k = A \cdot e^{-E_a/RT}$, where k is rate constant; A is the total numbers of double collisions per second in 1 cm^3 of reaction system, A is a constant known as Arrhenius or frequency factor or A is a constant preexponential factor independent of the temperature and concentration; $\alpha = e^{-E_a/RT}$ is exponential factor, it is called Boltzmann factor and gives the fraction of collisions with energies greater then or equal to activation energy.

Two important conclusions can be drawn from the Arrhenius equation:

- a) at constant temperature greater the activation energy, slower is the reaction;
- b) as temperature increases, rate of reaction also increases.

As the rate constant k is a product of two multipliers A and $e^{-E_a/RT}$ the k is a measure of the number of activated molecules per unit volume or *it has a sense of the number of active collisions*.

The temperature generally affects the exponential factor to a greater extent than the preexponential one. It is explained that the elevation of the reaction rate with increasing of temperature only depends on increasing the fraction of active

collisions from total number of collisions. The higher temperature T , the less E_a/RT and the higher $A \cdot 1/e^{E_a/RT}$.

The following conclusions can be drawn from equation $k = A \cdot e^{E_a/RT}$:

1. Even a slight decrease in the activation energy increases the rate of reaction quite substantially.
2. The temperature generally affects the reaction rate to a greater extent when the activation energy of a reaction is higher.
3. Reactions with high activation energies proceed at low rates when the temperature is low, but the influence of the temperature on the rate of such reactions is usually more appreciable (the temperature coefficient γ is larger).

The Arrhenius equation shows that the rate constant of a reaction grows with a decreasing activation energy.

Calculation of Activation energies from the Arrhenius equation. Let us see how equation $k = A \cdot e^{E_a/RT}$ is applied for determining the activation energy. This equation is considerably simplified if the logarithm of the rate constant is taken as a function of the reciprocal absolute temperature:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad \text{or} \quad \lg k = \lg A - \frac{E_a}{2,3 R} \cdot \frac{1}{T}$$

Calculate the rate constant for different temperatures.

The experimental data $\frac{1}{T}$ and $\lg k$ usually give a straight line (fig. 9).

Hence the logarithm of the rate constant of a reaction is practically linearly related to the reciprocal temperature ($1/T$).

$$\operatorname{tg} \alpha = -\frac{E_a}{2,3 R}; \quad E_a = -2,3 R \operatorname{tg} \alpha \quad \text{at } 1/T = 0; \quad \lg k = \lg A$$

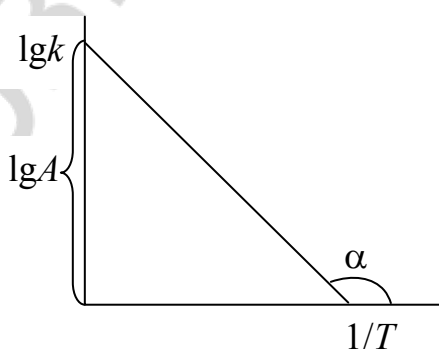


Fig. 9. The relationship between $\lg k$ and $1/T$

The collision theory gave an idea about active collisions and activation energy, proposed calculations for many reactions, but this theory is not free from limitations.

First of all the collision theory didn't explain the mechanism of the collision.

The collision theory doesn't explain reaction's mechanism, influence of a solvent and other factors on the rate of a reaction.

The collision theory only states that reaction can proceed after active collision from total number of collisions.

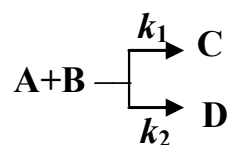
2.9. CONCEPT ABOUT KINETICS OF COMPLEX REACTIONS

Most reactions are complex.

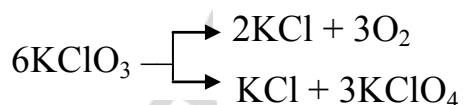
The kinetics of complex reactions consisting of simple reactions, connected in one way or another, depends upon the nature of their interrelation and on the ratio of their reaction rates. Typical forms of such interrelations are: *simultaneous, consecutive, conjugate, reversible* reactions.

The theory of these reactions is based on the principle that when several reactions occur simultaneously, each takes place independently and each obeys the kinetic equations of the simple reactions.

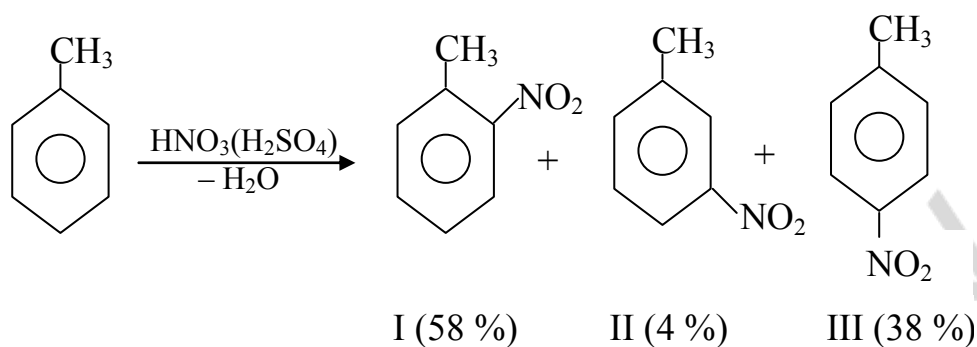
1. *Simultaneous reactions* are those of the type.



In such reactions the initial substance or substances can react simultaneously in different directions. An example of parallel reactions is the decomposition of potassium chlorate, which at moderate temperatures may occur in two parallel directions.



The other reaction is nitration of toluene. This reaction is the first stage for manufacture of novocain.



Toluene reacts with a mixture of concentrated nitric and sulphuric acids. The first product is a mixture of ortho- and para-nitro toluene (I, III). The latter product is very important for manufacture of anesthetic.

Simultaneous reactions are most frequently encountered in organic chemistry. For instance in the nitration of toluene with nitric acid in the presence of concentrated sulphuric acid the nitro group may occupy either the meta-, ortho- or the para-position (II, I, III).

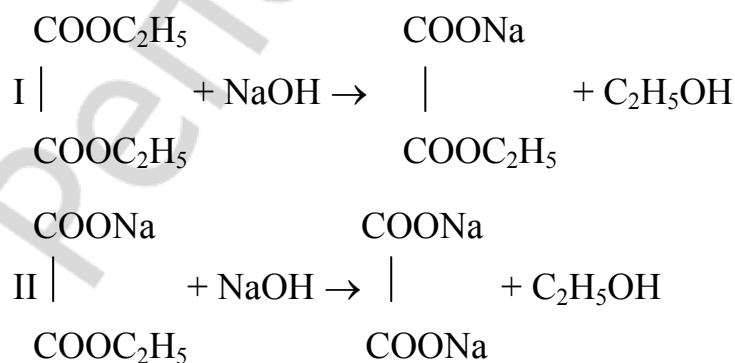
If the reactions differ considerably in rate the reaction with the highest rate is usually called the *main reaction* and the others *side reactions*. However, if the difference is not very great, the main reaction is considered to be that which leads to the desired product, although its rate may be lower.

2. *Consecutive reactions* are those of the type $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$, where B is an intermediate in the formation of C, and k_1 and k_2 are the rate constants of the two stages of the reaction.

Scheme is that for the simplest type of consecutive reactions. It occurs in two stages, each of which is a simple unimolecular reaction. In the general case the number of stages may be more than two, and the stages may be not unimolecular.

Consecutive reactions are very wide spread. Among them is hydrolysis of dicarboxylic acid esters of glycol esters or of diacyl chlorides. The kinetics of consecutive radioactive transformations may be considered as a particular case of the kinetics of a series of consecutive first order reactions.

A simple illustration of consecutive reactions may serve the saponification of diethyl oxalate by sodium hydroxide, which proceeds in two consecutive stages:



Calculation of the rates of consecutive reactions in the general form is very complicated. We shall only point out that *if one of the stages proceeds at a considerably lower rate than all others the over-all rate of the reaction will be determined by the rate of this stage.*

3. *Conjugated reactions* are defined as reactions of the type: $\mathbf{A} + \mathbf{B} \rightarrow \mathbf{M(a)} \rightleftharpoons \mathbf{A} + \mathbf{C} \rightarrow \mathbf{N(b)}$, of which one, for example (a), takes place only together with the other, i. e. induced by the other (b). In such cases the substance C is an initiator for the first reaction. An example of such reactions are: hydrolysis of ATP (b) and the synthesis of proteins and peptides (a) in the living organism.

The free energy released by hydrolysis of ATP is necessary for the synthesis of proteins and peptides in living organism.

□ $G < 0$ hydrolysis of ATP — exergonic reaction;

□ $G > 0$ formation of peptide bond — endergonic reaction.

4. *Reversible reactions.*

Reversible reactions proceed under given conditions both in the forward and reverse directions simultaneously $\mathbf{A} + \mathbf{B} \xrightleftharpoons[k_2]{k_1} \mathbf{C} + \mathbf{D}$, where k_1 is the rate constant of forward reaction; k_2 is the rate constant of the reverse reaction.

The state of a system when the rates of the forward and reverse reactions are equal: $V_1 = V_2$; $k_1 C(A)C(B) = k_2 C(C)C(D)$ is called a state of chemical equilibrium.

It is readily seen that on reaching a state of chemical equilibrium the concentration of each component of the reaction will remain constant.

Chemical equilibrium is dynamic, i. e. its setting in does not mean that the reaction has stopped.

Chemical equilibrium is characterized quantitatively by a quantity known as the *chemical equilibrium constant*.

The chemical equilibrium constant is the ratio of the rate constant of the forward and reverse reactions: $\frac{k_1}{k_2} = \frac{C(C)C(D)}{C(A)C(B)} = K_c$, where K_c is the chemical equilibrium constant expressed in terms of the equilibrium concentrations of the reactants and products.

The equilibrium constant determines the extent of a process by the instant of reaching the equilibrium state. The larger this quantity, the greater is degree of conversion of the reactants into the products.

The equilibrium constant depends on nature of the reactants and the temperature.

5. *Chain reactions.* Up to now, we dealt with chemical reactions proceeding comparatively simply. There is a broad group of reactions, however, that proceed in a more complicated way. Here, the formation of macroscopic amounts of the product is the result of a chain of elementary events of interaction. Such reactions are known as chain ones.

Chain reactions proceed with the participation of *active centers* — atoms, ions or radicals (fragments of molecules) having unpaired electrons and displaying, as a result, a very high reactivity.

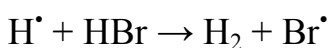
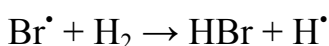
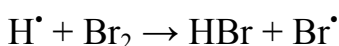
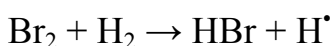
The active centers are the initiators of chains of consecutive transformations of substances.

A simple example of a chain reaction is the reaction between gaseous bromine and hydrogen expressed by the ordinary equation: $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$.

The chain reactions consist of some steps.

The first step — the initiation of the chain. Bromine molecules dissociate and this process can be expressed by the equation: $\text{Br}_2 \rightarrow \text{Br}^\cdot + \text{Br}^\cdot$.

The second step the propagation (and branching) of the chain.



The third step the breaking of the chain (or the termination of the chain): $\text{Br}^\cdot + \text{Br}^\cdot \rightarrow \text{Br}_2$.

The same mechanism can prevail for the reaction between hydrogen and chlorine, oxidation of hydrocarbons, burning, explosions, polymerization reactions.

This is why the theory of chain reactions is the scientific foundation of a number of important branches of engineering and chemical technology.

Radical reactions proceed in vivo under the affect of different free radicals OH^\cdot , HOO^\cdot , ROO^\cdot , O_2^\cdot and some other. Scientists came to the belief that accumulation of free radicals in intracellular fluids is one reason for aging.

Rate of radical reactions can be increased greatly under the influence of radiation. Even small dozes of radiation can accelerate generation of free radicals. Free radicals cause the destruction of cell membranes, suppress immune system of people, and cause different diseases. Radical reactions can be retarded by antioxidant substances: vitamins A, E, C and Selenium compounds.

Chains reactions also include nuclear chain reactions proceeding in atomic reactor or upon the explosion of an atomic bomb.

6. *Photochemical Reactions*. Photochemical reactions are reactions that take place under the influence of light (visible light, ultra-violet) or more seldom, infrared rays. Such reactions can occur in gases, liquids and solids. Molecules of reacting substances are excited by absorbing quanta of light under the photochemical effect of light, i.e. become reactive or decompose into ions and free radicals.

The photochemical reactions are characterized by quantum output (γ):

$$\gamma = \frac{\text{(an amount) a number of molecules of products}}{\text{an amount of absorbed quanta}}$$

The most important photochemical reaction is undoubtedly the photosynthesis taking place in plants.

This process is endothermal, taking place with increase in the Gibbs free energy ($\Delta G > 0$). It cannot occur in the absence of light. $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ under the action of solar light chlorophyll converts the CO_2 of the air into complex molecules of organic substances. In this case the light energy transforms into the energy of chemical bonds.

Photochemical reactions are highly varied. Among them are the photosynthesis of carbo-hydrates carried out by plants under the action of the sun's rays, the photographic processes, luminescence phenomena, decolourization of dyes, etc. Photochemical reactions also greatly differ chemically. Under the action of light synthesis (phosgene, hydrogen chloride), decomposition (hydrogen peroxide), oxidation, etc. may take place.

The photochemical reactions are applied in medicine — the oxidation of bilirubin at jaundice of premature babies, the photochemical processes underlie mechanism of vision.

2.10. CATALYSIS AND CATALYSTS

Substances that are not consumed in a reaction, but affect its rate, are called *catalysts*. The phenomenon of the change in the rate of a reaction under the action of such substances is known as *catalysis*. Reactions proceeding under the action of catalysts are called *catalytic*.

The action of a catalyst in the majority of cases is explained by the fact that it lowers or increases the activation energy of a reaction. The catalyst is called *negative*, when it increases the activation energy; the catalyst is called *positive*, when it lowers the activation energy (tab. 3).

In the presence of a catalyst a reaction proceed through other intermediate stages than without it, and these stages are more accessible from the energy viewpoint.

Table 3

Activation energy of catalytical and noncatalytical chemical reactions

Reactions	E_a , kJ/mol		Catalyst
	without a catalyst	with a catalyst	
$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	180	40	Pt
		8	Cu
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	750	55	I_2

The catalyst doesn't effect on the total number of collisions in practice but has effect on the activation energy.

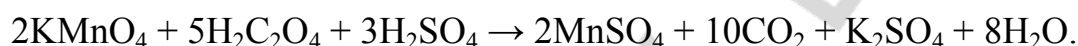
Catalysts have no effect on chemical equilibrium since they equally accelerate or lower the direct or reverse reactions. Catalysts only accelerate or lower the establishment of equilibrium in the system. *Catalysts have no effect on the equilibrium constant (K_c)*.

Depending on the physical state of the catalyst and reacting substances, *homogeneous and heterogeneous catalyses* are distinguished.

Examples of a *homogeneous catalysis* are: a) the oxidation of CO (in the gaseous state in the presence of water vapor) by oxygen $2\text{CO} + \text{O}_2 \xrightarrow{\text{H}_2\text{O}} 2\text{CO}_2$; b) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{NO}} 2\text{SO}_3$; c) the action of various enzymes in biological processes.

Examples of a *heterogeneous catalysis* are: a) the synthesis of ammonia over an iron catalyst $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$; b) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$.

Autocatalysis is a process when a product of a reaction acts as a catalyst. An example of autocatalytic reaction is:



Catalyst: Mn^{2+}

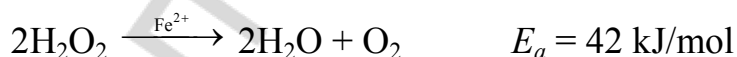
Catalysts are employed very broadly in the chemical industry.

2.11. ENZYMES

Catalysis plays a very great role in biological systems. Most chemical reactions proceeding in the digestive system, in the blood and cells of animals and man are catalytic reactions. The catalysts, which in this case are known as enzymes, are simple or complex proteins. Thus, saliva contains enzyme ptyalin, which catalyzes the transformation of starch into sugar. An enzyme in the stomach, pepsin, catalyzes the decomposition of proteins. The human organism contains about 30 000 various enzymes; each of them is an effective catalyst of the corresponding reaction.

Distinctive traits (properties) of enzymes:

1. *High catalytic activity. The high enzymatic activity.*



In the presence of the enzyme catalase (found, in particular, in the erythrocytes), this reaction can be effected at a much greater rate, yielding the same end products of hydrogen peroxide breakdown. Hydrolysis urea: by acid $E_a = 103 \text{ kJ/mol}$; by enzyme urease $E_a = 28 \text{ kJ/mol}$.

2. *Highly specific to substrate. High enzymatic specificity to substrate. High selectivity (one enzyme activates only one or two biochemical reactions).*

Enzymes exhibit specificity of action. In many instances, this property is the essential characteristic.

For example, pepsin splits the proteins of animal and vegetal origin but doesn't split carbohydrates or fats. Amylase splits starch, but doesn't split a saccharose although they are built of glucose residues.

3. *Enzymes act under mild conditions: body temperature 25–40 °C; normal pressure.*

4. *Enzymatic reactions proceed without side reactions (side effects).*

5. *The rate of any enzymatic reaction depends on the enzyme and substrate concentrations.* The greater the enzyme concentration the greater the rate of enzymatic reaction. i. e. the reaction rate is proportional to the concentration of the enzyme present. The enzymatic reaction rate is proportional to the substrate concentration too.

At low substrate concentrations the reaction rate is directly proportional to the substrate concentration $V = k_1C$ and obeys the first order kinetics. At high substrate concentrations, the reaction rate attains a maximum and becomes constant, independent of the substrate concentration $[S]$. In this instance, the reaction obeys the zero order kinetics: $V = V_{max} = k_0$ (as the enzyme becomes fully saturated with substrate) and is wholly determined by the concentration of enzyme (fig. 10).

a — first order reaction (of $[S] > K_m$, the reaction rate is proportional to the substrate concentration).

b — mixed order reaction.

c — zero order reaction ($V = V_{max}$, and the reaction rate is independent of the substrate concentration).

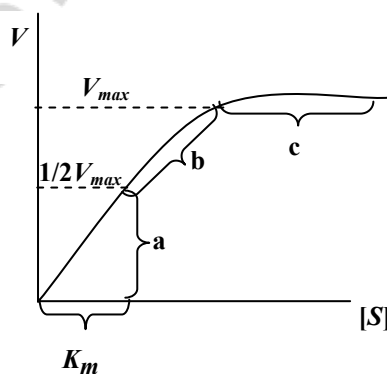


Fig. 10. Theoretical relationship between the enzymatic reaction rate (V) and the substrate concentration $[S]$ at a constant concentration of the enzyme

In their studies on enzyme saturation effect, L. Michaelis and M. Menten have developed a general theory of enzymatic kinetics.

They proposed the following chemical reaction $E + S \xrightleftharpoons[k_2]{k_1} [ES] \xrightarrow{k_3} E + P$, i. e. the enzyme E reacts with the substrate S to form an intermediate complex $[ES]$ which further dissociates into a free enzyme and the reaction product P .

V_{max} is the maximum rate of reaction for complete saturation of enzyme with substrate. The substrate concentration of which enzymatic reaction rate V is half the maximum rate i. e. $V = 1/2V_{max}$ is called by the *Michaelis constant* K_m .

K_m characterizes stability of enzyme-substrate complexes. The lower is K_m , the higher stability of a complex.

Factors affecting enzymatic reactions are:

1. *Temperature.*
2. *Acidity and basicity of medium.*
3. *Enzyme inhibitors.*

Enzymes work best at an optimum pH value, which varies from enzyme to enzyme. Most enzymes that are active within cells have a pH optimum fairly close to the range of pH within which cells normally function (fig. 11). For example, the pH optima of two digestive enzymes, pepsin and trypsin, occur at about pH 2 and pH 8 respectively.

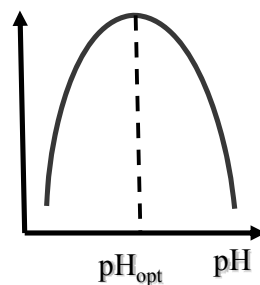


Fig. 11. The effect of acidity on enzymes' activity

We will consider two forms of inhibition (there are others):

1. Competitive inhibition (fig. 12).
2. Noncompetitive inhibition (fig. 13).

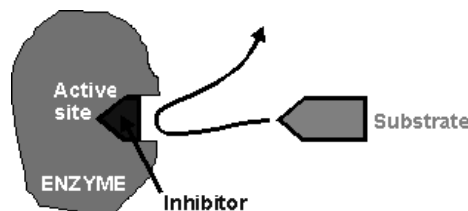


Fig. 12. Competitive inhibitors generally structurally similar to substrate and bind to active site — keeping out the substrate

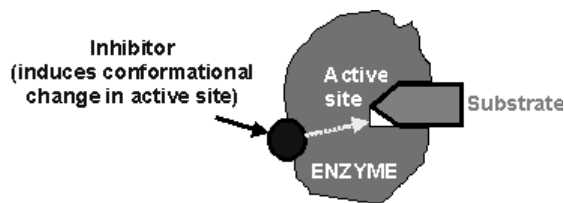


Fig. 13. Noncompetitive inhibitors bind away from the catalytic site but cause a conformational change to be transmitted to the active site

Practical application of Enzymes. Enzymes find wide application in many branches of food industry such as bread baking, brewing, wine production, tea production, tanning and fur dressing, cheese industry, cookery (in preparatory treatment of meat), etc. In recent years, enzymes are being increasingly used in chemical industry for carrying out chemical reactions such as oxidation, reduction deamination, decarborylation, dehydration, and condensation as well as for resolving and separating α -amino acid isomers for use in industry, agriculture and medicine.

At present, a new branch of knowledge, the industrial enzymology, is emerging, laying down the basis for further advance in biotechnology. An enzyme covalently bound («grafted») to an organic or inorganic carrier is called the *immobilized enzyme*. The technique of enzyme immobilization opens a route to the solution of key problems in enzymology including the provision for high specificity of enzymes and improvement to their stability, the ease of utilization and the feasibility of repeated use and application to flow processes of chemical synthesis. The industrial applications of such enzyme based techniques have become known as the *engineering enzymology*.

The immobilized β -galactosidase is used as means to decrease the milk sugar content in milk, which helps in dealing with the problem of lactose intolerance. Moreover, the milk thus processed can be stored in a frozen state for a longer period of time without thickening.

Cellulose can be converted to glucose through the use of immobilized celluloses. In principle, the engineering enzymology can provide a means for obtaining alimentary products, in particular, carbohydrates, from liquid fuel (petrol) by splitting it to glyceraldehyde and then proceeding, with the participation of enzymes, to the synthesis of glucose and starch.

The progress in enzymology is increasingly gaining ground in medicine, especially, in many aspects of prophylaxis, diagnosis, and therapy. A notable progress has been recorded in a novel branch of enzymology — *medical enzymology*.

Medical enzymology is now advancing in three major directions:

1. *Enzymopathology*, which is concerned with the investigation of enzymatic activity in norm and pathology. As has been ascertained many hereditary disturbances of metabolism originate in the defect of a definite enzyme. For ex-

ample a hereditary disease, phenylketonuria, manifested by neurologic disturbances, is the lost capacity of the liver cells to synthesize the enzyme that catalyzes the conversion of phenylalanine to tyrosine.

2. The second trend is *enzymodiagnosics* which is concerned with both the use of enzymes as selective reagents for identification and quantization of normal and abnormal chemical substances in blood plasma, urine, gastric juice (for example, for enzymatic urinary analyses of glucose, proteins and other substances, not detectable when they are in norm in urine, and the qualitative and quantitative analyses of the enzymes themselves in biological fluids under pathology. It should be remembered, however, that out of the whole wealth of enzymes (over 2000) that have been discovered in nature (and, partly, in the human organism), the diagnostic enzymology makes use of a rather limited set of enzymes and besides, for the diagnosis of a still smaller number of diseases (hepatitides, myocardial infarction, organic damage of the liver and others). Thus, the level of lipase, amylase, trypsin and chymotrypsin becomes drastically elevated in diabetes, malignancy of the pancreas, hepatic diseases, and other states.

3. The third trend in medical enzymology — *enzymotherapy*, i. e. the use of enzymes and regulators of enzymatic activity.

In the clinic, pepsin, trypsin and mixtures there of are used to treat the gastrointestinal tract. RNase, DNase, hyaluronidase, collagenases, elastases taken separately or in combination with proteins, are used for the treatment of wounds, inflammatory foci, skin burns, and for the removal of edemas, hematomas, keloid cicatrices (in pulmonary tuberculosis). Enzymes are also applied in the treatment of cardiovascular diseases and for the dissolution of blood clots, for these purpose the immobilized streptokinase has been obtained.

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термодинамики и кинетики**

**Elements of Chemical
Thermodynamics and Kinetics**

Учебно-методическое пособие
На английском языке

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