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Bioenergetics, one of the most important fields of biophysics, contains many assumptions that do not provide complete clarity regarding the actual phenomena of energy production in living organisms. This publication examines energy exchange processes in living organisms based on a number of hypotheses from the fields of physical and colloid chemistry, which are based on approaches to substantiating self-organization phenomena in catalytic reactions and thin aqueous films. This is a new direction toward creating a holistic concept of bioenergetics that links processes occurring at various levels of biological organization.

Key words: bioenergetics, thermodynamics, physical chemistry, phenomenon self-organization processes, catalytic reactions, thin water films.

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Abstract

Bioenergetics is one of the most important areas of biophysics, contains many provisions that do not give full clarity about the real phenomena of energy production in living organisms. This publication examines the processes of energy exchange in living organisms based on a number of hypotheses from the field of physical and colloid chemistry, which are based on approaches to substantiating the phenomena of self-organization in catalytic reactions and in thin aqueous films. This is a new direction on the way to creating an integral concept of bioenergy, linking the processes taking place at different levels of organization of bioobjects.

Keywords: bioenergetics, thermodynamics, physical chemistry, self-organization phenomena, catalytic reaction, thin water film

PREFACE

The term "bioenergetics" was first used by Nobel laureate A. Szent-Györgyi in a monograph published in 1957 and soon translated into Russian [1]. A significant milestone in the birth of bioenergetics was the publication in 1961 of Peter Mitchell's chemiosmotic theory [2], which explained the mechanism of respiratory and photosynthetic phosphorylation. The further entry of bioenergetics into biophysical science and its consolidation as one of the most important sections is associated with the name of V.P. Skulachev [3], who in 1968 proposed this name for a new scientific direction at a conference on oxidative phosphorylation in Polignano a Mare (Italy).

The term "bioenergetics" has been adopted not only by the official scientific community, but also by healers and psychics of varying levels and professional skill. Consequently, "bioenergetics" has come to be divided into "scientific" and "parascientific" branches. To be fair, it should be noted that there are a vast number of controversial and unclear issues in both fields. Therefore, a more rational and productive approach would be creative interaction between the aforementioned branches of bioenergetics, naturally within mutually acceptable areas.

Preface

This brief, collective monograph examines the problems of bioenergetics, drawing on classical chemical thermodynamics and chemical kinetics, focusing on the unresolved issues of this science. Specifically, it examines energy exchange processes in living organisms, drawing on a number of hypotheses in physical and colloid chemistry, which are based on approaches to substantiating self-organization phenomena in catalytic reactions and thin aqueous films.

The first edition of this monograph, published in 1994 [4], with a print run of 2,000 copies, has become a bibliographic rarity over the past quarter century. During that turbulent period in Russian history in the 1990s, the authors received no answers from the scientific community to the controversial questions they posed regarding bioenergetics. In 2018, an electronic copy of the book was posted in the National Electronic Library (<https://elibrary.ru>). To present the material with some additions [5] not included in the first edition, the authors decided to revise and slightly expand the material in the second edition. The authors are sincerely grateful to their colleagues at the Laboratory of Medical and Biological Technologies of the Federal State Unitary Enterprise Research Institute of Industrial and Marine Medicine of the Federal Medical and Biological Agency of Russia, Lyudmila Nikolaevna Milinevskaya and Larisa Vladimirovna Ilyina, for their assistance in preparing the monograph for publication. The authors express their deep gratitude to Evgenia Leonidovna Matyushenkova, a talented physician and researcher at the former Laboratory of Biotechnical Systems of the St. Petersburg Medical Academy of Postgraduate Education (now the I.I. Mechnikov North-Western State Medical University), thanks to whose efforts the first edition was prepared for publication.

books.

Authors

“Life does not contradict thermodynamics,
but the thermodynamic description is not
enough for understanding and explanation
biological phenomena...»

A. S. Davydov, 1986 [6]

INTRODUCTION

The basis of biochemistry, with its enormous diversity of research, laws, and methods offered by this science, is classical physical chemistry.

Classical chemical thermodynamics and the closely related classical chemical kinetics are used as the theoretical basis for most biochemical research. These studies assume the absolute validity and general applicability of the laws of classical physical chemistry to all chemical processes. However, they ignore the crucial fact that within physical chemistry itself, many of its laws are considered far from obvious, but rather debatable, and lacking clearly defined applicability boundaries. This applies, among other things, to such fundamental laws as the second law of thermodynamics for chemical processes and the thesis that a catalyst cannot influence the energetics (ΔG) of a chemical reaction by disturbing the reaction mixture from chemical equilibrium. There is also insufficient clarity regarding the energetics of electron clouds.

Introduction

in a steady state, while understanding that electron clouds are only a visual model reflecting the wave function describing the motion of an electron in an atom. It also cannot be unequivocally stated that all forces acting on electron clouds are potential forces for which the work does not depend on the shape of the path. On the contrary, it is quite possible that for a number of forces acting on electron clouds, the work depends on the shape of the path, and therefore, the energetic effect of a chemical reaction also depends on intermediate stages (including the stages of development of transition complexes of the substrate with the catalyst). This, in turn, means that the fundamental law of classical chemical thermodynamics—Hess's law—may have a very narrow applicability. Closely related to Hess's law is the thesis that catalysts cannot disturb the reaction mixture from chemical equilibrium, and therefore this classical

the thesis is not obvious.

Having been tested on a number of very simple chemical reactions, the laws of classical physical chemistry apparently cannot be mechanically transferred to all physical and chemical processes, much less to such a complex variety of them as is characteristic of living organisms. Considering that at present, the majority of biochemical processes are not yet reproducible "in vitro" under the model conditions required for a precise verification of the laws of classical physical chemistry,

chemistry, doubts about the legality of applying these laws for examining biochemical processes become even more obvious. Created decades, or rather centuries, ago, the classical theory of chemical thermodynamics is macroscopic. Classical chemical kinetics

in their quantitative models, they are also mainly macro-

typical. The mechanisms of catalyst action are unclear, and their effect on reaction rates is estimated as a simple decrease in E-activation, taken into account in calculations by the Arrhenius equation (this equation does not include parameters that determine cause-and-effect relationships in the behavior of individual molecules). It is possible that such macroscopic approaches are acceptable for assessing the behavior of simple molecules, but biochemical systems involve complex molecules (primarily enzyme proteins), and in this regard, the question of the applicability of the existing theoretical basis to the consideration of biochemical processes clearly arises.

Physical chemists tend to view biochemical processes as a source of new information that can be used to expand and modify the system of laws governing the energetics and kinetics of physicochemical processes, which is entirely justified. However, biochemical research is dominated by the mechanical transfer of all the laws of classical chemical thermodynamics and chemical kinetics to living organisms, and this primarily influences the concepts of bioenergetics.

Formally, classical bioenergetics associates the decrease in entropy ($\Delta S < 0$) in a number of the most important organizing (creative) biological processes with phenomena for which the law of chemical thermodynamics is valid:

$$\Delta G = \Delta H - T\Delta S.$$

Processes with $\Delta G < 0$ occur spontaneously; they can be coupled with processes having $\Delta G > 0$. In this case, the modulus $|\Delta G|$ in energy-generating chemical reactions is greater than $|\Delta G|$ in the creative bio-

Introduction

logical processes accompanied by a decrease in entropy ($\dot{y}S < 0$). Specifically, in most biological phenomena, various creative processes accompanied by an enormous increase in the complexity of the organization are explained by the fact that the heat of the reaction $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ is very significant and its $\dot{y}H = -2816$ [kJ/mol] [7, 8]. On the other hand, *the $\dot{y}H$* of the main energy-generating chemical reactions, their $\dot{y}S$ and $\dot{y}G$ are known, but the values of the decrease in entropy ($\dot{y}S < 0$) in creative biological processes are unknown ($\dot{y}S = k \ln W$

(for them, they were not directly determined). Consequently, estimates of $\dot{y}G$ in creative biological processes are also unreliable. In this regard, the classical thesis that, as a rule, the growth of the organization of biological objects is directly caused by heat release in the reaction of glucose oxidation,

highly questionable.

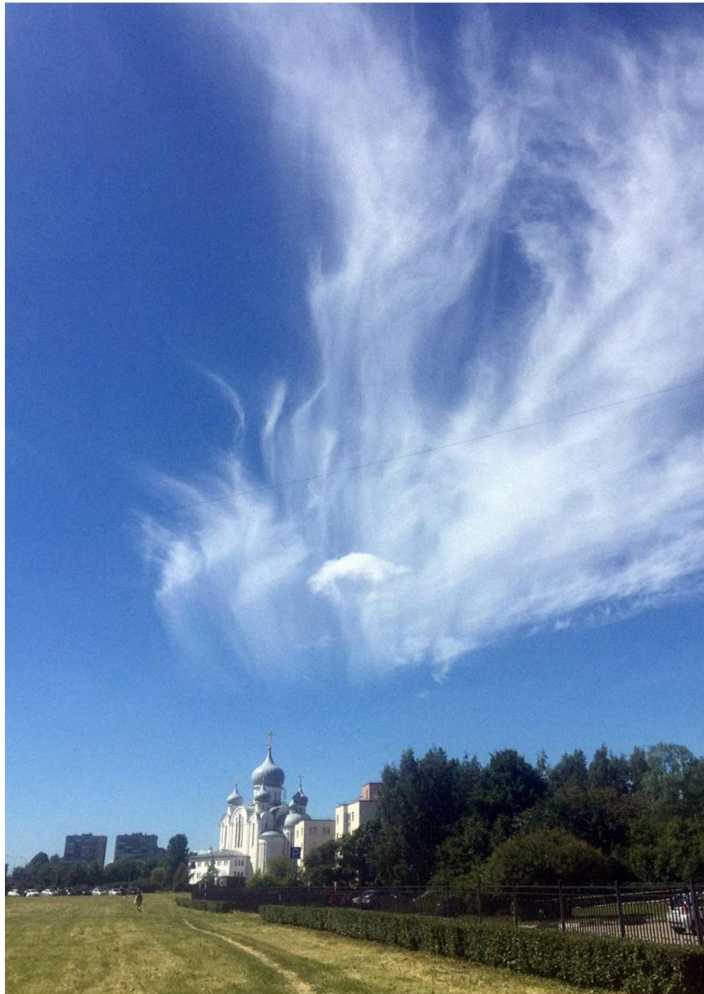
What is the result of applying the existing theoretical framework to bioenergetics? It consists of the emergence of a highly simplified model of energy production, distribution, transformation, and utilization in living organisms, in which the concept of self-organization and self-governance in biological objects is essentially ignored. Furthermore, the systems directly supporting the coupling of energy exchange processes have not been specifically identified, the body's responses to the effects of certain forms of energy (mechanical waves, electromagnetic radiation, constant magnetic fields, thermal energy, microquantities of chemical energy carriers) are not considered, and the pathways for generating certain forms of bioenergy are unknown.

Even macroscopic tests of energy balance have been carried out only for a few biological objects, in a narrow range of conditions, far from the native conditions of their life, and without taking into account many energy exchange processes.

Under these circumstances, it is difficult to speak of the existence of a holistic concept of bioenergetics that links the processes occurring at various levels of biological organization. Therefore, the existing concept of bioenergetics is relatively easily criticized, and attempts to revise its provisions are objectively justified.

In this paper, an attempt is made to consider a number of non-traditional (however, not going beyond the logic of theoretical constructions in chemistry) hypotheses in the field of physical and colloidal chemistry.

These hypotheses are based on the justification and consideration of self-organization phenomena in catalytic reactions and in thin aqueous films.



*Celestial Phoenix. Photo by L.V. Ilyina, St.
Petersburg, Piskarevka, June 2019*

Chapter 1

BIOLOGICAL ENERGODYNAMICS

1.1 ASSESSMENT OF ENERGY CONSUMPTION DURING MUSCLE WORK

One of the widely studied areas of bioenergetics is the elucidation of the mechanisms of muscle contractions. Known methods for assessing energy expenditure during muscular work are based mainly on the study of gas and heat exchange in the body.

organism.

Let us consider the results of classical experiments to determine the energy production of a living organism. Typically, in these experiments, the object under study is placed in a thermally insulated chamber, and the total energy production of the organism is judged by measuring the temperature in the surrounding environment, assuming that all the work performed is converted into thermal energy [9]. However, this latter assumption is not entirely obvious and is subject to debate.

Let us assume that in this experiment the biological object under study performed mechanical work, increasing the ambient temperature. We can say that all the kinetic energy it produced

energy is converted into thermal energy of the environment only if the resultant of all forces developed by the biological object is completely converted into thermal energy. For example, one can imagine the movement

the movement of a weightless piston in a thermally insulated cylinder filled with an ideal gas (this is a hypothetical process in which mechanical work should be completely converted into thermal energy). Since these conditions cannot be met in a real experiment, the estimate of the energy consumption of a biological object will obviously be underestimated.

With this in mind, it can be suggested that the well-known assessment of the energy production of a living organism by gas exchange, which practically coincides with the results of experiments to determine heat exchange [9], characterizes only part of the energy produced.

As follows from the consideration of classical bioenergetics experiments from the perspective outlined above, a full assessment of human energy expenditure during mechanical work is quite difficult. However, in a number of simplified biomechanical experiments, it is probably possible to judge with sufficient certainty the minimum energy expenditure for performing the corresponding mechanical work. Pull-ups on a bar were chosen as such a biomechanical experiment, since in this case all the work is aimed at overcoming gravity. The mechanical work (A) during pull-ups was calculated as $A = mgh$, and the power (P) was calculated as

$$P = \frac{mgh}{t} n,$$

where: m is the mass of the body, g is the acceleration of gravity, t is the total time, n is the number of pull-ups.

In the example of the experiment conducted, the subject $m = 80$ kg pulled himself up 0.5 m ten times, in an average of 17 seconds. Correspondingly, accordingly, with one pull-up he performed mechanical work $A = 80 \times 9.8 \times 0.5 = 400$ J, developing power

$$PB = m \frac{10 \times 80 \times 9.8 \times 0.5}{17} = 235$$

Considering that, according to classical bioenergetics, this mechanical work was mainly provided by the use of energy from glycolysis reactions and aerobic oxidation of glucose in muscle cells, we will calculate the amount of reagents ($C_6H_{12}O_6$; O_2) that muscle cells minimally need to use to provide such mechanical work. According to literary data [7, 8], in the reaction

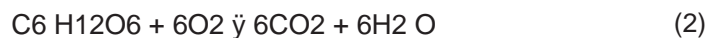
glycolysis



the standard change in free energy ΔG^0 will be:

$$\Delta G^0_{0.1} = -198 \text{ [kJ/mol]},$$

and in the reaction of aerobic oxidation of glucose, respectively:



$$\Delta G^0_{0.2} = -2872 \text{ [kJ/mol]}.$$

Based on the laws of physical chemistry, these values can be used directly to calculate consumption.

the concentration of reagents is unacceptable, since the energy effect reagent reactions depend on and the concentration $[C]$ of the both ΔG and the reaction products, and this dependence is expressed the more, the smaller ΔG [7].

At $\Delta G_{0.1} = -198$ [kJ/mol] and $\Delta G_{0.2} = -2872$ [kJ/mol], the influence of the $[C]$ of the reactants on the ΔG of the reactions is expressed very little (in the practically significant range of $[C]$ of the reactants and products). Let us confirm this with the corresponding calculations.

In glycolysis

$$\Delta G_{10^1} = \Delta G_{0.1} + n \cdot RT \ln \frac{[\text{CH}_3\text{CHOHCOOH}]^2}{[\text{C}_6\text{H}_{12}\text{O}_6]}$$

that is

$$\Delta G_1 = \Delta G_{0.1} + 2478 \ln \frac{[\text{CH}_3\text{CHOHCOOH}]^2}{[\text{C}_6\text{H}_{12}\text{O}_6]}$$

The results of calculating ΔG_1 for different ratios of concentrations of reactants and reaction products are presented in Table 1.

Table 1

$\frac{[\text{CH}_3\text{CHOHCOOH}]}{[\text{C}_6\text{H}_{12}\text{O}_6]}$	1	0, 1
$\frac{[\text{CH}_3\text{CHOHCOOH}]^2}{[\text{C}_6\text{H}_{12}\text{O}_6]}$	1	5×10^{-5}
ΔG [kJ/mol]	-198	-223

Therefore, for glycolysis, when the ratio $[C]$ of reactants and reaction products changes by 10 times, ΔG changes by 13% of $\Delta G_{0.1}$.

In aerobic oxidation of glucose

$$\dot{\gamma}G2 = -2872000 + 2478 \ln \left[\frac{[\text{CO}_2]^6 [\text{H}_2\text{O}]^6}{[\text{C}_6\text{H}_{12}\text{O}_6] \times [\text{O}_2]^6} \right], \text{ that is.}$$

$$\dot{\gamma}G2 = -2872000 + 2478 \ln \left[\frac{[\text{CO}_2]^6 [\text{H}_2\text{O}]^6}{[\text{C}_6\text{H}_{12}\text{O}_6] \times [\text{O}_2]^6} \right].$$

If the values of $[\text{CO}_2]$, $[\text{O}_2]$ in the cytoplasm of muscle cells are considered to be close to their values in blood plasma, then the following values should be entered into the formula [9]:

$$[\text{CO}_2] = 3 \times 1000 : 100 : 1000 : 22.4 = 1.34 \times 10^{-3} \text{ mol/l,}$$

which corresponds to a CO_2 concentration of 3% by V (3 ml CO_2 in 100 ml of solution).

$$[\text{O}_2] = 0.3 \times 1000 : 100 : 1000 : 22.4 = 1.34 \times 10^{-4} \text{ mol/l,}$$

which corresponds to an O_2 concentration of 0.3% by V (0.3 ml O_2 in 100 ml of solution).

The molar concentration of $\text{H}_2\text{O} = 1$.

$$16 \dot{\gamma}G2 = -2872000 + 2478 \times \ln \frac{(1.34 \times 10^{-3})^6 \times 6}{[\text{C}_6\text{H}_{12}\text{O}_6] \times (1.34 \times 10^{-4})^6}, \text{ those.}$$

$$\dot{\gamma}G2 = -2872000 + 2478 \times \ln(1 \times 10^6 : [\text{C}_6\text{H}_{12}\text{O}_6]).$$

Calculations of $\dot{\gamma}G2$ for different glucose concentrations are shown in Table 2.

Table 2

$[\text{C}_6\text{H}_{12}\text{O}_6]$	$\dot{\gamma}G2$ [kJ/mol]
0.005	- 2825
0.05	- 2830

As can be seen from Tables 1 and 2, the values of ΔG_1 and ΔG_2 depend little on the $[C]$ of the reactants and products of these reactions. This is very important, since the exact values of $[C_6H_{12}O_6]$, $[CH_3CHOHCOOH]$, $[CO_2]$, $[O_2]$ in the cytoplasm of muscle cells during the experiment under consideration are quite difficult to establish.

Next, based on the physiological norm, we assume that energy-generating reactions occur with the following ΔG :

$$\Delta G_1 = -225 \text{ [kJ/mol]}, \Delta G_2 = -2825 \text{ [kJ/mol]}.$$

With these ΔG_1 and ΔG_2 values, we calculate the consumption of $C_6H_{12}O_6$, and O_2 by the muscles during one pull-up and per second. Considering that glycolysis and aerobic glucose oxidation can make different contributions to providing muscle cells with energy, we will specify the percentages of anaerobic and aerobic energy supply in advance. Let's assume that $\% \text{ anaerobic} + \% \text{ aerobic energy supply} = 100$, which is consistent with classical bioenergetics.

Glucose consumption during glycolysis (anaerobic process) is calculated as follows:

$$M(C_6H_{12}O_6) = A_{\text{mech}} \times \frac{\% \text{ anaerobic}}{100} : \Delta G_1 \times 180,$$

where: $M(C_6H_{12}O_6)$ [g] is the mass of glucose, A_{mech} [J] is the work, ΔG_1 [J/mol] is the modulus of change in free energy.

During aerobic oxidation of glucose, we calculate the consumption of O_2 : %

$$\text{number of moles of } O_2 = A_{\text{mech}} \times \frac{\% \text{ aerobic} \cdot 100}{100} : \Delta G_2 \times 6,$$

moving on to gas volumes, we get: %

$$VO_2 = A_{\text{mech}} \times \frac{\% \text{ aerobic}}{100} : \Delta G_2 \times 6 \times 1000 \times 22.4,$$

where VO_2 [ml] is the volume of oxygen.

Thus:

$$M(\text{C}_6\text{H}_{12}\text{O}_6) = \frac{A_{\text{Mex}} \times \% \text{ анаэробн}}{125000},$$

$$V\text{O}_2 = \frac{A_{\text{Mex}} \times \% \text{ аэробн}}{2102}.$$

Let us calculate the possible consumption of O₂ and C₆H₁₂O₆ in our biomechanical experiment (Table 3).

Table 3

Ameh, [J]	% anaerobn.	M(C ₆ H ₁₂ O ₆) [G]	% aerobicn.	VO ₂ , [ml]
400 (for 1 pull-up)	10	0.03	90	17
	30	0.095	70	13
	50	0.159	50	9.5
	70	0.2	30	5.7
	90	0.29	10	1.9
235 (in 1 sec, Ameh, equal to power)	10	0.019	90	10.1
	30	0.056	70	7.8
	50	0.094	50	5.6
	70	0.13	30	3.4
	90	0.17	10	1.1

Knowing the consumption of C₆H₁₂O₆ by muscle cells during glycolysis and O₂ during aerobic oxidation of glucose, it is easy to calculate the minimum V of blood that must flow through the muscles that provide work during pull-ups (for 1 pull-up and for 1 sec).

Considering [C₆H₁₂O₆] in the blood = 0.005 with a molecular weight of glucose equal to 180 [9], 1 ml of blood contains

$$\frac{0.005}{1000} \times 180 = 9 \times 10^{-4} \text{ g glucose.}$$

The volume of blood that must flow through the muscles to deliver glucose to muscle cells is designated as $V_{cr}(C_6H_{12}O_6)$ and is calculated as follows:

$$V_{cr}(C_6H_{12}O_6) = \frac{M(C_6H_{12}O_6)}{9 \times 10^{-4}},$$

where: $M(C_6H_{12}O_6)$ in g, $V_{cr}(C_6H_{12}O_6)$ in

ml. The concentration of O_2 in the blood is 19% of V (taking into account that associated with Hb) [9]. Therefore, 1 ml of blood contains: O_2 , 19

$$\frac{19}{100} = 0.19 \text{ ml } O_2.$$

The volume of blood that must flow through the muscles to deliver O_2 to the muscle cells is designated as V_{KpO_2} .

$$\text{This volume will be: } V_{kr O_2} = \frac{VO_2}{0.19} \text{ ml}$$

Using the data in Table 3 for M , $C_6H_{12}O_6$ and VO_2 , the blood we calculate volume required for glucose and O_2 transport is calculated (Table 4). Table 4 shows that the

volumes of blood required to flow through the muscles performing pull-ups are quite large. Thus, during one pull-up, 89–322 ml of blood (depending on the % of anaerobic and aerobic energy production) should flow through these muscles, and 53–188 ml of blood in 1 s. With an average cardiac output of 70 ml, this corresponds to 0.8–4.6 left ventricular stroke volumes. Taking into account the distribution of blood flow in the body, the specified volume of blood delivered to the working muscles in real conditions

Biological energy dynamics

conditions is impossible. It should be noted that the figures in Table 4 correspond to the minimum costs of $C_6H_{12}O_6$ and O_2 for the production of E.

Table 4

Ameh, J	% anaerobe	M $C_6H_{12}O_6$, G	VO_2 , ml	VO_{kp} $C_6H_{12}O_6$, ml	$V_{kp} O_2$, ml
400 (for 1 pull-ups- (vanie)	10	0.03	17	33	89
	30	0.095	13	105	68
	50	0.159	9.5	177	50
	70	0.2	5, 7	222	30
	90	0.29		322	10
235 (in 1 sec)	10	0, 019	10.1	21	53
	30	0.056	7.8	62	40
	50	0.094	5.6	104	29
	70	0, 13	3.4	144	18
	90	0, 17		188	5.8

Since it is known that the efficiency of using $\dot{y}G1$ and $\dot{y}G2$ in the synthesis of ATP is not very high (about 40%) [8], and the efficiency of using $\dot{y}G$ of the reaction $ATP + H_2O \rightarrow ADP + H_3PO_4$ in myofibrils during muscle contraction is also far from 100%, then it can be concluded that in reality at least 2 times more blood should flow through the muscles directly providing pull-ups in comparison with the values indicated in Table 4. That is, a level of blood flow should be ensured that far exceeds the physiological capabilities of the cardiovascular system.

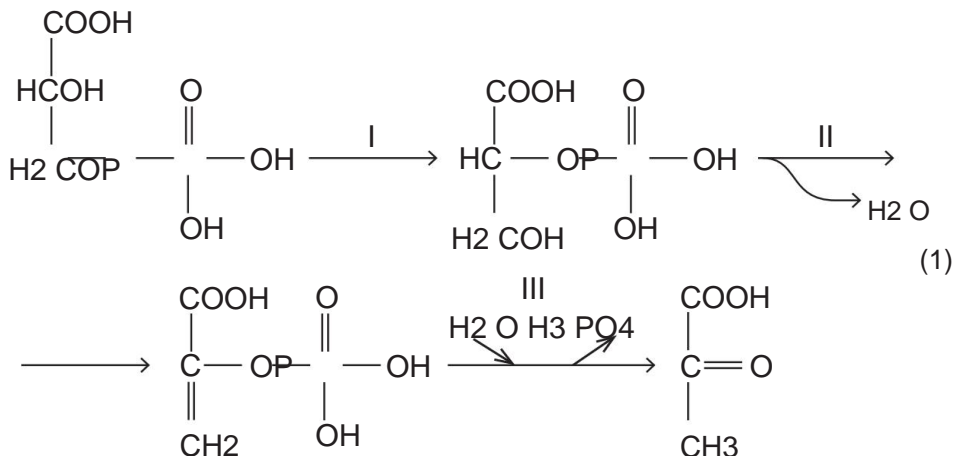
The conclusion that follows from the biomechanical experiment is the following. Traditional energy production pathways in muscle tissue—glycolysis and aerobic glucose oxidation—do not provide sufficient energy for a person to perform even moderate muscular work. This suggests that muscle cells obtain significant energy independent of biological oxidation and glycolysis occurring directly in the working muscles.

1.2 ENERGY DYNAMICS OF BIOCHEMICAL REACTIONS

Along with the biomechanical experiment discussed above, we will also analyze the energetics of a number of known biochemical reactions from the standpoint of classical theory. We will focus on well-studied carbohydrate metabolism reactions, in particular, individual reactions of glycolysis, the Krebs cycle, and gluconeogenesis.

neogenesis.

During the exchange of phosphoglyceric acid the following reaction occurs:



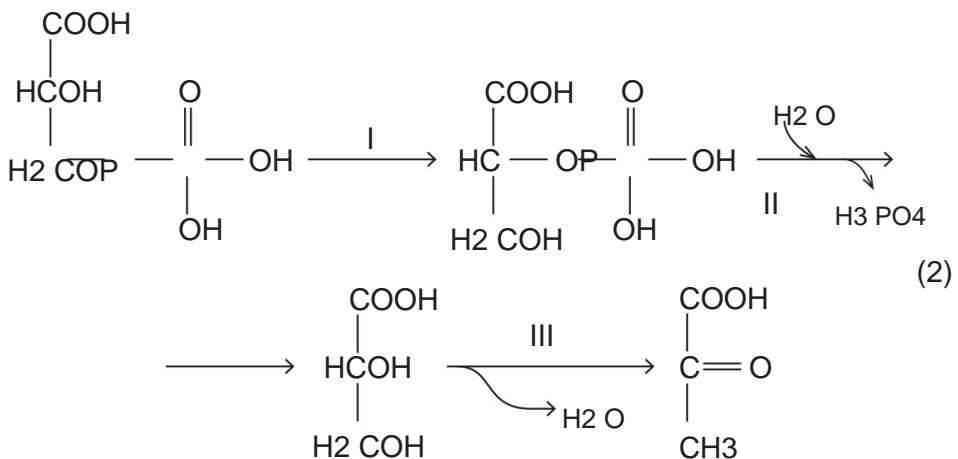
 Biological energy dynamics

For stages I, II, III of this reaction, the values of $\dot{y}G_0$ are respectively equal to: +4.4 kJ/mol, + 1.84 kJ/mol, - 61.9 kJ/mol [8]. Accordingly, for the overall reaction (1)

$$\dot{y}G_0 = + 1.84 + 4.4 + (- 61.9) = 55.7 \text{ kJ/mol.}$$

Let's consider this process taking into account Hess's law, according to which the energy effect of a reaction depends only on the starting materials and the final products. To verify this, let's analyze the course of a similar overall reaction (2) through other intermediate stages,

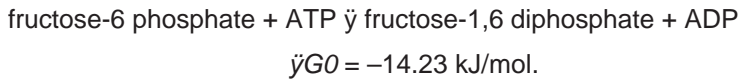
namely:



It is known [8] that at stages I and II $\dot{y}G_0 = +4.4$ and -17.5 kJ/mol. It is easy to show that, according to Hess's law, at stage III $\dot{y}G_0 = -55.7 - (4.4 - 17.5) = -42.4$ kJ/mol. Knowing the structure of pyruvic and glyceric acids, such $\dot{y}G_0$ is difficult to predict. Consequently, it can be concluded that Hess's law is not applicable here, and the energy effect of these reactions is apparently explained by the action of enzymes.

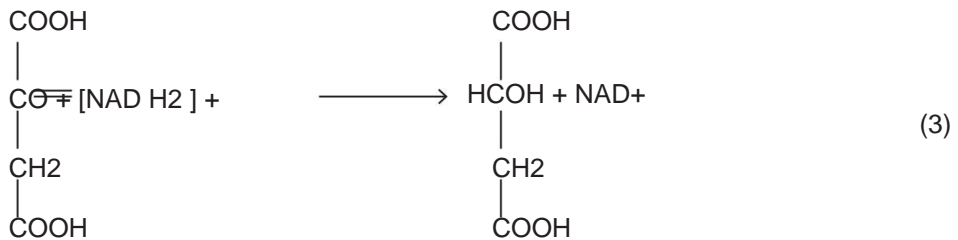
It should be noted that the reversibility of a number of biochemical reactions. The value of ΔG depends not only on ΔG .

So, in the reaction:



This reaction is poorly reversible [8].

However, reaction (3) of reduction of oxaloacetic acid, which occurs under the action of enzymes during oxidation sugars and gluconeogenesis:



$$\Delta G^0 = -30 \text{ kJ/mol,}$$

is quite easily reversible, despite the higher value of ΔG^0 [8]. The possibility of the influence of enzymes on chemical

The equilibrium is confirmed in a number of other processes.

Let us consider in more detail some oxidation-reduction reactions, based on the following premise. In oxidation-reduction reactions, the KR usually differs significantly from 1, due to which the reversibility of oxidation-reduction reactions is low. In this case, shifts in chemical equilibrium to the right and left are possible either by creating sufficiently high [approx.]

[rest.] or ([rest.]/[approx.]) [7], or due to conjugation of the react-

tions with $\dot{y}G > 0$ and $\dot{y}G < 0$, or by using non-traditional sources of chemical energy that change the redox reactions in the desired direction.

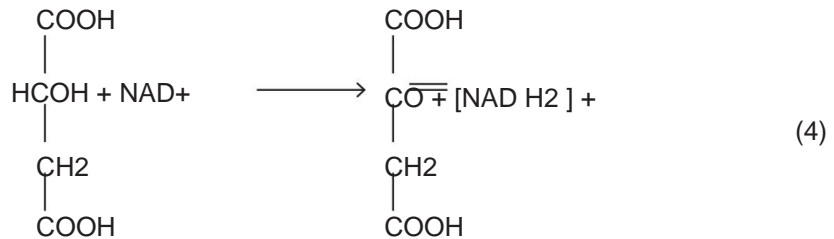
However, in a living cell, the reversal of oxidation-reduction reactions with significant CR is quite common [8].

If, in a cell, the equilibrium of such reactions shifts depending on the needs of the organism by changing the [ok.]/[reduced] ratio, then the question arises about the methods of organizing highly hermetic reactor chambers that allow local maintenance of the required [ok.]/[reduced] ratios, and powerful (to create a high concentration gradient) transport systems of oxidizing and reducing agents. It should be taken into account that in the cell, opposite oxidation-reduction reactions with different [ok.]/[reduced] — ([reduced]/[ok.]) occur at high speeds and simultaneously, which are created fairly quickly in local "hermetic" reactor chambers. Based on the fact that we are talking about reactions in the range of $KP = 10^{-6}$ – 10^{-10} , it can be assumed that the regulation of the [ok.]/[reduced] ratio by the cell is not sufficient to ensure shifts in the chemical equilibrium in the required direction.

The coupling of reactions characterized by the indicated CR with reactions having $\dot{y}G < 0$ suggests the existence of corresponding coupling systems. For the reactions under consideration, such systems have not been studied, and their presence is only an assumption [8].

In this regard, let us consider a number of oxidation-reduction reactions. During the oxidative decarboxylation of pyruvic acid, an intermediate reaction occurs

the oxidation reaction of FAD H_2 , NAD^+ . FAD where the oxidizing agent is $\text{H}_2 + \text{NAD}^+ \rightarrow \text{FAD} + [\text{NAD H}_2]^+$, however, under similar conditions in the respiratory chain, the reverse reaction $\text{FAD} + [\text{NAD H}_2]^+ \rightarrow \text{FAD H}_2 + \text{NAD}^+$ occurs. This fact is difficult to interpret from the standpoint of classical theory. In the Krebs cycle, the well-known reaction (4) of malic acid oxidation, the reverse of reaction (3), occurs spontaneously in the mitochondria.



$$\Delta G^0 = +30 \text{ kJ/mol.}$$

The equilibrium constant of this reaction (K_{P1}) is determined expression:

$$K_R = e^{-\frac{\Delta G^0}{RT}},$$

where: ΔG^0 is the standard change in free energy, R is the universal gas constant, T is the absolute temperature.

$$K_R = e^{-\frac{30,000}{2478}} = 5.52 \times 10^{-6}.$$

At equilibrium for reaction (4) the concentration ratio is equal to $\Delta\Delta$, i.e.:

$$\frac{[\text{COOHCOCH}_2\text{COOH}] [\text{HAD H}_2]^+}{[\text{COOHCHOHCH}_2\text{COOH}] [\text{HAD}^+]} = K_R = 5.52 \times 10^{-6}.$$

To shift the chemical equilibrium to the right in such a reaction during its spontaneous course, it is necessary to create conditions when:

$$\frac{[\text{COOHCHOHCH}_2\text{COOH}][\text{NAD}^+]}{[\text{COOHCOCH}_2\text{COOH}][\text{NADH}_2]} > 1/KR.$$

Considering that in mitochondria $\frac{[\text{NAD}^+]}{[\text{NADH}_2]} < 1$, required

Creation $\frac{[\text{COOHCHOHCH}_2\text{COOH}]}{[\text{COOHCOCH}_2\text{COOH}] \ln} > 1/\ddot{y}$ at $1/\ddot{y} = 181052$.

parallel with reaction (4), the opposite reaction (3) of gluconeogenesis occurs, the equilibrium in which, as is known, is also shifted to the right.

Since, from the point of view of classical chemistry, a shift of equilibrium to the right in both opposite reactions (3 and 4) due to the creation in one solution (in the mitochondrial matrix) of the corresponding concentrations of their reactants and products is impossible [7], it is quite natural to assume that these reactions are catalyzed by different enzymes. It is possible that these enzymes use some as yet unknown transformations of chemical energy to shift the chemical equilibrium in the desired direction.

To summarize the analysis conducted in this section, we can conclude that there is insufficient correlation between the energy expenditure of working muscle and the energy production of classical biochemical reactions. The course of a number of biochemical reactions is not consistent with Hess's law; some reactions may have variable KP. There is also no clear connection between the reversibility of reactions and their $\ddot{y}G0$.

All this indicates the presence and determining influence of some specific factors on speed and energy

Chapter 1

the energetics of biochemical reactions. To elucidate the possible mechanisms of such influence, we will first consider individual theoretical aspects of the energetics of catalytic processes.

Chapter 2

PHENOMENON OF CATALYSIS

2.1 MODERN PROBLEMS OF SCIENTIFIC THEORY

Catalysis is the phenomenon of acceleration of chemical reactions by substances present in contact with the reactants, but which do not change their chemical properties as a result of the reaction. According to the existing theory of catalysis, after a complete cycle of intermediate chemical interactions, the catalyst restores its chemical composition. This definition does not contain any indication of the reason why such an intermediate interaction between the catalyst and the reactants causes the acceleration of a chemical reaction [10]. "The catalyst opens a new reaction pathway" (the transformation of the initial substances into the final ones), which is significantly different from the non-catalytic route [11]. This difference lies in the fact that the catalytic and non-catalytic pathways are realized through a different sequence of elementary stages, one of which is limiting and determines the rate of the entire process as a whole [12].

Information about the acceleration of chemical reactions under the influence of certain specific substances (catalysts) has been available since the time of the alchemists of the 15th–16th centuries. To designate this phenomenon, the great Swedish chemist J. Berzelius introduced the term catalysis in 1835 (from the Greek $\kappa\alpha\tau\alpha\lambda\upsilon\sigma\iota\varsigma$ — destruction) [13]. The problems of catalysis received the highest attention from most of the leading figures in chemistry of the 19th–20th centuries. The first Nobel Prize in Chemistry in 1909 was awarded to the founder of the basic concepts of catalysis, the outstanding German chemist F.W. Oswald. Theoretical and practical issues of applying catalytic processes continue to be on the agenda to this day, since the overwhelming majority of chemical, pharmaceutical, biological, food, and other technologies rely on the use of various types of catalysts. In recent years, Nobel laureates in this field have been Grubbs R. et al. (2005) for the discovery of the mechanism of some reactions of the metathesis process and the development of heterogeneous ruthenium, molybdenum and tungsten industrial catalysts for this process; Ertl G. (2007) for discoveries in the field of solid surface chemistry, which led to the creation of effective catalysts.

lyzers.

A significant contribution to the development of theoretical ideas about the phenomenon of catalysis was made by the works of N.D. Zelinsky, one of the founders of organic catalysis [14]; the multiplet theory of A.A. Balandin [15]; the electron theory of F.F. Volkenshtein [16]. According to the definition of A.A. Balandin: “Catalysis is the effect of a substance on a reaction, selectively changing its kinetics, but preserving its stoichiometric and thermodynamic conditions; this effect consists in replacing some elementary processes with others, cyclic ones, in which

an active substance is involved. The introduced substance is called a catalyst, it does not change quantitatively as a result of the reaction and does not shift the equilibrium" [15].

Five theories of hetero-

Genetic catalysis: multiplet theory, active ensemble theory, statistical theory, electron theory, and radical or chain theory. The normal evolution of our understanding of catalysis, theories of catalytic processes, conclusions, and generalizations, despite the enormous amount of research on the genesis, activity, activation, and poisoning of catalysts, is hampered by the lack of a unified view of the process mechanisms.

"It is interesting that within the framework of the theories of catalysis, the inadequacy of the generally accepted theory of chemical reactions appears even more obvious. Chemical research into catalytic reactions has shown that they proceed through intermediate compounds which, in heterogeneous catalysis, have significantly lower kinetic energy and the concentration of which, according to thermodynamic considerations (a sharp decrease in entropy during formation), should be significant.

but lower than the original ones.

Thus, chemical catalysis—the acceleration of a reaction, compared to its non-catalytic pathway within the framework of accepted general ideas about chemical reactions (the rate of a chemical reaction is proportional to the concentration and kinetic energy of the reacting particles)—contradicts the basic accepted model of a chemical reaction" [17].

In fact, the mechanism of catalysis is currently unknown [18].

Chemistry is a natural science, but not an exact one. Therefore, many Key chemical concepts can be given several different definitions [19].

"The absence of a scientific theory capable of predicting the catalytic properties of substances is precisely what has given rise to the notion, often encountered in the specialized literature, of catalysis as more of an art than a science. The century and a half history of catalysis as an independent branch of chemistry shows that all known catalysts were discovered either by chance or intuitively, empirically. The objective reason for such an unusual situation in modern science should apparently be sought in the very nature of catalysis and the astonishing diversity of catalytic processes. Even now, when the latest experimental methods make it possible to approach the study of catalytic processes, as well as the catalysts themselves, at the atomic-molecular level and in real time, Nature does not reveal the secret of how it does it" [10].

It should be noted that the fundamental works on physics
The development of the catalytic mechanisms of catalysis dates back to the first two-thirds of the 20th century. Looking through the proceedings of the 10th International Conference "Mechanisms of Catalytic Reactions," held in October 2016 (Russia) [20], for example, it becomes apparent that the bulk of the very interesting papers presented were devoted only to specific applied issues of catalysis. Fundamental works illuminating the mechanisms of catalysis, or introducing at least new hypotheses for the discussion of this issue, have not been observed in recent years. It is possible that the material presented in this book will, to some extent, fill this gap in physical chemistry.

Modern developments in scientific research in the field of catalysis are associated primarily with the use of computer technologies for modeling the stereochemistry of catalytic reactions and studying the atomic-molecular structure of catalysts. Attention is drawn to

energetic and crystallographic features of the structure of the organization of catalysts. One of the fundamental laws of chemical kinetics, the Arrhenius law, relates the reaction rate constant to the energy characteristic inherent in a given reaction, called the activation energy, which

paradox in turn is directly related to the energy properties of the surface structure of the catalyst (kinetics of surface reactions) [16, 21].

In this context, Taylor's active center theory (proposed back in the 1920s) continues to be discussed. This theory suggests the presence of active centers in a catalyst, which are atoms located on its surface, above the average surface level and forming a kind of protrusion. Such protrusions can possess free valences and form reactive intermediate compounds. It is quite clear that the surface of a solid is energetically non-uniform. However, the question remains unclear: what are these "active centers"? [17].

One gets the impression that, overall, catalysis as a phenomenon is too diverse in the kinetics of physicochemical and biological (enzymatic catalysis) processes to fit within the framework of a single scientific definition. In fact, the scientific definition of catalysis, given in 1835 by J. Berzelius as the general property of materials (catalysts) of varying structure and chemical composition to accelerate chemical reactions without undergoing their own chemical transformations, has not undergone any fundamental changes to this day.

Apparently, the solutions to this problem require new theoretical approaches, physicochemical concepts and hy-

hypotheses. Perhaps, we should recall the resonance theory in chemistry proposed by Nobel Prize winner in chemistry L. Pauling [22]; consider the existence of the phenomena of "polymorphic resonance", which, according to A.P. Smirnov, "underlies catalytic reactions in which the catalyst serves as a kind of frequency transformer in wave energy processes" [23]. From the standpoint of the electron theory of catalysis, the following remain little studied: the electron-proton effect and hydrogen atom transfer reactions (electron + proton) [24]; the possibility

the possible role of the phenomenon of plasmon resonance on the crystalline surfaces of catalysts [25]; spectral-dynamic dispersion of the active centers of catalysts, etc.

The structure, form of an object and its functions (internal and external) are inseparable - this is a general philosophical position.

The structure (shape) of an atom of any substance determines its stability and specific functional properties in interaction with other atoms, such as, for example, the spectra of emission and absorption of energy. Each polyatomic molecule is a set of coupled harmonic or anharmonic atomic oscillators integrated into a single molecular oscillator. From the same position, i.e., as a certain set of interacting oscillators, one can consider a cluster, a crystal, and, in general, any macroobject. Various types of molecular deformations, the presence of impurities, changes in the positions of atoms cause oscillations with different frequencies; each such natural oscillation of a certain frequency is called a mode. Combinations of modes create a common set of frequency spectra of an object and its own functional quality in interaction with substances with similar emission and absorption spectra [26].

It's possible that the mechanism of interaction via spectral-phase "patterns" of molecular oscillations plays a leading role in catalytic processes. This may be especially true for biological catalysts—enzymes—which differ from inorganic catalysts in their higher selectivity.

Based on the concept of living matter as a system in which self-organization processes occur, it can be assumed that it is the diversity of enzymes and highly selective enzymatic reactions that makes this kind of process possible.

2.2 CATALYTIC PROCESSES IN BIOENERGY. HYPOTHESIS OF A SHIFT IN CHEMICAL EQUILIBRIUM

Energy processes of life in biology

The chemical world is directly connected with the phenomenon of catalysis—enzymatic catalysis. J. Berzelius pointed out: "In living plants and animals, thousands of catalytic processes occur between tissues and fluids, carrying out a large number of different chemical syntheses from a single starting material" [13].

Based on classical chemical kinetics [7, 27–30],

The talizer cannot shift the chemical equilibrium because
It cannot accelerate a forward chemical reaction without accelerating the reverse reaction to the same degree. The reason for this phenomenon can be seen as follows. The development of the substrate-catalyst complex in the forward and reverse reactions goes through the same stages. This means that the energetic difficulties in the formation and development of this complex during

The forward reaction's advantages are equivalent to the energetic difficulties encountered in its formation and development in the reverse reaction. Consequently, an increase in the forward reaction's ease of progression due to a catalyst means an equal increase in the reverse reaction's ease of progression with the same catalyst.

Let us consider a hypothetical isomerization reaction $A \rightleftharpoons B$ in the presence of catalyst K . In general, the direct reaction $A \rightarrow B$ proceeds through the following intermediate states:

dii:



where: C is an intermediate product of the reaction $A \rightarrow B$, K_1 is the intermediate state of the catalyst in the development of the transition complex.

The reaction $B \rightarrow A$ proceeds similarly in reverse order:



Moreover, the energy of *the* AK , AK^{\ddagger} , and BK complexes, which determines the ease of catalysis, affects the forward and reverse reactions equally. Consequently, a catalyst cannot increase the rate of reaction $A \rightarrow B$ without increasing the rate of reaction $B \rightarrow A$ to the same extent. Therefore, catalyst K cannot shift the chemical equilibrium in the reaction $A \rightleftharpoons B$.

Thus, classical chemical kinetics does not assume the possibility of a shift in chemical equilibrium under the action of the action of catalysts and their associated influence on the energetics of chemical reactions. Therefore, to explain processes such as the biochemical reaction under consideration

oxidation of oxybutanedicarboxylic (malic) acid, necessary
we need to put forward new hypotheses, in particular those concerning

Catalysis that goes beyond classical physical chemistry. Such a hypothesis could be the assumption that catalysts exist that can shift chemical equilibrium and influence the energetics of chemical reactions. These catalysts can presumably be divided into three main types.

- 1st type - catalysts that shift chemical equilibrium due to self-organization phenomena in the development of a complex of the substrate with the catalyst, in which anti-entropic phenomena arise, allowing the catalyst to accelerate the forward reaction to a greater extent than the reverse.
- 2nd type – catalysts that shift chemical equilibrium using the antientropic phenomenon, which consists of an uneven distribution of reagent molecules (substrates) by kinetic energies.
- 3rd type – catalysts that use quantum-chemical energies when acting on a substrate.

Thus, at least three mechanisms of catalytic action can be proposed, due to which

it becomes possible to increase the energy of reaction products without supplying traditional forms of energy to the reactants.

The proposed catalysts of types 1 and 2 utilize thermal energy. They are also allowed to utilize dissipated thermal energy, i.e., the thermal energy of a system in a state of equilibrium, in order to convert it into more valuable forms of energy (for example, into energy stored during ATP synthesis). Catalysts of type 3 must also be able to increase thermal energy.

system, changing the sign of \dot{H} of chemical reactions. Of course, catalysts of the 3rd type would allow shifting the chemical equilibrium.

With such catalysts, it is possible to create chemical engines whose operation is consistent with the law of conservation of energy, albeit at the expense of consuming E from unconventional sources. In practical terms, they can be considered as highly efficient engines. In living organisms, they are proposed to be considered as ATP synthesizers in closed life-support systems.

Let us consider the action of hypothetical catalysts of type 1 using the example of the same isomerization reaction $A \rightleftharpoons B$.

In the development of a substrate complex with a type 1 catalyst The manifestation of self-organization (control) processes is assumed. In the reaction $A \rightleftharpoons B$, the process will proceed through the following stages: $A + K \rightleftharpoons AK \rightleftharpoons CK1 \rightleftharpoons BK2 \rightleftharpoons B + K$.

In this case, the presence of molecule A in the complex with the catalyst is considered a control signal for modification of the catalyst molecule. Under the influence of this control signal, the catalyst molecule will change in such a way (conformationally, in the structure of the electron layers, etc.) that the formation of complex $BK2$ after the appearance of complex $CK1$ is facilitated. This ensures accelerated progression of the process $CK1 \rightleftharpoons BK2$.

This is the first control signal in the operation of the catalyst. The second The following phenomenon is assumed to be the second control signal. After the decomposition of the $BK2$ complex, the catalyst will return to its original state ($BK2 \rightleftharpoons B + K$), and in the K state it will not be able to react intensively with the B molecule due to steric hindrance. The formation of complex B with the catalyst is facilitated only after the control action on

The catalyst of molecule A only at the stage when the intermediate product is converted into the final product (at the stage $CK1 \rightarrow BK2$ in the forward reaction). Since in the reverse reaction the formation of complex B with the catalyst will be hindered, this will ensure the preferential acceleration of the forward reaction $A \rightarrow B$ by the catalyst and, accordingly, a shift in the equilibrium in the reaction $A \rightarrow B$ towards the product (B).

It is very important to substantiate the possibility of controlling the operation of the catalyst by means of low-energy control actions. actions that are much lower in ΔE than the main processes in reactions $A \rightarrow B$. This possibility exists when using minor changes in the conformation of the catalyst molecule in the control processes, during which steric hindrances for the formation of a complex of the catalyst with the B molecule appear (at the stage $BK2 \rightarrow B+K$) and are eliminated (at the stage AC , for the stage $SK1 \rightarrow BK2$).

Steric hindrance to the formation of complex B with the catalyst prevents the binding of B and K molecules, without direct energetic counteraction between the reaction $B + K \rightarrow BK2$ and the catalyst's conformational change, which creates this steric hindrance. It is quite natural that the change in the energy of the controlling effects is quantitatively much smaller than in the main reactions $A \rightarrow B$.

Part of the chemical energy of the reaction $A \rightarrow B$ can be used for control actions. It is also possible to use dissipated thermal or electromagnetic energies of the environment. The necessary changes in the conformation of the catalyst molecule are entirely possible, given that conformational changes in large molecules under the influence of collisions with other molecules are not

are chaotic.

Let us consider the rationale for the possibility of the existence of type 2 catalysts.

Let us return again to the isomerization reaction $A \rightleftharpoons B$.

Let us assume that the energy of molecule B is somewhat less than the energy of molecule A , and accordingly the equilibrium in the reaction $A \rightleftharpoons B$ is somewhat shifted towards product B . When one molecule of A passes into one molecule of B , energy $EA-B$ is released, and for the reaction $A \rightleftharpoons B$ to proceed, one molecule of A requires activation energy E_{A-B} , which is equal to

also the activation energy for the elementary act of the reaction $B \rightleftharpoons A$ (Fig. 1).

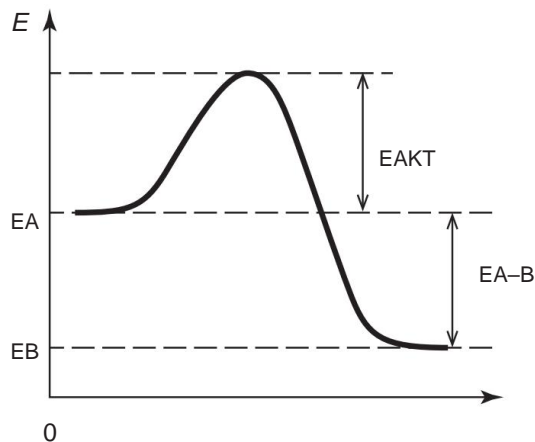


Fig. 1. Change in the potential energy of the system of molecules A and B during the reaction

Let us assume that the energy for the reaction $B \rightleftharpoons A$ comes only from the thermal motion of the molecules. Let us denote the kinetic energy of one molecule as E_{kin} . It follows that the reaction $A \rightleftharpoons B$ involves molecules of A for which $E_{kin} > E_{AKT}$ (Fig. 2a), and the reaction $B \rightleftharpoons A$ involves molecules for which

for which $E_{KIN} > (E_{AKT} + \Delta E_{A-B})$ (Fig. 2b). Let us assume that an isolated system contains molecules A, and that different molecules of A have different E_{KIN} . It should be taken into account that the distribution of molecules by E_{KIN} also depends on the structure of the molecules. Let us denote the number of molecules in the system that have similar kinetic energies as N . The dependences of N on E_{KIN} for different substances are naturally different and quite complex (approximately such a dependence can be represented in accordance with Fig. 2a).

Some of the A molecules with $E_{KIN} > E_{ACT}$ enter into the reaction $A \rightarrow B$. As the reaction $A \rightarrow B$ proceeds, the total number of A molecules decreases (and, accordingly, the concentration of A molecules), the total number of B molecules increases (and, accordingly, the concentration of B molecules), and the temperature of the reactant mixture also increases. A situation arises where the number (and concentration) of reactive A and B molecules is equalized (Fig. 2b). Chemical equilibrium arises in the reaction $A \rightarrow B$ [7].

Let's introduce a catalyst into the system that reduces the activation energy of the forward and reverse reactions by the same amount (which is consistent with classical chemical kinetics). Under its influence, E'_{ACT} appears

$$E'_{ACT}, \text{ i.e. another active energy}$$

such that $E'_{ACT} < E_{ACT}$. After this, the situation in the equilibrium system will change. The number of molecules A and B capable of entering into the reactions $A \rightarrow B$ and $B \rightarrow A$ will increase, and the concentrations of reactive molecules A and B will increase accordingly.

If the $N(E_{KIN})$ dependencies were linear and the value $(\Delta N / \Delta E_{KIN})$ was the same for substances A and B, then the reduction in activation energy to the value E'_{ACT} would not entail a change in the ratio of the number (and concentration) of reactive molecules A and B, but the dependences of N on E_{KIN} are, of course, nonlinear and different for different substances, which entails other changes (Fig. 2c).

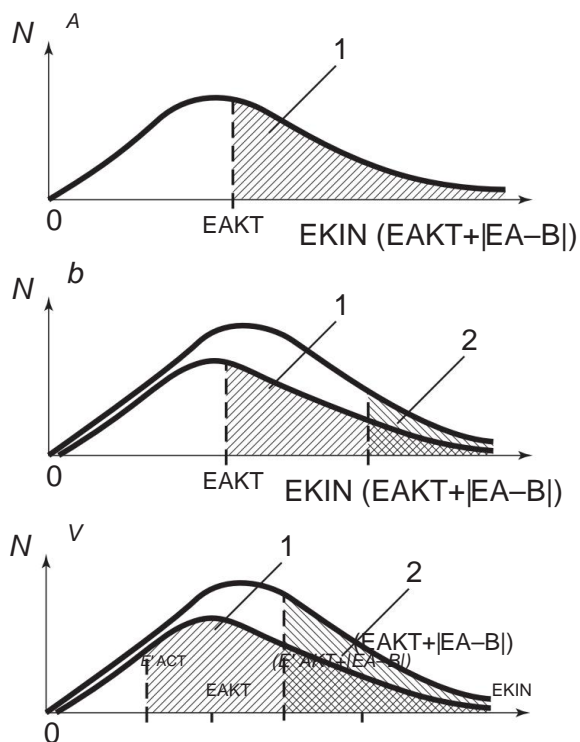


Fig. 2. Distribution of reagent molecules A and B by kinetic energy in the reversible reaction $A \rightleftharpoons B$. The shaded area is the number of reactive molecules.

- Initial distribution of reagent A molecules;
- distribution of molecules by kinetic energy in a state of equilibrium;
- change in the ratio of reactive molecules A and B after introducing a catalyst into the equilibrium mixture

When the activation energy shifts to the E_{ACT} level, the ratio of the numbers and concentrations of reactive molecules A and B will change, indicating a shift in chemical equilibrium. This is because the uneven and complex distribution of molecules by kinetic energy is essentially an entropic effect, which can be considered a consequence of the self-organization of "chaotically" moving molecules. It follows from this that catalysts that lower the energy barriers of the forward and reverse reactions

by the same amount, should also shift the chemical equilibrium in reactions where the distribution of reagent molecules according to the E_{KIN} is uneven and different for the starting materials and reaction products.

Next, we will analyze the catalysts of type 3 on the principle of the absolute possibility of their existence.

Energy of a quantum-chemical nature can apparently be used in strictly directed effects on electron clouds in a substrate-catalyst complex [7, 27, 28]. To substantiate this possibility, let us first consider a number of phenomena.

Electron density movements during chemical reactions are largely due to electrostatic forces—the attraction of electrons to nuclei and the mutual repulsion of electrons from each other. However, the distribution of electron density is also affected by other forces, the action of which is very complex and, apparently, allows for control effects that can significantly influence the movement of electrons with little energy expenditure on control actions. Let us consider an example. In the interaction $2Na^{\circ} + Cl_2 \rightleftharpoons 2Na^+Cl^-$, the ionized compound $NaCl$ appears, the electron density on the bonding orbital is practically

is practically completely drawn to Cl^- from Na^+ . But this cannot be a consequence of a stronger attraction of the Na electron to the Cl nucleus than to the Na nucleus due to electrostatic forces. The charge of the Cl° nucleus is balanced by the charge of the Cl° electrons, and the displacement of the electron density forms an excess negative charge on Cl and a positive charge on Na, which entails the formation of a compound that should not be electrostatically stable. The electrons in the Cl^- anion should "repel" while simultaneously being attracted to the Na^+ cation. Nevertheless, the NaCl compound is ionized, therefore, forces exist in the molecules that are capable of overcoming electrostatic forces; in contrast to the latter, the nature of these forces may be more complex. It is possible that these are not potential forces and can be controlled by releasing different energies under the same energy but different direction of influences. This creates the preconditions for the operation of type 3 catalysts. For example, if these non-electrostatic forces are weakened by controlling the NaCl compound, the reaction $2\text{Na} + \text{Cl}^- \rightarrow 2\text{Na}^\circ + \text{Cl}^\circ_2$ will occur, which will also be exothermic. Non-potential forces, for which the work depends on the shape of the path, may well be important in systems using non-traditional chemical energy. If these forces influence the movement of electron density, counteracting electrostatic ones, then in this case the electrons in the same atoms can behave in opposite ways depending on factors containing controlling effects.

laziness.

It is quite possible to use it as an unconventional energy, the energy of the wave process inherent in electrons. If, with the help of a control action, we convert a standing wave (an electron in a stationary state) into a moving

wave (the electron changes orbital), then we can use To use the energy of the wave process, initially inherent to the electron, to move it to an orbital with higher energy. Of course, it is necessary to expend energy on the control action, but this energy expenditure may be small. Apparently, in the steady state, electrons constantly receive energy to maintain the wave process, since it does not decay, despite the fact that electrons can interfere with it during mutual collisions. It is possible that in the steady state, electrons constantly receive energy for the wave process from a certain region and re-emit it during the wave process to some other region. If we take into account that electrons from the outer layers penetrate to the nucleus and return, we can conclude that the situation of counteraction of electrostatic and other forces that shape electron orbitals is not stable. Changes occur largely due to energies not taken into account by classical theory, which can be used with strictly directed effects on electron clouds, which is presumably provided by type 3 catalysts. Thus, the possibility of influencing the behavior of electron clouds through very low-energy control actions is fundamentally evident.

2.3 ON THE PHENOMENA OF SELF-ORGANIZATION OF PHYSICAL AND CHEMICAL PROCESSES IN LIVING ORGANISMS

Taking into account the theoretical possibility of energy production by living organisms due to self-organization phenomena

physicochemical processes (which was discussed earlier),

It is very important to assess the role that such processes play and can play in bioenergetics.

As the biomechanical experiment examined shows, glycolysis and aerobic oxidation of glucose often do not allow for compensation of energy expenditure in muscle cells, while the reserves of macroergs in cells, as is known, are insufficient for long-term muscular work.

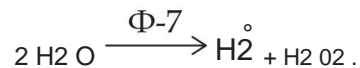
The conclusion suggests itself about the existence in muscle cells of sufficiently powerful energy sources or energy converters that are independent of glycolysis and aerobic oxidation of glucose, the contribution of which to the production of bioenergy changes depending on the circumstances and is maximum under extreme conditions.

by intensity and duration of loads.

It is quite logical to assume that such energy sources exist in other cells, thanks to which the living organism

The body can withstand extreme stress from starvation and hypoxia. From an evolutionary perspective, such alternative sources of bioenergy should be closely linked to ATP synthesis systems. Let's consider a possible option for incorporating an alternative energy source into the cellular energy metabolism system.

Let us assume that mitochondria contain the enzyme F-7, which ensures the reaction:



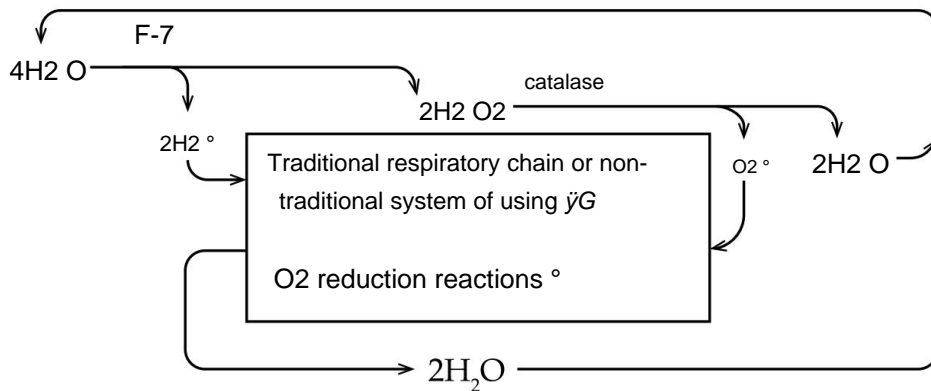
Considering the significant $\dot{\gamma}\text{H}^\circ$ in such a reaction, the enzyme should most likely be considered a type 3 catalyst (according to the above classification), using energies of a quantum-chemical nature.

Next, the already known enzyme catalase ensures the reaction $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$.
 H_2O_2 is fed into the respiratory chain (optimal-After this H_2O_2
 The most important, from the point of view of ATP production, during biological oxidation is apparently the reduction of NAD^+), and O_2 is supplied to the final link of the respiratory chain to the corresponding cytochrome.

Thus, the chemical energy released in the non-traditional way via the F-7 enzyme can be converted into the energy of ATP molecules using the usual coupling systems in the respiratory chain.

Along with the traditional use of H_2 and O_2 in the mitochondria, and it is possible that they may be involved in other processes that require energy expenditure as forms of chemical energy.

In summary, such a path can be represented as follows diagram:

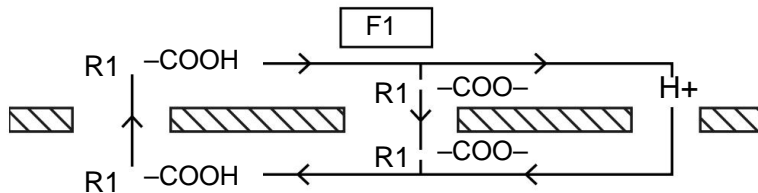


The existence of such an energy supply system is indirectly confirmed by the fact that the enzyme catalase plays an important role in maintaining mitochondrial function. It is also important that under hypoxic conditions, the danger increases.

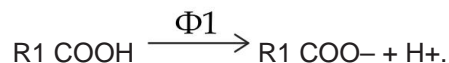
damage to biological structures by H_2O_2 . However, this raises some confusion from the standpoint of classical chemistry, since with a deficiency of an oxidizing agent (O_2) and an excess of reducing agents (substrates of the respiratory chain), the spontaneous formation of partially reduced forms of oxygen (H_2O_2) should be hindered rather than facilitated. Therefore, it can be assumed that H_2O_2 is not formed spontaneously during hypoxia, but is an intermediate metabolite of the energy-producing system used by the cell under extreme conditions (hypoxia).

Along with ensuring the functioning of the respiratory chain in mitochondria, the energy supply systems of cells, in the presence of the physicochemical processes discussed above, can produce ATP in other ways.

Using catalysts of types 1, 2, and 3, it is theoretically possible to carry out the reaction $ADP + H_3PO_4 \rightarrow ATP$ solely through non-traditional chemical energies, since these catalysts, for example, can constantly maintain a proton flow through the cell membrane. At the same time, opposite reactions must occur on opposite sides of the membrane, ensuring the presence of a transmembrane $[H^+]$ gradient and, accordingly, a constant H^+ flow through the membrane.



F1 is an enzyme that shifts the equilibrium in the dissociation reaction of a weak acid:

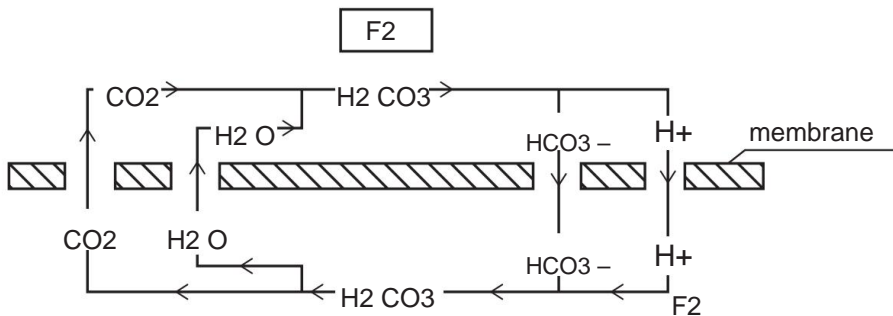


The enzyme F1, being on one side of the membrane, will ensure an increase in $[H^+]$ on this side; on the opposite side of the membrane, equilibrium in the reaction:



returns to the value at which $[H^+] < [R1\text{ COOH}]$, which accordingly manifests itself in the possibility of spontaneous transport of H^+ , $R1\text{ COO}^-$, $R1\text{ COOH}$ through the membrane. One can also consider methods of approaching the provision of circulation of substances through the membrane, for example, according to the following

diagram:

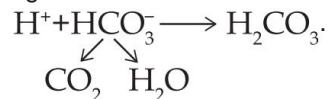


F2 is an enzyme that shifts the equilibrium in the reaction:



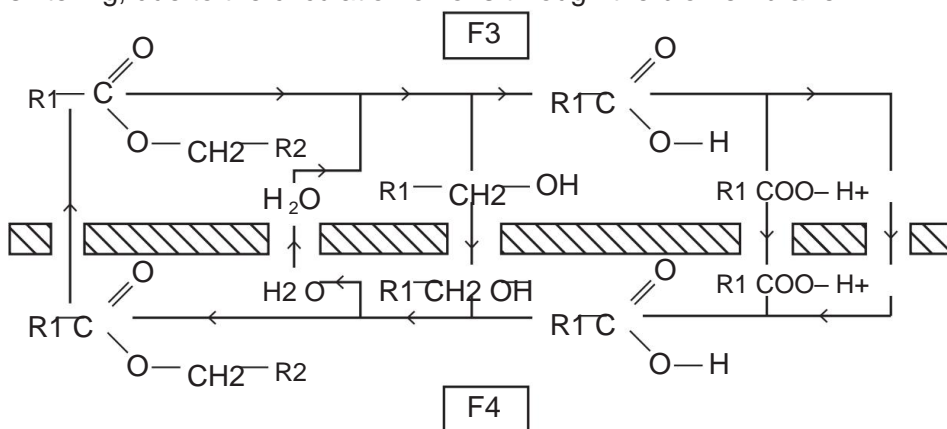
and being on one side of the membrane, increases $[H^+]$.

the flow of H^+ and HCO_3^- ions, the predominant course of the reaction occurs through the membrane occurs After

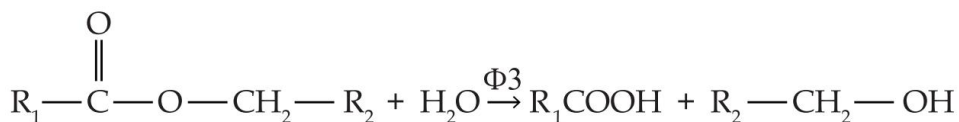


Accordingly, circulation of substances through the membrane occurs.

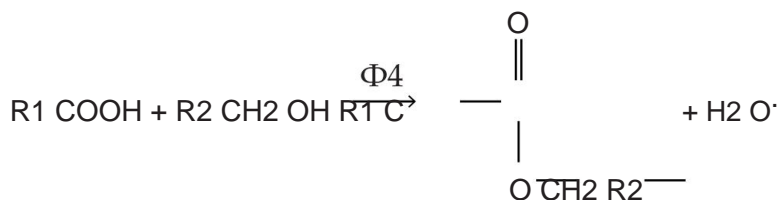
Let us give a few more possible options for energy supply.
sintering, due to the circulation of ions through the biomembrane:



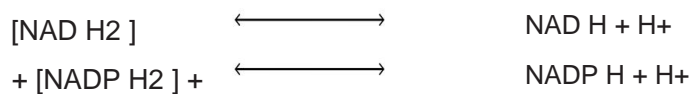
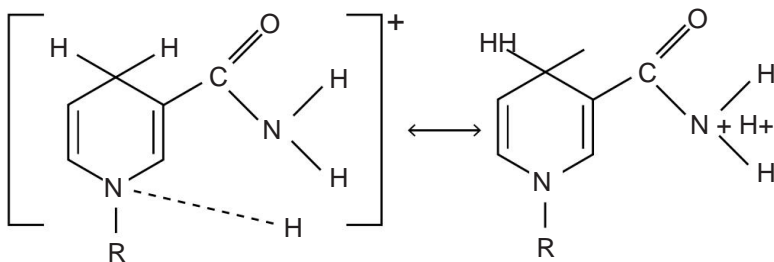
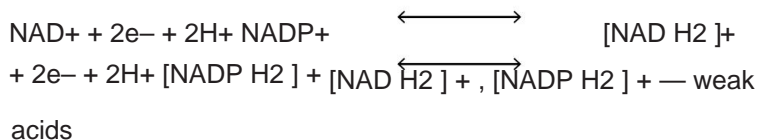
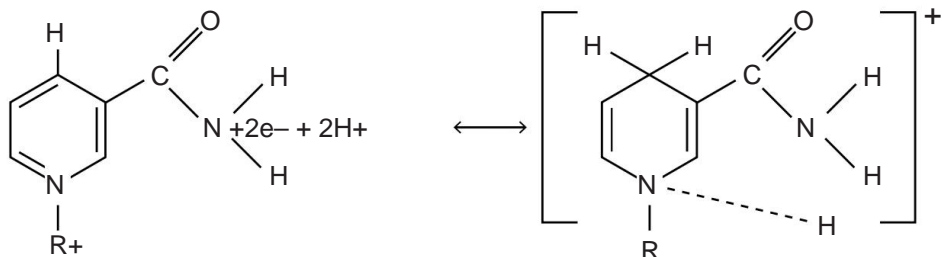
FZ is an enzyme that mainly provides hydrolysis of the ester:



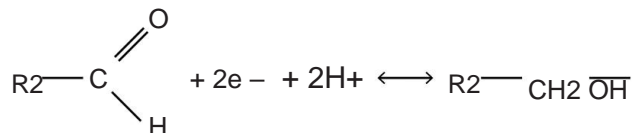
F4 is an enzyme that provides the synthesis of a complex ester:



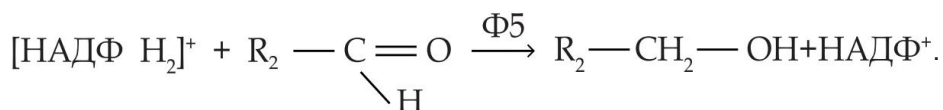
The existence of the F4 enzyme is not so doubtful, since the energies released by such catalysts, judging by the examples considered, can be quite significant. Another option could be the following process:



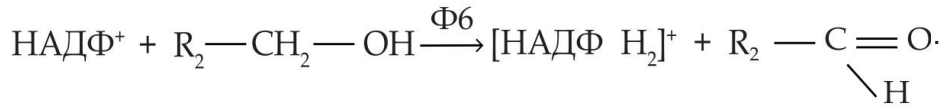
a reaction takes place in the cells



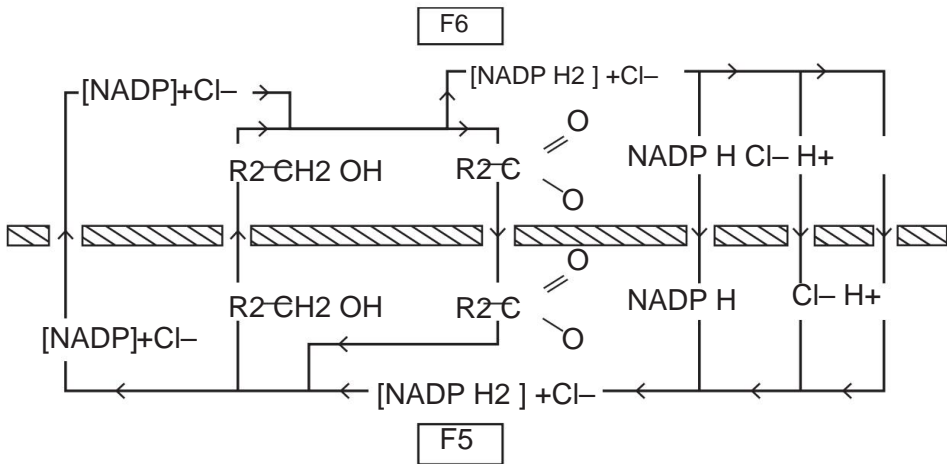
Let us assume that F5 is an enzyme that provides mainly basically, the reduction of the aldehyde in the reaction:



F6 is an enzyme that mainly provides oxidation alcohol (reverse reaction):



It is acceptable to use enzymes that carry out the same reactions using $[\text{NAD H}_2]^+$, NAD^+ according to the following scheme:



Thus, providing the H^+ current by any of the methods considered in conjunction with ATP synthesis can create conditions for this synthesis only through non-traditional chemical energies.

2.4 DEDUCTIVE CONSIDERATION OF THE PHENOMENON OF CATALYSIS IN THE ASPECT OF BIOENERGY

In the previous section, a number of hypothetical options for incorporating something “non-traditional” into the normal cellular energy exchange system were considered, in relation to the use of ATP.

and the reaction of glycolysis, the energy source provided by the phenomenon of catalysis. It should be noted that the above hypotheses about the possibility, under certain conditions, of shifting chemical equilibrium by a catalyst and the phenomena of self-organization, as

The following discussions on the phenomenon of catalysis are based on the traditional need to ensure their conformity with the law of conservation of energy and the principles of thermodynamics. Nevertheless, let us examine these fundamental principles of modern physical science from the perspective of the limits of their applicability in the real world.

2.4.1 Law of conservation of energy in thermodynamics

The law of conservation of energy states that in an isolated system the amount of energy remains constant while it is possible to transform energy from one form to another. The laws of conservation of energy, momentum, angular momentum, and electric charge are valid for any isolated systems [31, p. 602]. Note that an isolated system is a physical abstraction, since such systems do not actually exist in Nature. "A complete description of a physical system is possible only

within the framework of dynamic laws that determine in detail the change in the state of the system over time. However, in many cases the dynamic law for a given system is unknown or too complex" [31, p. 602]. Nevertheless, the law of conservation of energy has been formulated, to varying degrees, for its various forms: mechanical, thermodynamic (the first and second laws of thermodynamics), electrodynamic (Poynting's theorem), hydrodynamic (Bernoulli's equation), relativistic, optical, quantum-mechanical, etc. Since all of the above formulations are valid only

For a physical abstraction, i.e., for an isolated system, the formulations themselves apparently represent nothing more than physical abstractions. Thus, we can conclude that the law of conservation of energy and its applications to various forms of energy are valid only for isolated systems—physical abstractions.

According to A. Einstein: "Our ideas about physical reality can never be final. We must always be ready to change these ideas" [32, p. 61]. The same idea is reflected in the Physical Encyclopedia: "In connection with the development of the theory of gravitation, a further revision of views on the symmetries of space-time and fundamental conservation laws (in particular, the laws of conservation of energy and momentum) is planned" [31, p. 603].

This book focuses on examining thermodynamic processes in physical terms: heat, entropy, enthalpy, and work. Modern thermodynamics is based on the work of R. Clausius, S. Carnot, W. Thomson (Kelvin), and others. R. Clausius's postulate (the second law of thermodynamics) states: "Heat cannot be spontaneously transferred from a colder to a hotter body" [33, p. 12].

At the end of the 19th century, Nobel Prize winner in chemistry Wilhelm Ostwald introduced the concept of a perpetual motion machine, or rather a pseudo-perpetual motion machine of the second kind. Ostwald's idea was that since, according to the first law of thermodynamics, heat is equivalent to mechanical energy, all that was required of a perpetual motion machine of the second kind was the ability to ideally transform energy. Thus, "...without contradicting the first law, it is entirely possible to construct a machine that selects..."

extracting heat from a body that has the temperature of the surrounding air, or, for example, taking heat from water from large

reservoirs and performing mechanical work thanks to this" [34]. However, this idea of W. Ostwald contradicts the second law of thermodynamics.

But are these "principles" the absolute truth for Nature? A kind of "taboo" for scientific research? For example, K.E. Tsiolkovsky in the above formulation of the second law of thermodynamics according to Clausius saw, as he says, a "strange reservation": "Heat cannot by itself (spontaneously) pass..." [35]. He notes a similar kind of "strange reservation" in Thomson (Kelvin).

K.E. Tsiolkovsky writes: "Although we see from natural phenomena that these positions of thermodynamics seem to be justified and even seem to belong to the crude truths, obvious to everyone, such as the immobility of the Earth, the smallness of the stars, the existence of the celestial spheres, etc., were previously considered, but, in any case, we cannot consider the postulates of Clausius and Thomson to be successfully expressed. They would be accurate if they were free from the reservations indicated; but would they then be justified?" [35].

Based on his own calculations, K.E. Tsiolkovsky concludes that "Clausius's postulate in its pure form, without any reservations, is not justified. The force of gravity, as well as other causes—their number is unknown—violate it. That is why the reservation "by itself" is necessary to the postulate [35].

It should be noted that K.E. Tsiolkovsky's views on thermodynamic postulates were criticized by a number of scientists even during his lifetime. He may have made errors in some of his calculations, but constructing a model of boundless outer space as an isolated system is, at the very least, absurd. Therefore, in addition to K.E. Tsiolkovsky's undeniable contribution to astronautics, he can also be considered the founder of gravitational thermodynamics.

Modern humanity's knowledge of the physical world and its laws is still negligible. A well-known, and still highly relevant, assessment of the achievements of theoretical physics is given by one of the founders of its modern foundations, Nobel laureate in physics Richard Feynman. He writes: "...our vaunted modern physics—"

It's a complete scam: we started with magnetic iron ore and amber, and ended up with a lack of understanding of either. But in the process of studying, we learned a huge amount

"a huge number of amazing and very useful things for practice!" [36].

In the history of science there have always been clashes between various scientific schools, views, and principles of knowledge of Nature, often subject to opportunistic, political, psychological, and interpersonal contradictions in the scientific community, sometimes of a militant, aggressive nature. Nevertheless, any "taboos" on the natural function of man—his consciousness and the ideas produced by this consciousness in the field of natural science are counterproductive for science itself and the development of society.

society as a whole.

As experience shows, for example, a ban on registering inventions of a perpetual motion machine was imposed by the French Academy of Sciences back in 1775; nevertheless, even in this area numerous technical solutions of various kinds continue to appear, and their flow does not dry up despite

"scientific" dogmas.

Examples include the modern works of T.N. Morey [37, 38], the concept of energy inversions by Professor P.K. Oshchepkov, and the works of G.B. Lesovik and colleagues, who described a quantum heat engine [39]. The devices of P. Correa and A. Correa [40], and Yu.A. Efimov have been patented.

and Marina M. Yu. [41]. The inventions of John Searle [42], the magnetic field transgenerator of A. A. Melnichenko [43] and many others are well known. An informative review and personal research in this area are given in the book by A. V. Frolov "New Energy Sources" [44].

It is beyond the authors' competence to analyze the above and other ideas, hypotheses, and technical solutions in this area. However, it is obvious that the very existence of the Universe and matter as such is on a cosmic scale.

down to the microworld of atoms and elementary particles, there is "eternal" movement in its various manifestations (rotation, vibrations, fields and radiation, chemical and nuclear reactions, etc.), accompanied by the inversion of energy forms.

In all the above discussions, the question of the source of the "inexhaustible" energy, the surrounding space, and the physics of its transmission remains open. "The difficulty of imagining a non-mechanical medium capable of transporting energy and momentum gave rise to various mechanical models of the ether as a medium transporting electromagnetic interactions." However, the ether models had to be abandoned due to their contradiction with Einstein's principle of relativity [31, pp. 55-56]. Einstein's principle of relativity is presented in this case as an absolute truth, although it is well known that throughout the existence of the theory of relativity, there have been many of its opponents. A real alternative to Einstein's theory could have been, for example, the ballistic theory of W. Ritz (BTR) [45].

Walter Ritz (1878–1909) was a Swiss physicist and mathematician, and a fellow student of Albert Einstein. Ritz's theory of the theory of electrons is based on the hypothesis that all elementary charges (electrons) constantly emit tiny elementary charges.

ionic particles (reons) flying through space in all directions at the speed of light. The existence of corresponding antiparticles—areons—emitted by positrons is also assumed. According to V. Ritz's hypothesis, streams of reons and areons carry light, determining its speed, and are responsible for gravitational and magnetic effects. It is possible that due to V. Ritz's early death, his theory was long forgotten.

Essentially, without going into the details of the BTRs filling space, according to this theory, "reons" and "areons," which have dimensions orders of magnitude smaller than those of an electron, form a kind of medium filling space, similar to a hypothetical ether. The virtual particles of the physical vacuum can be considered in the same light. "In Maxwell-Dirac electrodynamics, the physical vacuum is a 'boiling broth' of virtual particles and antiparticles—

electrons and positrons, whose lifetime is determined according to the Heisenberg uncertainty principle" [46].

To sum up this brief excursion into theoretical physics, we can paraphrase the previous phrase and conclude that modern theoretical physics also represents a kind of "boiling broth" of hypotheses, theories, opinions, denials and assertions, given the uncertainty and meagerness of objective knowledge about natural phenomena on the scale of the Universe.

2.4.2 The mechanism for implementing Hess's law and the second law of thermodynamics

The application of Hess's law and the second law of thermodynamics to the consideration of catalytic reactions leads to the conclusion that it is impossible for a catalyst to influence a chemical reaction.

equilibrium. Indeed, when formally applied

Applying these laws to the analysis of catalytic processes makes it easy to conclude that catalysts have no influence on chemical equilibrium. However, a detailed, informal analysis of the role assigned to Hess's law and the second law of thermodynamics in the theory of catalysis reveals many controversial aspects, which forces a more cautious approach to the well-known classical thesis that a catalyst accelerates the onset of chemical equilibrium without being able to shift it. Oddly enough, classical theory does not contain consistent, deductive proof of the impossibility of shifting chemical equilibrium by catalysts.

It should be said that the following reasoning is valid in all points are consistent with the law of conservation of energy and with the principle of least energy.

Even without going beyond classical physical-chemical theory, it is possible to prove in several ways that the analog of Hess's law (the law of additivity) is not applicable to Gibbs free energy. Then, to substantiate the possibility of disturbing physical-chemical systems from equilibrium using catalysts, using energy sources not considered in classical chemistry (it is important to note that these phenomena are known in chemistry, but not as energy sources).

Hess's law suggests that the change in enthalpy in a In zyciochemical processes, the enthalpy depends only on the initial and final states of the system. This means, among other things, the following: If the enthalpy decreases at some stage of the process, it is converted into thermal energy, which can be used at the next stage of the process to increase the enthalpy of the next intermediate product.

It's easy to see that without this possibility, the change in enthalpy in a physicochemical process would depend on the intermediate stages. If we apply similar reasoning to entropy, it turns out that, unlike enthalpy, increasing at any stage of the process does not transform into some physical carrier that can compensate for this increase at subsequent stages (i.e., decrease entropy further). This is completely consistent with the second law of thermodynamics.

2.4.3 Dependence of the change in Gibbs energy on the intermediate stages of the physicochemical process

From the two theses considered, which correspond to the classical theory, follows a conclusion that clearly contradicts it: that the change in Gibbs energy in a physicochemical process depends on the intermediate stages. This means, for example, that catalysts (including enzymes) can shift the chemical

equilibrium by changing transition complexes and other intermediate reaction products.

The reason (according to classical theory) is that it is the Gibbs energy (not the enthalpy) that determines chemical equilibrium.

Thus, the classical physical-chemical theory turns out to be internally contradictory, actually admitting (as strange as it may sound) the possibility of the existence of chemical "perpetual motion machines" of the second kind, the action of which is based on the imbalance of entropy when carrying out "the same reactions" with different catalysts (or without a catalyst). It should be borne in mind that we are not talking about the fact that some

and the same reaction products can have different entropy in the

depending on the intermediate stages of the reaction. It is assumed that That obtaining the same products at different intermediate stages of reactions requires different expenditures of organizing (controlling) actions, or, in other words, "anti-entropy" (information) to compensate for the different increases in entropy at certain stages of these reactions (while the same products with identical entropy will be obtained). This conclusion is based on the fact that the law of conservation of entropy is not provided for, among other things, by classical physical chemistry.

Thus, even without going beyond the framework of classical physical chemistry, it is easy to prove the possibility of shifting chemical equilibrium by catalysts, which is equivalent to the creation of chemical "perpetual motion machines", in this case, of the second kind.

No less obvious is the proof of the possibility-
The potential for shifting chemical equilibrium by catalysts is associated with the nonlinear distribution of molecules by kinetic energies. If a catalyst is introduced into an equilibrium mixture of reversibly reacting substances, reducing the activation energy of both reactions by the same amount, which corresponds to classical concepts, then, due to the nonlinear (and different for different real substances) distribution of molecules by kinetic energies, the number of reactive molecules entering into the forward and reverse reactions will change differently. Under these conditions, the catalyst will disturb the system from chemical equilibrium. Such catalysts are referred to above as type 2 catalysts.

The above reasoning also does not go beyond the framework of classical theory and at the same time allows us to substantiate the possibility of creating chemical "perpetual motion machines" of the second kind.

2.4.4 Quantum-chemical structures as a source of non-traditional energy

According to classical physicochemical theory, electrons in molecules (and atoms) are constantly in a wave process (even in stationary states). At the same time, the electron wave encounters destabilizing influences, which can lead to energy losses (for example, during chaotic intermolecular contacts during thermal motion). It is natural to assume that the electron

constantly receives energy to maintain the wave process from one region of physical space and constantly re-radiates it to another region of physical space. The complex nature of the formation of electron clouds (waves) and their dynamic ordering indicate that the energy exchange between regions of physical space and the electron is subject to certain specific patterns.

and is probably regulated, i.e. it can be assumed that quantum chemical structures are self-organizing systems.

Conclusion. The above considerations suggest that quantum-chemical structures contain effects governing the flow of energy in physical space, supporting the fundamental property of electron quantum-wave duality. Under these conditions, the application of Hess's law to physicochemical systems is possible only in special cases (as to energetically open systems), and the application of the second law of thermodynamics to them is also possible only to a limited extent (as to self-organizing systems).

The presence of self-organization phenomena in quantum chemical structures can be considered as a deviation from the 2nd law

thermodynamics (for quantum-chemical, not heat-exchange processes), which leads to the dependence of dH on the intermediate products of chemical reactions, i.e., to deviations from Hess's law, which is sometimes considered the equivalent of the first law of thermodynamics for physicochemical processes. Thus, deviations from the second law of thermodynamics in the field of quantum-chemical processes lead to deviations from the first law of thermodynamics (for thermochemical processes).

These conclusions were reached based on deductive reasoning consistent with classical physics and taking into account known facts from the field of quantum chemistry. With regard to the action of catalysts, the following conclusion is possible. The shift in chemical equilibrium during catalysis is associated with the differential use of the energy of physical space under the influence of self-organizing quantum chemical structures. The action of such catalysts (type 3 catalysts—see above) can lead to a significant increase in the energy of the reaction products.

2.4.5 Activation energy and self-organization in quantum chemical structures

An important fact indicating the susceptibility of quantum-chemical structures to control effects is the following:
ing.

As is well known, activation energy characterizes reactions, not reactants. Obviously, the same molecules behave differently (with respect to the formation of activation energy) depending on the molecules they encounter. This is easily substantiated by the assumption that

the structures on which the activation energy depends are subject to

Control effects occur, and molecules exchange control effects upon contact, which leads to the formation of different activation energies. For example, catalyst molecules, through their control effects on reactant molecules, reduce EACT.

The susceptibility of Eact to control effects allows suggest the possibility of shifting the chemical equilibrium by catalysts, which is most clearly demonstrated when considering catalysts of type 1 (see above).

The shift in chemical equilibrium by type 1 catalysts is achieved by the fact that the development of the transition complex between the substrate and the catalyst in a reversible reaction proceeds through different stages in the forward and reverse reactions. This is achieved through low-energy control actions.

Considering that, theoretically, engines that use type 3 catalysts are comparable in power to conventional chemical engines (i.e., these are very powerful engines), let us consider in more detail the possible mechanism of action of type 3 catalysts.

Let us consider, to some extent, the behavior of electrons in terms of self-organization. It is quite obvious that An electron constantly receives energy to maintain the wave process. It is also obvious that in a stable state, an electron is not a moving wave. There is no indication that the energy capable of disrupting the oscillatory process and converting a standing wave into a moving one is directly related to the energy of these waves. On the contrary, the opposite is more natural: some very insignificant control action can be capable of converting an electron from a standing wave to a moving one (as is possible with other waves encountered in physics).

Let us assume that after the electron is transferred from the standing wave into a moving one and its spontaneous transition to another orbital (with a different energy), the quantum-chemical structure within which this process occurred will disintegrate under the influence of low-dE controlling influences. Subsequently, conventional energy barriers may appear in this quantum-chemical structure, including those preventing the electron from re-entering its previous orbital. In this situation, controlling influences on the electron cloud lead to the use of non-traditional energy for the chemical reaction, in which the dE of the quantum-chemical structures can be either negative or positive.

Let us now analyze the extent to which these processes can be supported by the action of catalysts. Obviously, the catalyst molecule must enter into wave interaction with the reactant molecules. In the general case, it can do this with the appropriate fixation of the reactant molecules on the catalyst molecule. Further, the process of combining the electronic structures of the reactant and catalyst molecules is apparently associated with the presence of electron clouds with sufficiently labile wave parameters in the catalyst molecule, which favors

which allow the catalyst's electrons to come into contact with the reactant molecules' electrons. After this, low-dE control signals should be generated in the catalyst's electron clouds, transferring the standing electrons

waves in moving ones.

The appearance of such signals is not surprising; disturbances in an ordered wave process can be introduced by various influences, for example, when the conformation of the catalyst molecule changes during chaotic collisions with other molecules.

The nature of the resulting moving electron waves depends largely on the electron structure of the catalyst molecule (as well as the electron structure of the reactant molecules). It is natural to assume that, under these circumstances, the electron density may be redistributed in such a way that, in the event of decomposition of the reactant-catalyst complex, the electrons will end up in orbitals corresponding to the desired products of the chemical reaction.

Consequently, if one-way conductivity of moving electron waves is ensured in a catalyst molecule (or in the transition complex as a whole), this will ensure the decomposition of the transition complex after the moving electron waves, using non-traditional energy, create a corresponding redistribution of electron density in the transition complex, and before the electrons return to their initial state. The existence of such one-way conductivity of moving electron waves in molecules can be ensured due to the fact that electron behavior, as is known, obeys complex laws, and the parameters of the wave process are related to the electron energy in both directions, and the electronic structure is not uniform with respect to energy and wave formation. Under these conditions, the stability of the electronic structure may depend on the sequence and parts of the sequence in which certain disturbances appear.

Thus, the movement of an electron wave in one direction may not lead to significant destabilization of the electronic structure of the transition complex, but its movement in the opposite direction can destabilize the transition complex and cause its disintegration.

Therefore, within the transition complex of the molecule-
the catalyst molecules and the reagent molecules are quite possibly

The existence of structures that ensure one-way conduction of moving electron waves is a reasonable hypothesis. The existence of a catalyst that, through controlled actions, generates a moving electron wave and, at the appropriate moment, also through controlled actions, destroys the transition complex is quite logical. Such a catalyst is capable of increasing the energy of chemical reaction products using non-traditional quantum-chemical energies.

In this regard, it is possible to assume the following functional model of the catalyst molecule of type 3.

2.4.6 Functional model of type 3 catalyst

The molecule of such a catalyst must contain the following systems. System 1, which ensures preliminary mutual fixation of the molecules of the reactants and the catalyst. System 2, which ensures the electronic docking of the molecules of the reactants and the catalyst. System 3, which ensures the appearance of the corresponding moving electron waves in the transition complex. System 4, which ensures

unilateral conductivity of moving electron waves in the transition complex.

It should be expected that the requirements for individual correspondence between the parameters of these systems and the catalyzed reaction are different for different systems.

System 1 can have different specificity depending on the mode of intermolecular interactions between the catalyst and reagents.

System 2, which is presumably a quantum-chemical structure with labile wave parameters, can

can, in this regard, provide electronic docking of molecules-catalysts with different reagent molecules, i.e. it may not be specific for each catalyzed reaction.

The redistribution of electron density in transition complexes is directly determined by system 3, therefore, it must individually correspond to the nature of the catalyzed reaction.

System 4, apparently, can also be stereotypical in many catalysts that facilitate various reactions. If system 4 is absent from the considered functional model, then such a catalyst will accelerate only those reactions that lead to a decrease in the energy of the products. Consequently, the proposed hypothesis allows us to substantiate the mechanism of action of conventional catalytic

tori, but along with this, it also allows for prediction the existence of catalysts that affect chemical equilibrium and can increase the energy of reaction products without consuming thermal energy from the environment (this is typical for type 3 catalysts).

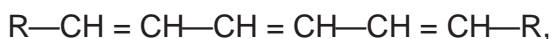
2.4.7 Active center of the enzyme

Let us compare some properties of enzymes with the functional model considered.

It is known that the composition of the active centers of enzymes, catalyzing The cysteine residue containing the SH group is present in the molecules that mediate very different reactions. This circumstance may be consistent with the model under consideration if we assume that the SH group contains electron clouds with highly labile wave parameters, i.e., plays the role of system 2.

Let us assume that protein molecules, due to the properties of their primary structure, may contain long delocalized bonds (running along the polypeptide chain). However, unlike typical delocalized bonds,

in molecules like:



where these bonds can be stable, in the polypeptide

Chains of delocalized bonds do not have such obvious prerequisites for stable existence. The formation and decay of such electronic structures (boundary, resonant structures) occurs without the supply of external energy (spontaneously). It is important that a large delocalized bond can decay by a chain mechanism with directional transfer

energy.

This allows us to assume that the polypeptide chain can, on the one hand, generate various moving electron waves (the parameters of which depend on the structure of the protein) in long delocalized bonds and, on the other hand, these delocalized bonds can easily be destroyed (reversibly) under the influence of minor control effects.

Consequently, the structure of enzymes allows us to assume the existence of systems 3 and 4 in them as well.

Thus, in the active center of the enzyme one should expect to find systems 2 and 1, and in other parts of the protein molecule - to find systems 4 and 3. Having analyzed a number of properties of enzymes, it is not difficult to find confirmation that the active center of the enzyme actually determines the catalytic action only partially. For example, it is obvious that there are many different ways to reproduce similar

The spatial orientation of the molecules that make up the active center (amino acid residues, heme-like structures, metal ions, H₂O molecules, etc.) should be very large. In other words, the number of protein chain variations in enzymes with similar catalytic activity at similar active centers should be very large. The structural diversity of isoenzymes should approach the structural diversity of enzymes, but this is not the case in reality.

On the other hand, according to the functional model of the catalyst molecule discussed earlier, the enzyme's active center, containing systems 2 and 1, is no longer considered to be the part of the enzyme molecule that primarily determines the type of catalyzed reaction and its rate. On the contrary, such an active center merely ensures the initial placement (due to system 1) and electron docking (due to system 2) of the reactant molecules with the enzyme molecule. Further action on the reactant molecules, which directly accelerates a particular chemical reaction, is provided by systems 3 and 4, which may be located outside the active center and include a significant portion of the enzyme molecule (this applies primarily to system 3). Consequently, to catalyze a particular chemical reaction, it is not enough to reproduce only the enzyme's active center; it is important to create appropriate structures that also include other parts of the protein molecule (possibly a large portion of it). Also, by analyzing the properties of real protein molecules, it is possible to assume that the reproduction of the active center may not require such a large number of amino acids in the entire enzyme molecule, i.e., from an evolutionary point of view, the appearance of huge

enzyme molecules containing one (small) active center.

In this regard, it is logical to assume that the catalytic process directly involves a large portion of the enzyme molecule, not just the active center. An obvious way for this portion to participate in catalysis is by generating moving electron waves in unstable delocalized bonds toward the active center (and the substrate molecule). Consequently, the functional model of the catalyst molecule is consistent with many properties of enzymes. On the other hand, this model suggests the possibility of shifting chemical equilibrium by catalysts (including enzymes), since protein catalysts, based on their structure, provide the prerequisites for finding systems 1, 2, 3, 4.

Let us now analyze the extent to which the considered model corresponds to the properties of metallic catalysts. As is known, a metallic crystal contains a highly developed system of multielectron (delocalized) bonds, which are also highly labile. This suggests the existence of system 3 in every metallic crystal. For a metallic crystal to acquire catalytic activity, it is necessary to create systems 1 and 2 within it, i.e., sorption centers and electron clouds with particularly labile wave parameters in the region of these sorption centers. For a metallic crystal to acquire the properties of a type 3 catalyst, it is necessary to create system 4 within it, i.e., quantum-chemical structures with one-way conductivity of moving electron waves that would be associated with the sorption centers.

Considering the relatively low ordering of the electronic structure in a metallic crystal, it should be expected that

that they are characterized by systems of type 1, 2, 3, but systems of type 4 are uncommon, i.e. metal catalysts can very rarely be catalysts of type 3 (unlike proteins).

Thus, the assumptions about the mechanism of action of type-3 catalysts discussed earlier are consistent with many properties of real catalysts. The hypothesis about the mechanism of action of these catalysts, from the rather obvious premise of wave interaction between the electrons of the catalyst and the reactant, derives the thesis that under these conditions, the catalyst can easily influence the dG and dH of chemical reactions.

The analysis of the problem presented in this section is purely deductive. It consistently traces the interrelations of Hess's law, the second law of thermodynamics, the phenomena of activation energy formation, and the phenomena of molecular distribution by kinetic energy. It follows from this that conditions are theoretically possible under which catalysts are capable of shifting chemical equilibrium.

Such catalysts can presumably be divided into at least three types, depending on the phenomena they exploit to shift chemical equilibrium. As is well known, studies of the mechanism of catalyst action within the framework of classical chemical thermodynamics have not yielded significant progress over many years. It is possible that the mechanism of catalyst action does not correspond to classical chemical thermodynamics, in which case attempts to study it within a traditional theoretical framework are unpromising.

Clearly, self-organization phenomena in catalytic processes (including enzymatic processes) require detailed study. The theoretical considerations presented in this section provide a rationale for this direction in catalyst research.

Chapter 3

PHYSICOCHEMICAL KINETICS LIQUID DIELECTRICS

3.1 THEORETICAL ASPECTS OF KINETICS STRUCTURING OF MOLECULES IN LIQUID DIELECTRICS

In general, a liquid can be considered as a medium consisting of various reagents and products of physical and chemical mic processes, with the participation of various supramolecular associations (as well as from non-associated molecules), which has thermal and quantum energy to support continuous spontaneous development (self-restructuring). It can be said that liquid clusters are a reaction mixture characterized by autocatalytic phenomena due to the possibility of forming low-energy control processes during physicochemical reactions using their energy effect, and which is at the same time provided with energy sufficient for the catalyzed reactions to proceed [4, 5].

Given the complexity and wide variety of reactants and products of such reactions, it should be assumed that the liquid is generally a reaction mixture that will never reach a state of equilibrium.

Liquid clusters, including film structures, are formed under the action of various intermolecular interaction forces (mainly donor-acceptor bonds, dipole-dipole bonds, dipole-induced dipole bonds, dispersion forces) [47]. Regardless of the predominance of these or other interactions, it can be said that if even two non-associated liquid molecules join, the velocity of thermal motion of such a cluster will be lower than that of non-associated liquid molecules. In this case, when this cluster collides with a non-associated liquid molecule, it (the non-associated molecule) will lose some of its speed and, on the other hand, a dipole may be induced in it. Both of these circumstances contribute to the inclusion of this molecule in the cluster. In this way, a three-molecular liquid cluster will be formed, and in a similar manner, a fourth non-associated liquid molecule will join it, etc., which will mean spontaneous growth

a liquid cluster surrounded by unassociated liquid molecules.

This phenomenon can be modeled through the distribution of kinetic energies of unassociated and clustered liquid molecules. The kinetic energy of an unassociated liquid molecule upon contact with a cluster will be distributed throughout the cluster as the kinetic and potential energy of associated molecules (already in the cluster). This will lead to the inclusion of this molecule in the cluster (based on the principle of least energy).

Physicochemical kinetics of liquid dielectrics

The process of cluster growth will continue until its "surface" area is such that the probability of breaking the bonds of one liquid molecule with the cluster is equal to the probability of forming bonds of an unassociated liquid molecule with the cluster. This probability depends on

statistics of the quantum and thermal distribution for a given liquid cluster and unassociated liquid molecules. It is important to consider that as the liquid cluster grows, these distributions will change, and this, in turn,

affects the speed and direction of cluster development, in this regard, it is obvious that the development of liquid clusters is probabilistic in nature and is not equilibrium.

It is also important that in different parts of the cluster the nature of intermolecular interactions will generally be somewhat different, which is associated with the specific orientation of the dipoles (this depends, in particular, on their shape). Thus, it can be said that in the general case, liquid clusters

The steps are anisotropic.

It is very important to take into account that in the environment of unassociated liquid molecules and liquid molecules included in the cluster,

the ratio of the significance of thermal and quantum statistics

distributions in the general case will be different.

Typically, for liquid molecules included in a cluster, the role of quantum statistical distributions increases, while thermal distributions decrease. Moreover, the pattern of thermal and quantum statistical distributions required for cluster formation differs from the pattern of thermal and quantum statistical distributions required for a particular cluster transformation (for example, for its disintegration). Taking this into account, it can be said that the process of cluster formation occurs with

one relationship between the importance of thermal and quantum sta-

The quantum distribution is different, while the decay process is different. Moreover, the probability of some cluster transformation (including decay) usually depends on quantum distributions more than the probability of a given cluster forming from unassociated molecules. This increases the role of the mutual quantum influences of liquid molecules on each other (which largely ensures cluster stabilization).

Consequently, a liquid cluster is more likely than unassociated liquid molecules to undergo a change that can be classified as a multimolecular concerted quantum transition (hereinafter referred to as MQT).

In the case of MSC, the primary factor is not the movement of molecules, but rather the change in their electronic structure. A change in the electronic structure of the liquid molecules within a cluster will cause a change in its size, shape, speed, and direction of translational and rotational motion, etc. (these changes will then be secondary).

The relationship between the significance of quantum and thermal statistics
Since the quantum distributions in the environment of non-associated liquid molecules and in the cluster are different for different types of intermolecular interactions, it can be assumed that it is maximum for donor-acceptor bonds, which have a purely quantum nature.

An important argument confirming the major role of the MSC in the development of liquid clusters is the abrupt nature of the motion of Brownian particles. Considering that the size and mass of a Brownian particle are poorly comparable to the size and mass of an individual liquid molecule, but are comparable to the size and mass of liquid clusters, it can be assumed that the abrupt changes in tra-

Projections of Brownian particles can be caused by the following reasons:

- the formation of huge imbalances in the collisions of individual liquid molecules on different sides of a Brownian particle during their chaotic thermal motion

research institutes:

- a sharp change in the trajectory of a Brownian particle during the transformation of the surrounding liquid clusters, which occurs due to the MCSP (i.e., in a jump-like manner, which is typical for quantum processes).

The first reason is unlikely, since its existence is extremely

While this is not difficult from a purely statistical standpoint, the second reason may occur when the quantum properties of liquid clusters are sufficiently pronounced. From these considerations, it can be assumed that Brownian motion is primarily a quantum process associated with the spontaneous transformation of liquid clusters.

Taking into account the kinetics of growth and destruction of liquid clusters, the following conclusion can be made. The least mutual damage will be caused to each other by transforming

Liquid clusters, between which are layers of unassociated liquid molecules, which can most easily change their size and shape without significantly affecting the liquid clusters. This system will be the most stable. Such a system can be created artificially in a liquid, for example, by applying electromagnetic or mechanical waves.

Let's take a closer look at water clusters. For water, hydrogen bonds are of the greatest importance (they are donor-acceptor bonds). Unlike other types

Intermolecular bonds characteristic of liquids are short-range, highly directional, saturable intermolecular bonds that are highly dependent on quantum statistical distribution (much less on thermal statistical distribution) and subject to control effects that occur in quantum chemical structures.

The energy of hydrogen bonds is quite significant (higher than the energy of most other types of intermolecular bonds characteristic of liquids). Hydrogen bonds between water molecules are formed by the acceptance of two electron pairs from the 2S and 2P atomic orbitals of oxygen into two antibonding molecular orbitals of covalent bonds.

oxygen-hydrogen.

Two hydrogen bonds (formed by two water molecules) are not identical, in one the electron pair is accepted with the 2S, and in the other with the 2P orbital of oxygen, therefore, the similarity of the two hydrogen bonds directly depends on the degree of SP hybridization in the water molecules.

Assessing the degree of hybridization is currently one of the most controversial areas in the theory of molecular structure. Hybridization theory is sometimes confirmed, sometimes not, but it is a convenient model reflecting the profound rearrangement of atomic orbitals that occurs when an atom transitions from a normal to an excited state. This allows us to assume the following. It is the degree of hybridization (in this case, SP) that is the link in water clusters that is most susceptible to low-energy (controlling) effects and statistical quantum distributions. Accordingly, a very promising approach is

The development of water clusters is considered depending on

from the degree of hybridization of electrons in a water molecule (water cluster).

A change in the degree of hybridization means a change in the length of both hydrogen bonds (one will decrease, the other will increase), a change in the energy of both hydrogen bonds (one will increase, the other will decrease), and a change in the bond angles (not only for hydrogen bonds, but also for covalent bonds). These are the most pronounced effects that a change in the degree of hybridization will have on a water cluster. It should be noted that an increase in the length of a chemical bond usually reduces its strength, and a deviation of the bond angle from some optimal value also destabilizes the chemical bond.

Taking the above into account, let's consider more complex water clusters. Water clusters spontaneously grow to a certain size. If each unassociated water molecule included in the cluster forms two hydrogen bonds with one water molecule already in the cluster, a ribbon-type cluster will form. If one water molecule included in the cluster forms two hydrogen bonds with two unassociated water molecules (when they are included in the cluster), a cluster with a branched structure will form.

The probability that two hydrogen bonds will form with two different water molecules is higher, the longer the time interval between the formation of the two hydrogen bonds. During this time, the second molecule must have time to occupy a position in which its acceptor orbitals (and donor electron clouds) will be spatially aligned with the donor electron clouds (acceptor orbitals) of the counterpart molecule. Theoretically, an increase in this

time interval will occur when the degree of hybridization in a molecule already included in the cluster decreases.

A very important question is the possibility of spontaneous chain depolymerization of water entering into a cluster with its parallel chain polymerization, during which another cluster is formed (spontaneous chain reaction of the transition of one cluster to another).

Theoretically, such a possibility exists for various liquids; given that water is characterized by donor-acceptor intermolecular bonds (hydrogen bonds), it should be expected that this effect will be quite pronounced in water. The main mechanisms for the formation of MCSP in water can be assumed to be a change in the degree of hybridization and the interconversion of hydrogen bonds into covalent bonds and vice versa. The interconversion of hydrogen and covalent bonds may underlie the high-temperature superconductivity of water.

By fixing a proton at one end of a chain water cluster, a negative charge can be obtained at the other end of the cluster in a time typical for the ICM, i.e., in a time typical for quantum transitions. After this, the fixation of the con-

the terminal proton can be removed and the cluster relaxes with the restoration of charge balance, if the fixation is not removed, the excess electron can be fed into the electrical circuit and the charge will return to the terminal proton from the electrical process.

waterman.

If we are not talking about pure water, but about alkaline solutions, this will allow negative charges to easily form at the ends of chain clusters. It is important that for a cluster, transferring charge, during the entire act of charge transfer (along the cluster) at its other end (to which the charge is transferred)

(series) the hydroxyl anion, which could create the preconditions for reverse charge transfer, did not appear.

Based on data on surface phenomena, it can be said that the most labile water clusters are those located at phase boundaries (e.g., liquid–vapor). Clusters in pure water and in water containing impurities differ to varying degrees depending on the nature of the impurities, their concentration, and the physical effects exerted (or previously exerted) on the water (e.g., water temperature).

Obviously, the most pronounced impact on water clusters is exerted by substances that enter into chemical reactions with water, such as fluorine, oxygen, ozone, alkali metals, and others (upon contact with them, water is transformed into another chemical substance). The second most significant impact on water clusters is exerted by substances characterized by hydrogen bonds (acids, alkalis, alcohols, etc.).

A specific reagent that changes almost all water clusters, mainly due to hydrogen bonds, is unstructured water.

A typical case here is the condensation of water vapor (vapors lack liquid clusters) on water droplets (containing clusters, like other forms of water in the liquid state). In this case, structured water comes into contact with unstructured water, which, theoretically, should form clusters significantly different from the previous ones. In this situation, the condensation of water vapor should proceed differently depending on the type of clusters already formed in the liquid phase. Accordingly, the condensation of water vapor will differ on different hydrophilic surfaces. Strictly speaking, portions of water having a different or similar structure at

contact will interact with unpredictable (within statistical distributions) changes in clusters.

Thus, in addition to the properties common to various structuring liquids, the structure of water has a number of important features. Theoretically, if a large liquid cluster undergoes a certain MCS initiated by a charge at one end, and the MCS leads to the formation of a similar charge at the other end of the cluster, this will mean charge transfer at a rate characteristic of this quantum transition. This can provide effects of local superconductivity in the liquid. The most pronounced

The self-development processes of liquid clusters should be expected in thin water films.

3.2 WAYS OF ENERGY CONVERSION OF WATER FILMS

Let us consider the possibility of using the mechanical energy of moving liquid layers in thin aqueous films as one of the non-traditional sources of bioenergy.

To do this, we will substantiate two assumptions.

1. A thin water film is characterized by self-organization phenomena (anti-entropic phenomena), which include balance of the processes of chain disorganization and chain self-organization of the film structure.
2. A thin water film is an anisotropic liquid a structure capable of responding to the chaotic effects of molecules in the environment (during their thermal movement) more ordered (mainly in the longitudinal direction) movements of molecules in the film structure.

Let us consider the possibility of film formation in the absence of the effect of self-organization phenomena [48–50].

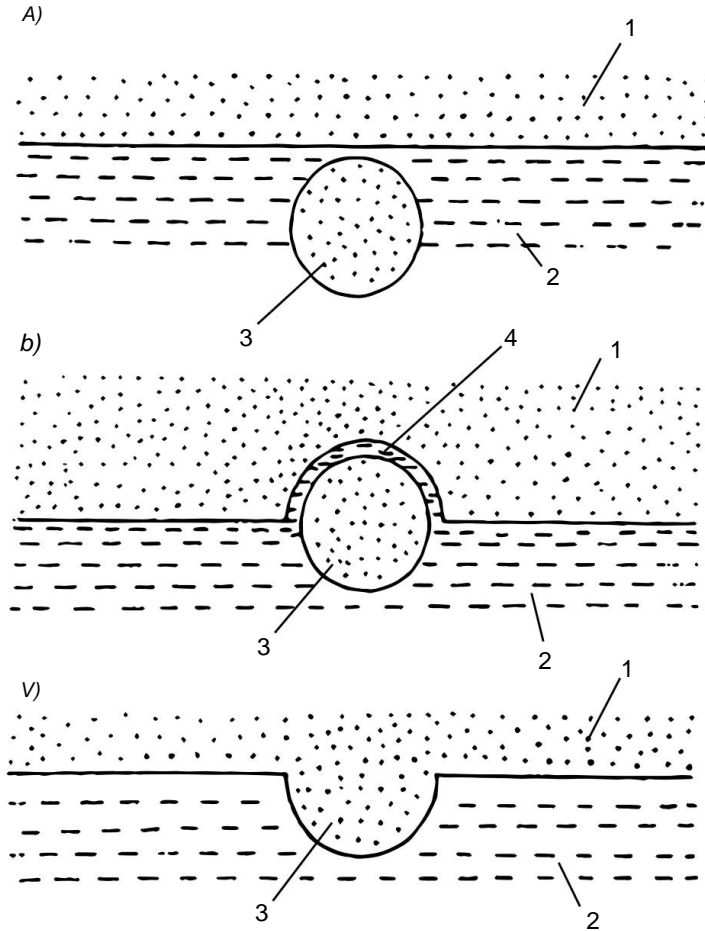


Fig. 3. The process of a bubble emerging from water: 1 – air, 2 – water, 3 – air bubble, 4 – film structure

Let us assume that an air bubble rises through a layer of water, at the upper boundary of which there are molecules of

surface-active agent (surfactant) in sufficient concentration (Fig. 3a).

Area (S) of water/air contact (total surface and bubble) should be kept to a minimum:

$$S_{\text{contact}} = S_1 + S_2 .$$

The situation changes when the bubble crosses the top layer of water, forming a film (Fig. 3b).

The contact area S increases due to the protrusion of the liquid above the bubble (S_1 increases with the same S_2). In the absence of film formation above the bubble (Fig. 3c), its emergence allows the water/air contact area to continuously decrease, ultimately to S_1 .

Let us analyze the possible causes of film formation, taking into account the above points. Let us assume that film formation is ensured by the increased viscosity (strength) of the initial surface layer of water on which the surfactant molecules are adsorbed. However, when the film is formed, no qualitative

changes.

This assumption contradicts a number of facts.

Firstly, significant liquid currents, uncharacteristic of the original water surface, are visually detectable on the film after its formation. This suggests that the film structure is maintained not by the passive strength of the initial surface layer, but by the dynamic stabilization of this thermodynamically unstable system (which is only possible through its self-organization).

Secondly, based on the stabilization of the film due to the high viscosity of the initial surface layer, it is difficult to justify

presence of surfactant molecules on both sides of the film after its formation [50].

Third, the surface layer of water, given its initially high viscosity, should be difficult to overcome for air bubbles and other objects of similar size, shape, and mass floating to the surface of the water. However, this generally does not occur. For example, objects made of hydrophilic materials are not retained by the surface layer, meaning that, in most cases, an effect analogous to foaming is absent for them. This suggests that the leading role in the formation of thin water films is played by the properties of the phase boundary, rather than the initial strength of the surface layer of water.

Based on this, it can be assumed that when the path exits, As a bubble of air rises from the water, the thickness of the water layer above the bubble decreases, and upon reaching the appropriate (small) thickness of the water layer, a qualitative change in the modes of intermolecular interactions occurs, transforming the water into a highly viscous, dynamically stable state. Surfactants are also necessary for this; however, what is important is not the initial viscosity of the surface layer formed by water molecules and surfactants, but the dynamic stability of the resulting film structure (Fig. 4).

Dynamic stability of a thermodynamically unstable system presupposes compensation for disorganization processes.
self-organization processes.

Chain disorganization can be seen in direct observation when a "black film" is formed. "Black" areas, appearing on a small part of the film surface, spread

are spread over the area, the thickness of the liquid layer in them decreases until a rupture occurs [49, 50]. At the same time, other parts of the film-

The sections where "black" areas did not appear show no signs of disintegration. This indicates that film disintegration is accelerating in the part where it was not promptly compensated for by self-organization processes, and that the disorganization process developed spontaneously, that is, it was a chain reaction.

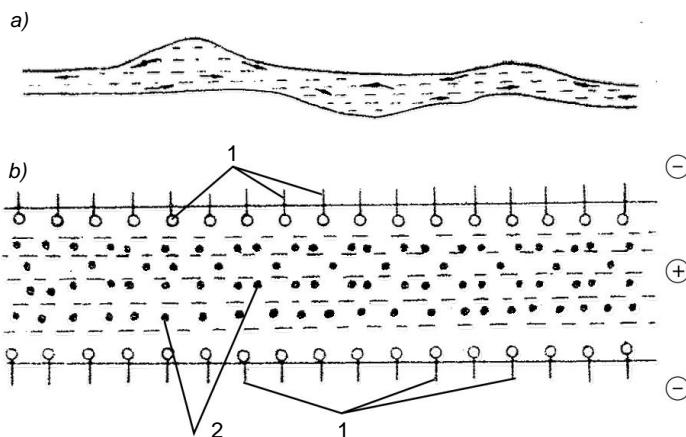


Fig. 4. Water film diagrams:

- a) section of a thin film with a symbol for liquid micro-displacements;
- b) film structure with anionic surfactants: 1 - anionic surfactant molecules, 2 - cations (counterions)

In this regard, it is quite natural to assume that the processes of self-organization of the film, capable of compensate for chain disorganization, are also chain-like, which allows the film to return to its original state from some stages of its disorganization.

Thus, the existence of the film can be represented in the form of alternating chain processes of its disorganization.

organization and self-organization, corresponding to self-oscillations of macroscopic transfer of liquid layers in a film structure.

Now let us justify the assumption that the film can-
can convert the energy of the chaotic motion of gas molecules in the surrounding environment into the energy of directed movement of liquid within its structure. The fact that the film is
An anisotropic liquid is quite obvious. Significant displacements of liquid along the film are easily observed visually. Similar displacements of liquid across the film are impossible due to the film's geometric dimensions. Therefore, the destabilizing effect of air molecules on the film, whose chaotic impacts on the film could theoretically serve as the primary cause of its chain disorganization, entails displacement of the liquid layers, primarily in the longitudinal direction, and its compensation by liquid currents during chain self-organization, also in the longitudinal direction (Fig. 5).

This means that chaotic effects of environmental molecules on the water film can create more directed movements of liquid in it.

From the phenomena considered it follows that the film can serve as an anti-entropic structure in which the energy of intermolecular interactions (quantum-chemical and thermal) is converted into the kinetic energy of macroscopic directed movements of liquid layers.

Let us consider possible ways of using this energy by the cells of living organisms.

These cells contain a number of organelles that are structurally related to highly concentrated emulsions in which the existence of aqueous films is possible. A thin aqueous film can

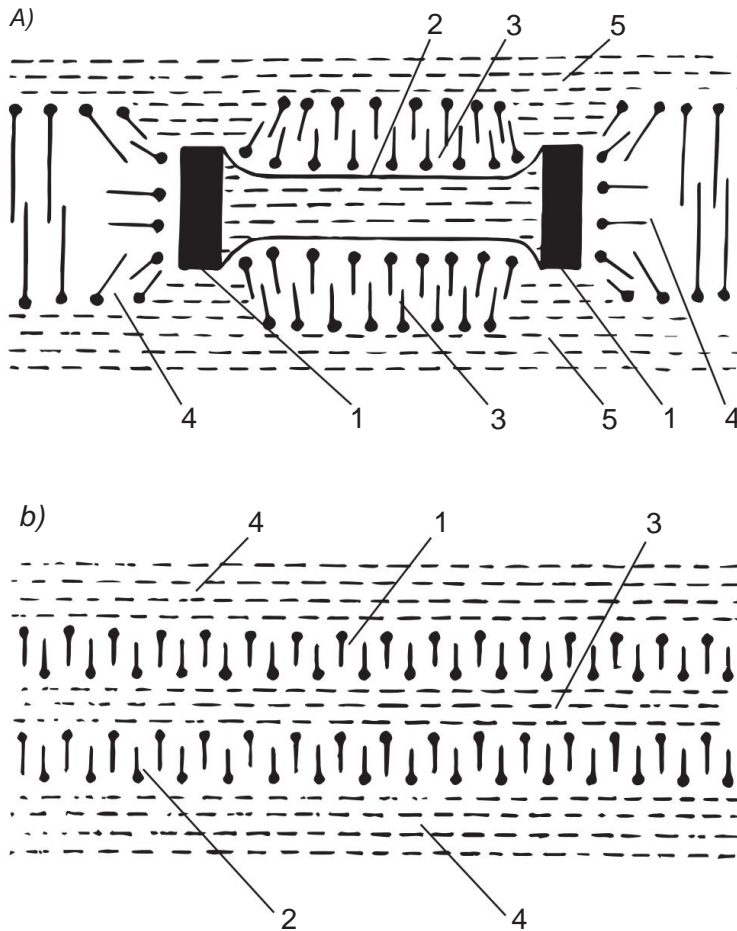


Fig. 5. Schemes of water films: a)

water film in a biomembrane:

- 1 - protein molecules, 2 - film structure,
 - 3 - surfactant molecules surrounding the film structure, 4 - lipid bilayer of the membrane;
- b) aqueous film between membranes of adjacent cells: 1, 2 - membranes of adjacent cells, 3 - thin aqueous film, 4 - water in non-film (thick) layers

exist in many biomembranes, as well as between biomembranes: in mitochondria, the nucleus, the Golgi complex, chloroplasts, at the border of neighboring cells.

The energy conversion pathways of aqueous films may vary. Considering that the film structure is stabilized, in part, by ionic surfactants present in biomembranes, it can be concluded that the film can directly generate EMF. A prerequisite for the generation of EMF may be the fact that the charges in the film are not uniformly distributed [49, 50], and if it is stabilized by anionic surfactants, its surface will be negatively charged. The latter is due to the fact that surfactants do not penetrate the internal layers of the film liquid, while cations from the dissociated ionic surfactant can do this (Fig. 46). In this case, the presence of self-oscillations of liquid currents in films leads to oscillations of unbalanced electrical charges. This, in turn, ensures the generation of alternating EMF and electromagnetic radiation, the amplitude and frequency of which correspond to the amplitude and frequency of mechanical oscillations of the liquid. By means of such a mechanism, water films associated with biomembranes can act as generators of EMF, as well as generators and receivers of electromagnetic radiation in a wide range of frequencies (including in the radio range). Along with electromagnetic radiation, during self-oscillations in the film structure, one can assume

detect the presence of radiation into the environment and mechanical waves. In this case, thin film structures can also have the properties of generators and receivers of mechanical, including sound, waves [51]. It is also possible that self-oscillations of films in biomembranes create changes in the geometric parameters of cells during their movement.

The area of biomembranes taking into account the endoplasmic reticulum is enormous, so it is possible that a significant part of the body's energy is produced by film water.

Let us consider the bioenergetic processes that can occur in cell membranes during functioning. such hypothetical energy sources.

Ion transport can directly utilize the alternating electromotive force generated by self-oscillations of the liquid in a film stabilized by ionic surfactants. Thus, the localized generation of excess negative charge on one side of the membrane in the region of an ion channel allows the corresponding cations to be transported through it. This ion channel is energetically passive, but by utilizing the energy of the film structure, it can act as an active transporter of the corresponding ions.

The movement of liquid layers in a film stretched between protein molecules results in the transfer of kinetic energy to them, which can lead to a change in their conformation and ensure the operation of protein systems for the active transport of substances (Ca^{2+} , Na^+ , K^+ , H^+ , H_2O , etc.). Similarly, it is possible to provide energy for the operation of protein pores to facilitate the diffusion of substances along a concentration gradient.

Thus, if we consider a water film as a self-organizing system with self-oscillations of liquid layers in its structure, then we can assume that the totality of such films is capable of providing energy for the processes of generating (and receiving) electromagnetic radiation, sound waves, active transport of ions, the creation of membrane electrical potential and facilitated diffusion of various substances through the corresponding pores [6]. In general, the transformative properties of many tissues of a living organism

can be considered from the standpoint of biophysics of layered-periodic structures [54].

It is important that in these processes the functioning of film self-oscillating systems does not require energy supply from traditional sources of bioenergy (ATP hydrolysis, tissue respiration, etc.).

3.3 HYDRATE SHELL OF THE ENZYME AS A SOURCE OF ENERGY FOR ENZYMATIC REACTIONS (HYPOTHESIS)

Let us assume that in a certain water cluster [52, 53] a chain or simultaneous change in the degree of hybridization (SP) of the electron clouds of oxygen atoms (in water molecules) occurs. Obviously, this will lead to a change in the water cluster, which can alter the conformation of the molecule hydrated by it. Despite the fact that the very concept of hybridization of valence atomic orbitals, as noted above, is only a convenient model for explaining the electronic structure of molecules, it creates the basis for constructing a possible system of energy production at the biomolecular level.

It is important that the initiation of such relaxation may require less energy than is released during it, as well as its reversibility and the possibility of energy release during both the direct and reverse transition (two-way relaxation). If we assume that the described processes take place in the hydration shells of biomolecules, then this allows us to put forward a hypothesis, the essence of which can be formulated as follows: *"Water clusters of the hydration shell of the enzyme are capable of*

to reversible relaxation, during which the substrate and enzyme

energy can be supplied that allows the activation energy to be exceeded.” It can also be assumed that in an enzymatic reaction the sign of $\ddot{y}H$ can change from (+) to (-).

The reversible reaction of water clusters (in accordance with the hypothesis) may be associated with a change in the degree of hybridization of the S and P electron clouds of the oxygen atom included in the H₂O molecule, due to low-energy control effects.

We will proceed from the logical hypothesis that S and P hybridization is not complete, and therefore the former S-electron pair will penetrate the nucleus better than the former P-electron pair. At the same time, the former P-electron pair will be more strongly shielded from the nucleus. Accordingly, two types of water clusters—*isomers*—will appear. Their properties cannot be identical, and the difference will be exacerbated if the degree of hybridization of the S and P electrons in the oxygen atom is me-

to take care of.

Let's assume that the protein portion of an enzyme can influence the degree of hybridization, which, accordingly, initiates the restructuring of water clusters in the enzyme's hydration shell, accompanied by the release of energy. This relaxation of water clusters can be reversible, and the reverse restructuring will also proceed with the release of energy.

This energy can be used to overcome the Eact of the fermentation reaction and to increase the energy of the products of the fermentation reaction (change of sign of $\ddot{y}H$).

Thus, according to the proposed hypothesis, the enzyme can draw energy for enzymatic reactions from its hydration shell. It should also be taken into account that restructuring the hydration shell will alter the conformation of the protein portion of the enzyme.

CONCLUSION

To sum up, we can say that by using the idea of self-organization as the basis for the bioenergetic model, we can significantly expand the scope of consideration of energy exchange processes in biological objects, linking phenomena characteristic of different levels of life organization.

Let us list these (previously considered) self-organizing phenomena.

Nation:

1. Low $\ddot{y}E\ddot{y}$ control effects on the catalyst molecule during the catalytic act, taking into account that the macromolecule (enzyme) is anisotropic with respect to changes in its conformation, and these changes are less chaotic than chaotic motion micromolecules of the environment, inducing a change in the conformation of the macromolecule.
2. A complex, nonlinear dependence $N(EKNH)$ for molecules of reagents and products of chemical reactions, which is antientropic and allows the catalyst to unevenly change $[C]$ of reagents for the forward and reverse reactions while decreasing $EKAT$ in each of these reactions by the same amount.
3. The existence of low $\ddot{y}E\ddot{y}$ control effects on the electron cloud, under which it transitions

Conclusion

from a standing wave (an electron in a stationary state) into a moving wave (the electron changes orbital). In this case, to change the orbital of the electron, energy is constantly supplied to it, providing a wave process in the electron in a stationary state.

tionary state.

4. The possibility of controlling the balance of various forces affecting the electron by low $\ddot{y}E\ddot{y}$ control actions, assuming that a number of forces acting per electron are not potential forces.
5. Self-organization during the formation of thin water films. Chain disorganization, compensated (before film disintegration) by chain self-organization phenomena, signifies the presence of mechanical self-oscillatory processes arising spontaneously under the influence of chaotically moving molecules in the medium surrounding the water film, or due to the thermal motion of molecules in the film itself, as well as due to changes in the modes of intermolecular interactions within it.

The application of these hypotheses in the field of physical and colloidal chemistry will allow us to develop new theoretical justifications for bioenergetic processes and expand the scope of consideration, modeling, forecasting and practical application of bioenergetic phenomena.

Consideration of bioenergetics phenomena taking these hypotheses into account presupposes the advancement of a concept of bioenergetics that is fundamentally different from the classical theory, based on the thesis of self-organization in living organisms at all levels, including the molecular level. Possible sources of bioenergy are traced, associated with the use of enzymes and ion transmembrane transporters, associated

with thin aqueous films, which makes it possible to link the biochemical and cellular levels of organization in terms of energy exchange. Along with this, the possibility of using thin-film structures as receivers of energy-generating and information signals, which are

Electromagnetic radiation, including radio waves, and mechanical waves (sound). It is also believed that the body may produce radiation in the radio range, as well as in the infrared and ultrasound ranges.

When discussing the bioenergetics of humans and higher animals, it is necessary to consider the regulatory and controlling role of the psychophysical component present in the biological processes of energy metabolism. Even in the simplest organisms, bioenergetic processes cannot be reduced to a simple set of laws of physicochemical kinetics. At the same time, processes in living matter are inherently oscillatory: "...the surface

cells are constantly in a state of movement and "trembling." These phenomena play a fundamental role in the normal and pathological physiology of the cell" [55, p. 116–

117]. All systems, organs, and tissues of any living organism function within a characteristic spectrum of biorhythms, determining the functional state of the organism as a whole. "Health is an optimal relationship between the interconnected rhythms of the physiological functions of the organism and their correspondence to the regular fluctuations of the habitat" [56, p. 32]. It has been established that bioenergetic processes and biorhythmodynamics closely correlate with a person's mental states, which determine his energy potential, level of adaptability, and performance [57].

Conclusion

In conclusion, it should be emphasized that the above-mentioned directions and hypotheses concerning the field of bioenergetics are only prerequisites for moving towards the creation of a holistic model of energy exchange processes in biological objects.

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Designations and abbreviations

NOTATIONS AND ABBREVIATIONS

A	mechanical work of
ADP	adenosine diphosphoric acid
ATP	adenosine triphosphoric acid
$[M]$	molar concentration of a substance
e^-	electron
E	energy
E _{KIN}	kinetic energy
E _{AKT}	E activation
ΔG	change in free energy in a chemical process
ΔG^0	standard free energy change
g	acceleration
h	height
K_p	equilibrium constant of the reaction
k_B	Boltzmann constant
MSCP	multimolecular coordinated quantum transition
	nicotinamide adenine dinucleotide
ABOVE NADP	nicotinamide adenine dinucleotide phosphate

Designations and abbreviations

n	number (quantity)
N	the number of corresponding molecules in the system
surfactants	surfactants
R	gas constant
ΔS	change in entropy
t	time
T	temperature °K
F	enzyme
V	volume
FAD	flavin adenine dinucleotide
W	number of microstates of physicochemical systems

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About the authors



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Table of contents

Preface	5
Introduction	7
Chapter 1. Biological Energy Dynamics	13
1.1 Assessment of energy costs during muscle work	13
1.2 Energy dynamics of biochemical reactions	22
Chapter 2. The phenomenon of catalysis	29
2.1 Modern problems of scientific theory	29
2.2 Catalytic processes in bioenergetics. Hypothesis on the shift of chemical equilibrium	35
2.3 On the phenomena of self-organization of physicochemical processes in living organisms	45
2.4 Deductive consideration of the phenomenon of catalysis in the aspect of bioenergetics	52
2.4.1 Law of conservation of energy in thermodynamics	53
2.4.2 The mechanism for implementing Hess's law and the second Law of Thermodynamics	58
2.4.3 Dependence of the change in Gibbs energy on the intermediate stages of a physicochemical process	60

2.4.4 Quantum-chemical structures as a source of non-traditional energy	62
2.4.5 Activation energy and self-organization	63
2.4.6 Functional model of type 3 catalyst	67
2.4.7 Active center of enzyme	68
Chapter 3. Physicochemical kinetics of liquids	
dielectrics	73
3.1 Theoretical aspects of the kinetics of structuring of molecules in liquid dielectrics	73
3.2 Pathways of energy conversion of water films	82
3.3 Hydration shell of the enzyme as a source of energy for enzymatic reactions (hypothesis)	91
	93
	97
	102
	104

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