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THERMODYNAMICS AS A BASE OF BEHAVIOUR OF INANIMATE AND ANIMATE NATURE

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Abstract. In this article the concept which allows to investigate the behavior of open (biological) systems by using the laws of unbalanced (classical) thermodynamics is examined. The second law of thermodynamics is applicable to open systems as well, provided that only in case of considering the whole system (continuum) “open system–environment” the total entropy will always increase. The law of temporary hierarchies allows to resolve quasi-closed thermodynamic systems in open biosystems and to investigate their development (ontogenesis) and evolution (philogenesis) by studying changes in the value of Gibbs’ specific functions of formation of any submolecular structure (including a population).

Keywords: thermodynamics, law, structure, biosystem, function of Gibbs, entropy, development, investigation.

Classical thermodynamics is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

Albert Einstein

1. General Methodological Aspects of Modern Thermodynamics

The concepts of classical and quantum physics allow one, either exactly or with a certain probability, to predict the state of macrobodies or microparticles. In particular, this concerns mechanical movement regularities which can be described by using spatial-temporal coordinates, the values of mass, velocity, pulse, wave characteristics, the knowledge of the fundamental type of interaction. However, there exist some processes which features cannot be explained by either classical physics or

quantum representations, *e.g.* the existence of bodies in different aggregation states, the appearance of elastic forces at deformations of systems, possible transformation of some compounds into others, *etc.* As a rule, these and similar processes are accompanied by transition of systems from one state to another one with changes in thermal energy. Such processes and most general thermal properties of macroscopic bodies are studied by the section of physics and chemistry called *thermodynamics* [1, 2, 9-11].

Thermodynamics studies a system, *i.e.* a body or group of bodies capable of changing under the influence of physical or chemical processes. Everything surrounding the system forms the external medium (environment). By a “body” any substance having a certain volume and characterized by some physical properties is usually understood. Thermodynamic systems can be homogeneous and heterogeneous. Every system is related with such a notion as the condition of a system, which represents a set of the quantitative values of all its thermodynamic properties. At change of at least one of these properties the system passes from one state to another. Usually, thermodynamic processes proceed at constancy of certain parameters of the system.

The bases of classical thermodynamics have been formulated in the works by Clausius, Van’t Hoff, Arrhenius, Gibbs, Helmholtz, le Chatelier, *et al.*, which describes processes depending on changes of the properties of systems in an equilibrium state. In other words, the thermodynamic description of systems and phenomena is based on the idea of an equilibrium state. Thermodynamics answers the question: where a process is directed before equilibrium is reached. Therefore it does not deal, in an explicit form, with time as a physical parameter and considers no mechanisms of processes. If a system infinitely slowly passes from one state to another through a continuous series of equilibrium states and if the

maximum work is thus done, such a process is called *thermodynamically equilibrium process*. Between two next states of equilibrium, the values of any functions of state of the system differ by an infinitesimal value, and it is always possible to return the system to its initial state by infinitesimal changes of the functions of state. The system can return to its initial state, having passed the same equilibrium states in the opposite direction, as in the direct one. Therefore, as a result of a *thermodynamically reversible process* the system and environment return to their original state, i.e. no changes remain in the system and environment. On the other hand, a process after which the system passes through a series of non-equilibrium states is called *thermodynamically non-equilibrium process*. If the system and environment cannot return to their original state, i.e. any changes remain in them, such a process is considered *thermodynamically irreversible*.

Thermodynamics only considers the initial and final states of a system which are characterized by special thermodynamic parameters. Usually, temperature, pressure, volume, and such *characteristic functions* as enthalpy, entropy, internal energy, Helmholtz free energy, and Gibbs thermodynamic potential act as such parameters of state. Just these functions and their values characterize the thermodynamic state of a system and cause the probability of proceeding of this or that process accompanied by changes of thermal energy. The functions of state allow establishing the direction of spontaneous processes and determining the degree of their completeness in real thermodynamic systems, e.g., Gibbs thermodynamic potential G can be used for exploring equilibrium (and quasi-equilibrium, as will be shown further) processes and closed (quasi-closed) systems, in which transformations proceed at constant temperature and pressure. Helmholtz free energy F is applicable to studying similar processes and systems at constancy of temperature and volume.

Thermodynamics is also a phenomenological science. This means that all physical quantities, functions and laws of thermodynamics are based on experience only, i.e. there is no strict theory concerning them. The sense of thermodynamics empirical provisions can be characterized as follows:

1) Unlike mechanical movement, all spontaneous thermal processes are irreversible (and, first of all, this applies to heat propagation in the environment).

2) According to various forms of movement and various types of energy there are also various forms of energy exchange. In classical thermodynamics, only two forms of energy transfer are resolved, namely, work and heat. Any kind of energy is an unequivocal function of the state of the system, i.e. the change of the energy does not depend on the way of the system transition from one state to another one. At the same time, heat and work are

unequal forms of energy transfer as work can be directly used for replenishment of the stock of any kind of energy, whilst heat – on replenishment of the stock of the system's internal energy only.

3) Any physicochemical system left to itself (i.e. in the absence of external forces and fields) always aspires to pass to the state of thermodynamic equilibrium; this state is characterized by the uniformity of distribution of temperature, pressure, density, and the concentration of components.

4) The characteristic functions of the state of system are interrelated by certain ratios, for example:

$$\Delta F = \Delta U - T\Delta S; \quad \Delta G = \Delta H - T\Delta S,$$

where ΔU , ΔH , and ΔS are changes of the internal energy, enthalpy, and entropy, respectively; T is absolute temperature, which points to their interconditionality and universality relative to the description of both initial and final state of the system.

The physical sense of the concepts of classical (equilibrium) thermodynamics is directly related with its three basic laws which are general laws of nature.

The second law of thermodynamics means that the processes of energy transformation can occur spontaneously only provided that energy passes from its concentrated (ordered) form to a diffused (disordered) one. Such energy redistribution in the system is characterized by a quantity which has been named as *entropy*, which, as a function of state of the thermodynamic system (the more energy irreversible dissipates as heat, the higher entropy is). Hence it follows that any system whose properties change in time aspires to an equilibrium state at which the entropy of the system takes its maximum value. In this connection, the second law of thermodynamics is often called the law of increasing entropy, and entropy (as a physical quantity or as a physical notion) is considered as a measure of disorder of a physicochemical system.

In connection with the notion of entropy, the notion of time gets a renewed sense in thermodynamics. As was already mentioned, the direction of time is ignored in classical mechanics, and it is possible to determine the state of a mechanical system both in the past and in the future. In thermodynamics, time acts as an irreversible process of entropy increasing in the system, i.e. the higher the entropy, the longer time interval has been passed by the system in its development.

It is also necessary to note that there are four classes of thermodynamic systems in nature:

a) isolated systems (upon transition of such systems from one state into another no transfer of energy, substance, and information through the system's borders proceeds);

b) adiabatic systems (no heat exchange with the environment);

- c) closed systems (no substance transfer);
- d) open systems (which exchange substance, energy, and information with the environment).

Such a classification of thermodynamic systems, at first sight, leads to a seeming contradiction between the general principle of relativity in nature and the validity of the second law of thermodynamics for whole nature. The matter is that ignoring exchange processes the second law of thermodynamics is directly applicable to systems a) and b) only, for which entropy either is constant, or (which is much more often) increases: $\Delta S \geq 0$. This means that in such systems the changes are characterized by increasing disorder (chaos) in them until the system reaches thermodynamic equilibrium (or its entropy reaches its maximum value). In open systems entropy may decrease. The latter fact, first of all, concerns biological systems, *i.e.* living organisms that are open non-equilibrium systems. Such systems are characterized by gradients of the concentration of chemicals, temperatures, pressure, and other physical and chemical quantities. In this regard, a seeming contradiction appears between the second law of thermodynamics and biological ordering.

The recovery from such a contradiction can be found in the use of the concepts of modern (*i.e.* non-equilibrium) thermodynamics which describe the behavior of open systems always exchanging energy, substance, and information with the environment. Schematically, the mechanism of interaction of an open system with the environment can be represented as follows. First, such a system at its functioning takes substances, energy, and information from the environment, and then gives it the used ones (naturally, in other types and forms). Second, all these processes are also accompanied by entropy production (*i.e.* energy losses and the formation of various wastes). Third (and this is most important), the formed entropy (characterizing a certain degree of disorder), without collecting in the system, is released into the environment, and the system takes from it new substances, energy, and information necessary for its optimum performance. All this allows drawing a conclusion that open system, as a result of exchange processes, can be in a non-equilibrium state as well, for whose description new laws (in particular, non-equilibrium thermodynamics) are necessary.

The concepts of non-equilibrium thermodynamics in its application to biological systems were developed by de Donder, de Groot, Mazur, Glansdorff, and Prigogine.

Another recovery from the specified contradiction is connected with the development of the concept of thermodynamics based on the possibility to apply classical (*i.e.* equilibrium) thermodynamics to real (open) systems. The matter is that many facts are now known to allow, in a certain degree, to neglect the irreversibility of some physical processes and chemical transformations (*i.e.* to

study them in a certain approximation). In these cases it is merely necessary to establish such ranges of changes of the properties of a system within which it is possible to consider them as equilibrium ones. Usually, such states are called as quasi-equilibrium, when a process studied by changes of some parameter is steady and has such a time in comparison with which the times of other processes in the system are either very long or negligible. Such a concept underlies *the law of temporary hierarchies* [1, 2], which allows to resolve quasi-closed thermodynamic systems (subsystems) in open biosystems and to investigate their development (ontogenesis) and evolution (philogenesis) by studying changes in the value of Gibbs specific (per unit of volume or mass) functions of formation of a given highest monohierarchical structure from the monohierarchical structures of the lowest level. Proceeding from these considerations, it is possible to make two important conclusions:

1) in every specific case, depending on the chosen time scale (or process), this state of the system can be considered (with various degrees of the accuracy of approximation) equilibrium or non-equilibrium, *i.e.*, allowing to apply various ways of description depending on the character of the task to be solved;

2) the second law of thermodynamics is applicable to real (open) systems as well, provided that the whole system (continuum) "open system–environment" is considered; for such a set, the total entropy will always increase, as for the first component $\Delta S_1 < 0$, for the second component $\Delta S_2 > 0$, and at $|\Delta S_1| \ll |\Delta S_2|$ we have:

$$\Delta S = (\Delta S_1 + \Delta S_2) > 0$$

2. Thermodynamics of the Development of Biological Systems

The total number of live organisms in every biocenosis, the rate of their development and reproduction depend on the quantity of energy arriving into the ecological system, and the intensity of circulation of chemical elements and their compounds in it, which can be reproduced and used many times. Substance circulations and energy transformation in nature obey the fundamental laws of thermodynamics. At the same time, live organisms are open non-equilibrium macrosystems with gradients of the concentration of chemical substances, temperature, pressure, and electric potential. The possibility of spontaneous emergence of ordered dissipative structures owing to cooperative movement of large groups of molecules is shown in the works by Prigogine, Glansdorff *et al.*, who have created the bases of nonlinear non-equilibrium thermodynamics. Such self-organizing processes underlie a new interdisciplinary scientific lead called synergetics. Hence it follows that the

emergence of a certain order from disordered systems leads to a seeming contradiction between the second law of thermodynamics and the ordering of biological systems (entropy reduction). However, as was already told, if open systems are expanded by adding the environment to them, the second law of thermodynamics becomes applicable to such a continuum.

So, to prove that life in the environment does not contradict the second law of thermodynamics, it is necessary to proceed from that: i) entropy has a thermodynamic and (or) statistical sense only:

$$S_2 - S_1 = \int (dQ/T)_{rev}; \quad S = k \ln W$$

where the subscript *rev* indicates the reversible nature of the process; dQ is the change of the heat quantity; T – temperature; k – Boltzmann constant; W – the number of the microstates realizing the current macrostate of the system;

ii) according to the second law of thermodynamics, any evolving system aspires to an equilibrium state, in which all its physical parameters accept constant values; the state of equilibrium is reached when the entropy of the “system–environment” set becomes maximum.

In the recent years, achievements of the physics of biopolymers have promoted the development of the latest representations of the possibility to study biological systems and their evolution by means of classical thermodynamic techniques (Danielle, Denbigh, Mitchell, Gladyshev, *etc.*). The thermodynamic theory of life system evolution [1-8, 11] gives answers to the questions like: Why does evolution proceed? Where is it directed to? What is its motive power?

By now, a rather large amount of experimental data is accumulated to specify that phylogenesis, ontogenesis, and biological evolution as a whole have a strongly pronounced thermodynamic orientation. In a qualitative relation, the sense of evolution of living beings can be understood from the viewpoint of thermodynamics within the *structure formation model* (structures of highest hierarchies emerge from those of lowest hierarchies). According to this model, every natural hierarchical structure has the energy of its formation, average lifetime (relaxation), biomass volume, *etc.* This allows studying live systems as quasi-closed ones in some approximation. The common material at building of hierarchical structural levels in the course of biological evolution is chemical substance. Therefore, the physical theory of evolution of living beings is based on analysis and generalization of experimental data connected with transformations of separate chemical substances in the processes of transition from a simple structure to a more complex one. The most noteworthy facts consist in the following.

1) During their development, such biosystems as an organella, a cell, an organism tissue, the biomass of a population, *etc.*, are enriched with power-rich chemical substances to force out water. Therefore, the kinetic

features of an organism aging correlate with the changes of water and fat in it. The same concerns the water content in the brain of a living being (depending on the extent of its relative development). Despite the growth of the power consumption of the biosystem, its chemical stability decreases, and the thermodynamic stability of the supramolecular structures of the body tissues increases. It is also necessary to note that the quantity of water, organic and inorganic substances in biotissues are directly related with the values of the Gibbs specific functions G_{im} and G_{ch} of formation of supramolecular and chemical structures, respectively.

2) Data on the changes of the temperature of melting (denaturation) of biotissues in the processes of ontogenesis and phylogenesis are known.

3) Weber-Fechner law relates the reactions of biological systems to external influences of the environment (light, noise, ionizing radiation, mechanical tension, psychostresses, *etc.*).

4) A correlation between the characteristic sizes of structures of various hierarchies and the average duration of their life in a biomass has been experimentally established: lower-hierarchy structures live much shorter than higher-hierarchy ones in biosystems (Fig.). As was shown above, atoms, common molecules, macromolecules, microbodies, cells, tissues ... an organism, population *etc.* are meant under hierarchical structures. This, in essence, means that the evolution of lower-hierarchy structures proceeds much quicker than that of the organism itself, whose biomass serves as the environment for its atoms, molecules, cells, *etc.* Just in this connection, for every biosystem it is possible to isolate its habitation medium, *i.e.* a peculiar thermostat with certain parameters. Such quasi-closed subsystems possessing their own thermostats, uniting, form a thermodynamic system of a higher hierarchical level.

The main idea of the thermodynamic model of evolution of living beings, uniting all the listed facts, consists in the point that the Gibbs specific function of formation of a structure (ΔG) serves a quantitative measure of all changes (including the thermodynamic stability of the chemical, supramolecular and other structures). From the offered model follows the existence of a correlation between the Gibbs specific function of formation of chemical substances from atoms and molecules and the specific Gibbs function of formation of supramolecular structures from these substances. Therefore, the changes in G at formation of any supramolecular structure, including a population, serve as a measure of the extent of its evolutionary transformation.

Therefore, the life expectancy of biostructures (τ), arising on aggregation of chemical substances, supramolecular and other formations, is determined by the change of the Gibbs function G_{im} ($P = \text{const}$, $T = \text{const}$) at formation of these structures:

$$t \approx \exp(\overline{\Delta G_{im}} / RT)$$

where the symbol “ $\overline{\Delta G_{im}}$ ” means the specific character of G , the subscript im belongs to intermolecular interactions. According to the model,

$$\Delta G_{im} \rightarrow \min.$$

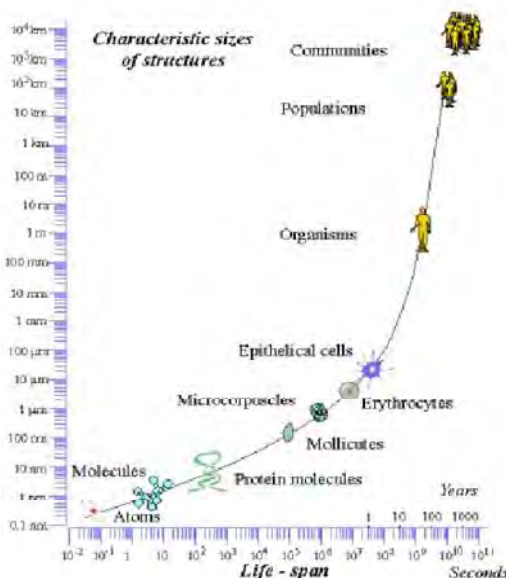


Fig. Correlation between the characteristic sizes of the structures of various hierarchies and their lifetime in the biomass. The dependence is expressed in logarithmic scales

Generalizing the foregoing, it is possible to present the model of biological evolution as follows. Under the influence of solar energy, thermodynamically stable substances convert into various products of photosynthesis, which, as a result of spontaneous “dark reactions” and according to the laws of chemical thermodynamics, are transformed into various substances. Further, under the laws of the so-called local thermodynamics of supramolecular processes (owing to the aspiration of the Gibbs specific function of biostructures to its minimum), more stable suprastructures are selected, which are accumulated in microvolumes and macrovolumes of systems. First of all, nucleic acids are selected, which structure and composition (because of the action of thermodynamic factors) slowly adapt to the environment, including the nature of proteins, whose structure is determined by DNA itself. This explains the feedback existence (having a thermodynamic basis as well) between the structures of proteins and DNA. Concurrently to synthesis processes, the disintegration processes of chemical compounds proceed. However, live systems resist it and aspire to preserve their state, which also has the thermodynamic nature, *i.e.* biosystems reproduce perishing supramolecular structures, and thermodynamics promotes selecting the most stable of them. So, it is thermodynamically favorable for macromolecular chains to

couple with similar chains and to surround themselves with the updated “young” substance of live organisms. Evolution selects those thermodynamically preferable ways of processes which promote cell fission and DNA preservation. All this proceeds on the background of parameter fluctuations of the environment (thermostats), which, together with other factors, provides life maintenance.

The physical essence of the model of evolution of biological systems can be understood on an example of the interconnected processes of formation (polymerization) and destruction (depolymerization) of such a known polymer as poly(acrylonitrile). If one analyzes the whole sequence of the processes including heterogeneous formation of solid poly(acrylonitrile) (accompanied by precipitation), its depolymerization (under the influence of light), polymerization of the again formed monomer etc., then, in a thermodynamic relation, these processes (of course, in a certain approximation) model the development of an organism and its evolution.

The proposed thermodynamic theory of biological evolution has a number of very interesting and important consequences for both science development and human life. One of them concerns the predefiniteness of the functions of DNA macromolecules in the emergence and development of living beings. If one assumes the thermodynamic orientation of life evolution, three conditions are necessary for DNA function realization, namely: i) the existence of an aqueous medium; ii) the chemical stability of AT and CG pairs; iii) surrounding of the DNA double helix with thermodynamically stable supramolecular structures. Therefore, the structure of the double helix in comparison with other supramolecular formations features an increased thermodynamic stability (expressed by the value of G_{im}), which causes the accuracy of replication and the high resistance to mutations. Just this “thermodynamic conservatism” of DNA determines the role of this biopolymer as the keeper of genetic information. Another major consequence of applied character consists in the possibility not only to estimate physiological age by means of Gibbs function but also to regulate it. The average life expectancy of an organism is determined by its hereditary signs and physicochemical and social conditions of the environment. Every instant of life (age) corresponds to the state of the organism characterized by a certain G_{im} value. Therefore, any change in the conditions of the environment leads to a change in the Gibbs specific function upwards or downwards. It is clear that at reduction of the value of Gibbs function (due to the transition of the biological system from one state to another one or, from the viewpoint of thermodynamics, from one thermostat to another one) an increase in the average life expectancy should follow.

The possibility of regulation of the physiological age of an organism is due to the correlation between the chemical and supramolecular components of the Gibbs specific function of formation of food biomass. In particular, if food possesses a lower caloric content, the value of Gibbs specific function becomes more and more positive (or less negative). On the other hand, at an identical caloric content of food, depending on the nature of the consumed biomass, various effects of “rejuvenescence” are reached. The gerontological action of some medicines can be explained (at a quantitative level) similarly.

Thus, it is possible to make some conclusions of both fundamental and practical character on the basis of the modern concepts of the thermodynamics and macrokinetics of live matter.

1. Life in the Universe (including Earth) arises and develops in full accordance with the universal laws of nature, in particular, the preservation laws, the second law of thermodynamics, and the law of temporary hierarchies.

2. All biological systems obey *the substance stability principle*, whose sense is that any structural unit of live matter (an atom, a molecule, ..., a cell, ..., a population...) is potentially thermodynamically limited in its interaction with both the structures of its “own” hierarchy and the structures of adjacent hierarchies. One of this principle’s consequences is the inverse relationship between the stability of chemical bonds in molecules and the stability of the corresponding intermolecular bonds (characteristic of supramolecular structures).

3. The evolution processes of animate nature, consisting of quasi-closed systems close to equilibrium, can be studied by the methods of phenomenological thermodynamics. This is confirmed by many experimental data which point to conclusion that live systems can participate in evolution not only under the influence of expansion work but also under the influence of such types of work (energy) as chemical, electromagnetic, gravitational, osmotic, etc.

4. Special “thermodynamically focused” diets promote reduction of the aging rate of living beings, including the man, and improvement of the quality of their life. *The anti-gerontological indicator* of any foodstuff (of either vegetative or animal origin) is caused by its chemical composition and the supramolecular structure contained therein, and also the ontogenetic and phylogenetic age of this product and the source of its origin (features of the environment). The quantitative characteristic of *the gerontological healthiness* of this or that foodstuff is, first of all, the minimum value of the specific Gibbs function of formation of its supramolecular structure.

5. The basic recommendations on dietary nutrition, directed to reduction of the risk of oncological diseases and their treatment, consist in the following:

- a sharp decrease in the use of sugar, milk, and dairy products;

- an increased quantity of green vegetables and some fruits of the bean family (soy, haricot, peas, etc.);

- certain restriction of the consumption of meat with preference to be given to cold water fish species (herring, tuna, cod, trout, salmon, etc.);

- of the highest gerontological and anti-cancer value are some food oils with a low hardening temperature whose value depends on the age and habitat medium of plants (258–243 K) (hempseed, linseed, sea-buckthorn, cedar, sunflower-seed, soy-bean oils);

- a sharp (threefold, fivefold, and even tenfold) increase in the consumption of the daily dose of vitamins C, E, PP (e.g., nicotinamide), A and B group, zinc and selenium.

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ТЕРМОДИНАМІКА ЯК ОСНОВА ПОВЕДІНКИ НЕЖИВОЇ І ЖИВОЇ ПРИРОДИ

Анотація. Розглянуто концепцію, яка дозволяє дослідити поведінку відкритих (біологічних) систем за допомогою законів нерівноваженої (класичної) термодинаміки. Показано, що другий закон термодинаміки можна застосовувати до відкритих систем за умови, що при розгляді всієї системи (континуум) «відкрита система–середовище» повна ентропія зростає. Встановлено, що закон тимчасових ієрархій дає можливість перетворювати квазізамкнуті термодинамічні системи у відкриті біосистеми і досліджувати їх розвиток (онтогенез) та еволюцію (філогенезу), вивчаючи зміни у величинах функцій Гіббса утворення будь-якої субмолекулярної структури (у тому числі населення).

Ключові слова: термодинаміка, закон, структура, біосистеми, функція Гіббса, ентропія, розвиток, дослідження.