# THERMOIMPULSE AS A TRUE EXTENSIVE MEASURE OF HEAT

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## Abstract

The expediency of replacing the Clausius entropy with a more adequate concept of "thermal impulse" as a measure of the amount of disordered motion in the system is substantiated. It is shown that the thermal impulse also exists in nonequilibrium systems, where it can also both increase and decrease. This makes it possible to solve the problem of thermodynamic inequalities, to return the concept of force to thermodynamics, to unify the methods for finding heterogeneous forces, to propose simpler criteria for the equilibrium, evolution and involution of each degree of freedom of the system separately, to substantiate the unity of the laws of transformation of any form of energy, to eliminate the blatant contradiction of thermodynamics with the nature of biological and cosmological evolution, etc. Other advantages of the thermal impulse are also revealed, which facilitate the proof of its existence, its applicability to thermally inhomogeneous media, physical visibility, measurability, ease of eliminating a number of paralogisms of thermodynamics, etc.

*Keywords:* entropy as a heat transfer coordinate and irreversibility criterion, its generalization to nonequilibrium states, elimination of its paradoxes and easing understanding.

## 1. Introduction.

More than 150 years have passed since the concept of entropy and the principle of its increase in irreversible processes entered the natural sciences [1]. However, disputes persist about the hidden meaning of this concept and about the physical foundations of the mentioned principle [2], which led to the loss of the former glory of the theory by thermodynamics, "whose conclusions will never be refuted by anyone [3]. In the extensive scientific and near-scientific literature, hundreds of books and thousands of articles are devoted to it, where these issues are discussed from various points of view [4]. Nevertheless, the inconsistency of the theory of thermal death of the Universe by R. Clausius [2] has not yet been satisfactorily proven, and "the glaring contradiction between thermodynamics and evolution [5] has not been eliminated. Meanwhile, the concept of entropy has crossed the boundaries of physics and penetrated the most intimate areas of human thought. Along with the thermodynamic entropy of R. Clausius, statistical, informational, mathematical, linguistic, intellectual, etc. entropies appeared, which further complicated the interpretation of this many-sided and poorly intuitive concept.

Against this background, tries to replace entropy with a more adequate parameter capable of both increasing and decreasing in evolution and involution remained practically unnoticed [6]. The need for this increased with the application of thermodynamic methods to biological and cosmological systems [5, 7], as well as to the study of the kinetics of various irreversible processes [8]. At the same time, paralogisms like the theory of the heat death of the Universe or the Gibbs paradox have arisen in almost every field of application of thermodynamics [9]. Entropy has become a "scapegoat" for "any and all" irreversibility and the "Achilles' heel" of thermodynamics [10].

One of the aims of this article is to reveal the duality and internal inconsistency of the concept of entropy as a parameter introduced by R. Clausius as the heat transfer coordinate, but, spontaneously increasing in any irreversible processes. Our main goal is to propose another, simpler and more understandable parameter that covers both these cases and cuts all paralogisms associated with entropy.

## 2. Inadequacy of entropy as a coordinate of heat transfer

Thermodynamics as one of the fundamental disciplines was formed at a time when, under the pressure of new experimental facts, the idea of heat as an indestructible fluid (caloric) collapsed, and with it, as it seemed then, the theory of heat engines based on its Carnot (1824) [2]. This prompted R. Clausius, the founder of equilibrium thermodynamics, to reconsider the concept of heat as a chaotic form of energy and define it as a quantitative measure of the heat transfer process [1]. The interpretation of heat as "energy in a state of transfer," i.e., a function of a process, at once limited thermodynamics to equilibrium systems and quasi-static (infinitely slow) processes. The fact is that in non-equilibrium systems, the change in entropy is due not only to heat transfer, but also to internal sources of frictional heat, electromagnetic heating, chemical reactions, etc. Such sources made it necessary to consider heat on a par with such phenomena as light, sound, electricity, and magnetism [2]. The understanding of heat as a "hidden" movement of a special kind, characterized by randomness, has survived to this day both in the concept of the heat capacity of the system and in the theory of heat transfer, which defines it as a process of exchange between bodies of internal thermal energy (according to the principle: you can only exchange what have both sides). Moreover, such an understanding turned out to be the only one acceptable for the thermodynamics of irreversible processes (TIP) [11, 12], which deals with the above-mentioned internal heat sources.

The replacement of the original concept of heat as a function of a state by heat as a function of a process gave rise to periodically arising discussions. They eventually led to an understanding of the need to distinguish between "body heat" as a quantitative measure of internal thermal energy, and "process heat" as a quantitative measure of heat transfer. In our works, this circumstance is emphasized by the fact that the heat of the body is denoted by $U_q$, and the heat of the process - by $Q$, and for infinitesimal increments the first one uses the sign of the total differential $dU_q$, and for elementary quantities of heat $đQ$ as a function of the process, the sign of the incomplete differential $đ$ due to its depending on the nature of the process [8]. The difference between them is that when the process terminates, the first remains unchanged, while the second vanishes.

The interpretation of heat $Q$ as a quantitative measure of heat transfer required the founders of thermodynamics to find a specific coordinate for this process, i.e., a parameter that necessarily changes during heat transfer and still is unchanged in its absence. To do this, R. Clausius had to confine himself to considering equilibrium systems to exclude the internal sources mentioned above, and to assume the existence of "equilibrium processes". This phrase included two incompatible concepts "equilibrium" and "process", since equilibrium in thermodynamics is understood as a state characterized by the termination of any macroprocesses [13]. This incompatibility can be verified by representing any extensive parameter of the system $\Theta_i$ (its mass $M$, internal energy $U$, the number of moles of $k$-th substances $N_k$, entropy $S$, electric charge $Q_e$, impulse $\boldsymbol{P}$, its momentum $\boldsymbol{L}$, etc.) in a continuous medium by the integral of its local density $\rho_i = d\Theta_i/dV$ and average density $\bar{\rho}_i = \Theta_i/V$ by the expression $\Theta_i = \int\rho_i dV = \int \bar{\rho}_i\, dV$. In this case

$$d\Theta_i/dt = \int [(d\,(\rho_i - \bar{\rho}_i\,)/dt]\, dV \equiv 0. \tag{1}$$

According to this identity, in a homogeneous medium, where the difference $(\rho_i - \bar{\rho}_i\,)$ vanishes everywhere, the integral (1) vanishes in the same way, i.e., the value $\Theta_i$ stays unchanged. Thus, in homogeneous systems, no processes (including heat transfer) are possible [8]. This means that, assuming the system to be homogeneous (internally balanced), R. Clausius "throws the baby out with the water", putting an insoluble internal contradiction into his theory. It resulted in the actual transformation of thermodynamics into thermostatics since it forced it to confine itself to infinitely slow ("quasi-static") processes. However, for such processes, the concept of their driving force, which appears in the laws of thermal conductivity, electrical conductivity, diffusion, viscous friction (including the "driving force of heat" by S. Carnot) has lost its relevance due to its infinite

smallness. Thus, the concept of force disappeared from thermodynamics, and with it, its ability to explain the cause of the occurrence of processes, reveal their "mechanism", direction, moment of completion, etc. For this, thermodynamics was forced to involve "from outside" physical kinetics, molecular- kinetic and statistical-mechanical theories. The possibility of defining equilibrium as the vanishing of the resultant force has also disappeared, which needed the use of conditions for the extremum of entropy or a series of thermodynamic potentials. This left an imprint on the entire system of substantiation of thermodynamics, including the proofs of the principles of the existence and increase of entropy [14].

One of the founders of thermodynamics, R. Clausius, used for this the theory of cyclic heat engines by S. Carnot (1824) [2]. In it, the thermal efficiency of its ideal cycle $\eta_t^K = 1 - T_2/T_1$ was decided by constant temperatures of the heat source $T_1$ and heat receiver $T_2$, and the condition of its maximum was expressed in the requirement of the absence of any decrease in the "driving force of heat" $T_1$ - $T_2$, not associated with the performance of work. In this case, representing any cycle as an infinite number of Carnot cycles with elementary quantities of input and output heat $đQ_1$ and $đQ_2$ and expressing its efficiency $\eta_t = 1 - Q_2/Q_1$ both in terms of temperatures $T_1$ and $T_2$, and through these heats [13], we have:

$$\eta_t = 1 - đQ_2/đQ_1 = \eta_t^K = 1 - T_2/T_1 \tag{2}$$

Such a proof, as far as we know, has met with no objections so far. Meanwhile, in the same way it was possible to prove the existence of another, more general, extensive measure of the quantity of thermal motion than entropy. If, for example, we consider a heat engine as a device that converts internal thermal energy $U_q$ into work (without replacing it with heat $Q$ as a function of the process), and substitute in (2) instead of $Q_1$ and $Q_2$ its quantity at the input and output of the heat engine $U_q'$ and $U_q''$, we find that $\oint đ(U_q/T) = \oint đP_q = 0$. We will find out the meaning of the parameter $P_q$ later. For now, we note that its existence as a ratio of two parameters $U_q$ and $T$ did not need to be substantiated at all.


### 3. Failure to divide energy exchange into heat and work

The proof of the existence of entropy by R. Clausius turned out to be inextricably linked with his idea of heat $Q$ and work $W$ as the only two possible ways of energy exchange between the system and the environment. This is reflected in the equation of the first law of equilibrium thermodynamics [13]:

$$đQ = dU + đW. \tag{3}$$

Meanwhile, the transition to the study of open systems exchanging matter with the environment led to the establishment of the fact that, along with heat transfer $Q$ and work $W$, there are two more types of energy exchange: the boundaries of a system characterized by a change in the composition of the system while its mass stays unchanged. At the same time, it turned out that "at the boundary where diffusion takes place" "the classical concepts of heat and work lose their meaning" [15].

The division of energy exchange into heat transfer and work has become even more problematic in complex (polyvariant) systems, in which, along with expansion work $đW_p = pdV$, other types of work are performed, including a special category of "technical" work $W^T$, which has passed into thermodynamics from mechanics (Л (Carnot, 1783; Poncelet, 1826) [2]. Such work was measured by the scalar product of the vector of the resulting force F and the displacement $dr$ caused by it of the object of its application $dW^T = F \cdot dr$. It was a quantitative measure of the process of transformation of external energy $E$ from its $i$-th form $E_i$ into $j$-th $E_j$, which is also a state function. Therefore, such work did not depend on the path of the process, and its elementary amount $dW_i^T$ was expressed by the total differential $dW_i^T = F_i \cdot dr_i = dE_i$. Such work was fundamentally different from the category of work that appeared in equation (3), primarily by the

vector nature of the coordinates $r_i$. This work was performed by external forces and had the meaning of a quantitative measure of the process of energy conversion, and not energy transfer, as the work of introducing a charge, $k$-th substance or volume (expansion work $dW_p = pdV$). These types of work, performed by internal forces and depending on the path of the process, should be called "non-technical" $dW_i^{\text{н}}$. Misunderstanding of their difference, i.e., the fact that "work is different from work", still prevents us from realizing that the true "watershed line" does not pass between heat $Q$ and work $W$, but between technical $dW_i^{\text{т}}$ and non-technical $dW_i^{\text{н}}$ types (categories) of work. Heat transfer should also be included among the latter since it is the work of introducing the amount of chaotic motion. For complex systems that perform both technical and non-technical types of work, there is no proof of the existence of entropy so far [13, 14]. We are not talking about non-equilibrium (spatially inhomogeneous) systems, where, in addition to external heat transfer, there are internal heat sources. Extrapolation of the concept of entropy to such systems continues to multiply the number of paralogisms, turning it into a "cancer" of thermodynamics [9].

It may seem that the severity of this problem can be largely smoothed out by the statistical interpretation of entropy as a measure of the thermodynamic probability of a state [2]. However, it also turned out to be incompatible with the concepts of "entropy flow" and "entropy production", which are used in nonequilibrium thermodynamics [11,12]. Moreover, no interpretation of entropy can prevent the transition of the joint equation of the 1st and 2nd principles of thermodynamics (3) into the inequality $TdS > dU + pdV$, which made it impossible to calculate energy exchange based on it, both in the framework of nonequilibrium thermodynamics and in other technical disciplines that study real processes.

All this forces us to start "from scratch" and return to the search for a more general parameter that could serve as an extensive measure of the internal thermal energy of the system $U_q$ of any (including open, polyvariant and nonequilibrium) systems.

## 4. True extensive measure of internal thermal energy

The desire to build a thermodynamic theory that is valid for the general case of open, non-equilibrium, polyvariant and isolated systems dictates the need to build it based on a deductive approach "from the general to the particular". This is exactly what "Thermokinetics" [8] is like as a unified theory of the processes of transfer and transformation of any form of energy, proposed by us in our doctoral dissertation [16]. It is based on the "principle of certainty of energy", according to which the number of arguments of energy as the most general function of the state of the system under study is equal to the number of independent (qualitatively distinct and irreducible to others) processes of its relaxation. This principle is proved by the "theorem on the number of degrees of freedom" of an arbitrary system, according to which the latter is equal to the number of independent (i.e., special, experimentally distinguishable, and irreducible to others) processes occurring in the system. Thus, any arbitrariness in the definition of the concept of energy is eliminated and "underdefinition" or "redefinition" of the system is prevented (i.e., tries to describe its state by a missing or excess number of variables), which is the main reason for the methodological errors of many modern theories [7].

To start "from scratch", let's return to the concept of "momentum" $P=Mv$ and "manpower" $Mv^2$, introduced by R. Descartes and G. Leibniz [2]. It is easy to show that Leibniz's "living force" is the internal energy of the disordered oscillatory motion of the particles that make up the system, regardless of its structure, homogeneity, and composition. Indeed, in an inhomogeneous system, its density $\rho = dM/dV$ becomes a function of spatial coordinates (radius vector r) and time t, i.e., $\rho = \rho\,(r, t)$, so that its total time derivative $d\rho/dt$ includes into itself the local $(\partial\rho/\partial t)_r$ and convective $(\partial\rho/\partial r)\,(dr/dt) = (v \cdot \nabla)\rho$ components:

$$d\rho/dt = v \cdot (\partial\rho/\partial r) + (\partial\rho/\partial t)_r \qquad (4)$$

This expression is a "kinematic" equation of the first order wave, in which $d\rho/dt$ plays the role of its damping function [17]. It describes a wave propagating from a source, which is illustrated in Figure 1. According to this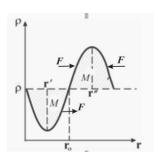 figure, a traveling wave is generated by the transfer of a certain amount $M$ of matter from a position with a radius vector $\mathbf{r'}$ to a position $\mathbf{r}$. The average velocity $\upsilon$ of this transfer is decided by the displacement ratio $\mathbf{r''}$- $\mathbf{r'}$ to the period of the wave $\nu^{-1}$ with frequency $\nu$ and is obviously equal to the propagation velocity of perturbations in the given medium. The modulus of this speed in any substance $\upsilon$ is related to the speed of light in a vacuum with a refractive index $n = c/\upsilon$, which gives the "living force" the meaning of the energy of the internal oscillatory motion of the system (its internal thermal energy $U_q$):



Figure 1. Wave formation

$$U_q = M\upsilon^2 = n^{-2}Mc^2. \tag{5}$$

This expression corresponds to the principle of equivalence of the energy $E_o$ and rest mass $M_o$ of A. Einstein, if we take the speed of light in the void as maximum ($n_o = 1$) and consider the identity for stationary systems $M$ and $M_o$, as well as $U_o$ and $E_o$. According to him, the internal thermal energy of a substance $U_q$ is expressed as the product of extensive and intensive measures of motion, which are the amount of motion $P = M\upsilon$ and the average speed of oscillatory motion $\upsilon$. Thus, the energy carrier of the chaotic form of motion in the $U_q$ system is the scalar momentum $\Theta_q \equiv P_q = M\upsilon$, which we called for brevity the thermoimpulse (i.e., the impulse $\mathbf{P} = M\boldsymbol{\upsilon}$, which has lost its vector nature due to the chaotic motion). It becomes possible to replace the entropy $S$ with this simple and intuitive parameter. The substantiation of the expediency of this will be the subject of the later part of this article.

## 5. The need to replace entropy with a thermoimpulse

In the extensive literature on entropy, tries to revise and generalize the basic concepts of thermodynamics are extremely rare. This can be explained by the extremely painful feeling of such attempts on the part of specialists and individuals who avoid at least a temporary loss of such a recognized support. As a result, errors accumulate, and it becomes more and more difficult to find the origins of apparently absurd conclusions.

An approach to this problem from the standpoint of the "certainty principle" reveals that R. Clausius from the very beginning went on the wrong path, leading away from the theory of heat engines of S. Carnot. This theory explicitly pointed to the temperature difference $\Delta T$ between the heat source and the heat sink as a condition for the emergence of a "heat driving force", and any decrease in it, not related to the performance of work, as the reason for a decrease in the efficiency of a heat engine [2]. This theory for the first time revealed the independence of the efficiency of an ideal cycle from the nature of the working fluid and showed ways to increase it, which were fully realized in the future in thermal power engineering. It was enough just to part with the idea of caloric as a weightless and indestructible liquid and consider it as a carrier of a special kind of motion, distinguished by its randomness.

However, R. Clausius went the other way, replacing the quantitative measure of the carrier of internal thermal energy $U_q$ with a quantitative measure of the heat transfer process Q, which made the entropy S a "scapegoat" for "any and every" irreversibility.

This was most clearly manifested in the entropy balance equation written by I. Prigogine in the form [18]:

$$dS = d_eS + d_uS, \tag{6}$$

where $d_eS = đ_eQ/T$ and и $d_uS = đ_uQ/T$ are the parts of the entropy change due to heat transfer $đ_eQ$ and internal heat sources $đ_uQ$, respectively.

Note that $d_eS$ and $d_uS$ are not partial differentials of entropy, which takes (6) out of the scope of the theory of differential calculus. However, it is even more important that any irreversible processes in it cause a change in the same parameter - the entropy $S$. Other parameters also have internal sources or sinks. Such are the numbers of moles of $k$-x substances $N_k$, which also change both because of chemical reactions and during diffusion of $k$-x substances through the boundaries of the system.

Further, according to (6), the entropy $S$ increases only because of the transformation of ordered forms of motion into chaotic ones. However dissipation is accompanied by the transition of energy into potential energy. In cutting metals, it was found that the ratio of the amount of dissipation heat released $Q^d$ to the work expended $W^r$, called the "heat output coefficient", is usually less than one. This means that part of the work of destruction of metals is converted into the potential energy of the chips, and not into heat. This circumstance manifests itself even more clearly in crushing materials, in which not only the temperature increases, but also the surface energy of the particles of the material. Thus, experience confirms that the increase in entropy is by no means the only consequence of the transformation of ordered forms into disordered ones.

Moreover, it turned out that thermal energy, already considered chaotic, can also be dissipated. Direct experimental confirmation of this circumstance was a series of experiments by L. Brovkin (1960, 1964) [18]. In them, in the gap of a densely packed roll of paper, cardboard, rubber tape and other sheet materials, along their entire length, a sensitive element of a resistance thermometer was laid. Then the roll was subjected to uneven heating from an external heat source, and in the later process of its cooling, a change in the resistance of such a "dispersed" thermometer, which characterizes the average integral temperature of such a system, was recorded.

The most surprising result of these experiments was a rather significant (up to 17%) rise in temperature during the first period of the roll relaxation process instead of the expected decrease. It continued for tens of minutes until the cooling of the sample began to predominate. This phenomenon, called by the author "the effect of the growth of the measured heat content", has not yet been satisfactorily explained. It becomes understandable only from the standpoint of nonequilibrium thermodynamics, which recognizes the existence of an ordered (potential) part of the internal energy of a thermally inhomogeneous system. Due to this ordered part of the internal thermal energy of the environment, heat engines do the work, and in this case, its kinetic part increases.

The fact that such relaxation processes do not contradict the principles of conservation and transformation of energy can be seen by being the "living force" as the result of the mutual transformation of ordered and disordered forms of energy:

$$dU_q \equiv dMv^2 = d(Mv^2/2) + \boldsymbol{F}\cdot d\boldsymbol{r} = dE^v + dE^r, \qquad (7)$$

where $E^v = Mv^2/2$, $E^r = \int \boldsymbol{F}\cdot d\boldsymbol{r} = \int \boldsymbol{v}\cdot d\boldsymbol{P}$ are the kinetic and potential energies of the system.

According to this expression, the ordered forms of energy $E^v$ and $E^r$ of an isolated system such as the Universe are in sum equivalent in size to its internal vibrational energy $U_q$ and, upon dissipation, can pass into it to the same extent as it does when it passes into ordered forms because of self-organization or as the vibrations decay. In other words, the law of conservation of energy does not exclude the circulation of energy forms due to the interconversion of the material and field forms of matter in the Universe. On the contrary, the transition of a part of the potential energy of the field form of the matter of an inhomogeneous Universe into the kinetic energy of ordered $E^v$ and disordered $U_q$ motion, and the latter into the potential energy of "inhibited" motion, is a manifestation of the laws of dialectics. It allows us to give energy the sense of a common measure of all forms of motion.

In this case, the representation of the "live force" in the form of the product of the thermoimpulse $P = Mv$ by the modulus of its average velocity $v$ allows us to give them the meaning of an extensive and intensive measure of internal thermal energy $U_q$, respectively. In this case, the

thermoimpulse $P_q$ will appear as a quantitative measure of the carrier of a given form of energy (briefly: energy carrier), and its potential $\psi_q \equiv \upsilon$ – a measure of the intensity of movement. If, in this case, one does not resort to the molecular-kinetic theory, but relies only on experience, then it is quite natural to consider $\psi_q$ as a measure of temperature $T$, and the momentum of one particle (molecule) $p = P/N$ as gas pressure. Since the number $N$ of particles in the volume of one mole of gas $V_\mu = 22{,}4$ m³/kmol is equal to the Avogadro number $N_A = 6{,}022169{\cdot}10^{26}$, then, taking atmospheric pressure $p = 101{,}325$ kPa and temperature $T = 273{,}15$ K as normal conditions, directly we come to the equation of state of an ideal gas $pV_\mu = R_\mu T$, in which the universal gas constant $R_\mu$ has the same value of 8314 J mol$^{-1}$ K$^{-1}$. By this representation, the absolute temperature $T$ should be measured not in Kelvins, but in m/s, so that the vibrational energy $U_q = PT$ is expressed in J. potentials $\psi_i$ - the meaning and dimension of the speed of the corresponding form of motion. This would mean a genuine revolution in the system of physical quantities, radically reducing the number of concepts and easing not only the transition from one discipline to another, but also the understanding of the physical essence of such energy carriers as an electric charge.

Another advantage of the thermal pulse is its ability both to increase in heat transfer, mass transfer and diffusion or during energy dissipation, and to decrease during damping of oscillations or during the transformation of disordered forms of motion into ordered ones. An example of such processes is the spontaneous evolution saw at all levels of the universe - from nucleosynthesis to the formation of stars and clusters of galaxies.

Replacing the entropy with a thermal pulse makes it possible to cut the incorrectness of expression (6). The total differential $dU_q = d(PT)$ should be represented as the sum of two terms:

$$dU_q = TdP + PdT. \tag{8}$$

Let us compare this expression with the total differential of the internal energy density $\rho_q = dU_q/dV$ as a function of the radius vector $\boldsymbol{r}$ of the temperature field and time $t$, which includes the convective $(\boldsymbol{v}\cdot\nabla)\,\rho_q$ and local $(\partial\rho_q/\partial t)_r$ components:

$$d\rho_q/dt = (\boldsymbol{v}\cdot\nabla)\,\rho_q + (\partial\rho_q/\partial t)_r. \tag{9}$$

The first term on the right side of (9) decides the flow of thermal energy $U_q$ through the boundaries of the system (which for the system corresponds to the heat exchange $đ_eQ/dt$), the second term determines the internal heat sources $đ_uQ/dt$. Thus, in nonequilibrium systems, heat transfer can also be expressed through a change in the parameters of the system $đ_eQ = TdP$ without the occurrence of thermodynamic inequalities [20].

It stays to be shown that the replacement of entropy by the thermoimpulse makes it possible to cut several other paralogisms that have arisen in thermodynamics when trying to use entropy as an extensive measure of thermal motion [9].

## 6. What does the replacement of entropy with a thermoimpulse give?

Thermoimpulse as an extensive measure of thermal motion has obvious advantages. This parameter does not require proof of its existence and has the degree of evidence that satisfies the concept of a phenomenological theory. It frees from the need to justify the applicability of the concept of entropy to systems far from equilibrium, since it also exists in systems with an arbitrary distribution of momentum between particles. This parameter specifies the meaning of the absolute temperature T as a measure of the intensity of thermal motion, equal to the average velocity $\upsilon$ of the disordered oscillatory motion of the particles that form the system. Understanding the thermoimpulse as a quantity of an oscillatory form of motion allows us to return to energy its original meaning of the most general measure of all forms of motion of matter and thereby put an end to the situation when "modern physics does not know what energy is" [21]. Finally, this parameter does not require the involvement of molecular-kinetic and statistical-mechanical theory

to interpret its physical meaning of thermodynamic parameters, which makes it a completely self-sufficient theory. Below we consider the most important consequences of such a replacement.

### 6.1. Elimination of inequalities in the mathematical apparatus of thermodynamics

It is known that the joint equation of the 1st and 2nd laws of thermodynamics in the case of irreversible processes takes the form of inequality [2,13]:

$$TdS > dU + pdV. \tag{10}$$

The reason for the appearance of inequalities is that in the absence of equilibrium, internal heat sources appear in the system, because of which $TdS > đQ$. Similar inequalities arise for other parameters $\Theta_i$, including its volume $V$, which can increase when the system expands into the void without performing work $đW_p^{\text{н}} = pdV$. This circumstance is the main obstacle to the application of the thermodynamic research method to other disciplines that study real (non-static) processes.

Meanwhile, another approach to the derivation of the basic equation of thermodynamics is possible, based on the representation of the internal energy of the system $U$ as a function of the quantities of motion of various kinds $P_i$ (including the thermoimpulse $P_q$). In this case, the energy of the system $U = \Sigma_i U_i(P_i)$, and its total differential can be represented as an identity [8]:

$$dU \equiv \Sigma_i \Psi_i dP_i, \tag{11}$$

where $\Psi_i \equiv (\partial U/\partial P_i)$ is the mean integral value of the generalized potential (absolute temperature $T$ and pressure $p$, chemical $\mu_k$, electric $\varphi$, gravitational $\psi_g$, etc. potentials).

As we can see, inequalities do not arise if we pass from the entropy $S$ and other coordinates of the energy exchange processes $\Theta_i$ to the quantities of motion $P_i$ of the corresponding degrees of freedom of the system, considering the internal sources of partial energy $U_i$. An equally important advantage of such a replacement is the possibility to introduce into thermodynamics the concept of a scalar (internal) thermodynamic force $F_i$ as a derivative of the momentum of a given kind $P_i$ with respect to time $F_i = dP_i/dt$. These forces buy a vector character with an uneven distribution of the density $\rho_i(r, t) = dP_i/dV$ of the momentum $P_i$ over the volume of the system $V$, which is accompanied by a shift in the position of its center $r_i$ from the first $r_{io}$ corresponding to a homogeneous state with a density $\rho_{io}(t) = P_i/V$. The position of this center in the current and homogeneous state is decided by the well-known expressions:

$$r_i = P_i^{-1}\int \rho_i(r, t)\,rdV;\ r_{io} = P_i^{-1}\int \rho_{io}(t)rdV, \tag{12}$$

where $r$ is the running (Eulerian) spatial coordinate; $t$ - time.

It follows from this that the redistribution of the energy carrier $P_i$ when the system deviates from a homogeneous ("internal equilibrium") state is accompanied by the appearance of a certain "moment of distribution" of the momentum

$$Z_i = P_i(r_i - r_{io}) = \int [\rho_i(r, t) - \rho_{io}(t)]\,rdV \tag{13}$$

with the shoulder $\Delta r_i = r_i - r_{io}$, which we called the "displacement vector" [8].

The parameters $Z_i$ have the meaning of the polarization vectors of the system in the most general sense of this term as the creation of its spatial inhomogeneity. The appearance of any $i$-th energy carrier $P_i$ of the distribution moment $Z_i$ with a shoulder $\Delta r_i$ makes its energy $U_i$ a function of two variables $P_i$ and $r_i$ (at $r_{io} = 0$), i.e., $U_i = U_i(P_i, r_i)$. In this case, $U = \Sigma_i U_i(P_i, r_i)$, and its total differential can be represented as an identity [8]:

$$dU = \Sigma_i dU_i \equiv \Sigma_i \Psi_i dP_i + \Sigma_i F_i \cdot dr_i, \tag{14}$$

where $F_i \equiv (\partial U_i/\partial r_i)$ are the forces characterizing the inhomogeneity of the $P_i$ field.

It follows that any force fields $F_i(r_i)$ *arise due to the uneven distribution of the energy carrier $P_i(r_i)$ in space*. In this case, the forces $F_i(r_i)$ buy a completely unambiguous meaning of the gradients of the corresponding energy form $U_i$. This puts an end to lengthy discussions about the origin of force fields, their materiality, the diversity of their nature, the "mechanism" of interaction (contact or exchange), its strength or weakness.

According to (14), the rate of change in the energy of the system can also be represented as the identity

$$dU/dt = \Sigma_i\Psi_i dP_i/dt + \Sigma_i F_i \cdot v_i, \text{ (Вт)} \tag{15}$$

Velocity $v_i$ can be decomposed into translational $w_i$ and rotational part $\omega_i \times \mathcal{R}_i$ (with angular velocity $\omega_i$ and instantaneous radius $\mathcal{R}_i$). Then we finally get:

$$dU/dt = \Sigma_i\Psi_i dP_i/dt + \Sigma_i F_i \cdot w_i + \Sigma_i \mathcal{M}_i \cdot \omega_i, \tag{16}$$

where $\mathcal{M}_i = F_i \times \mathcal{R}_i$ is the torque of forces $F_i$.

The three components of the right side of this expression are associated with a change in the momentum of the oscillatory $P_i^y$, translational $P_i^w$ and rotational $P_i^\omega$, respectively. Its main advantage is that it describes the processes in the system, without dividing them into an infinite number of elementary volumes $dV$ or particles of mass $dM$. This makes the number of degrees of freedom of the system finite ($i = 1, 2, …I$) and equal to $I = 3K\Lambda$, where $K$ is the number of system components ($k = 1, 2…K$), $\Lambda$ is the number of their phases ($\lambda = 1, 2…\Lambda$). Due to this, identity (16) describes systems with any finite set of properties, while applying to both continuum and corpuscular models. Thus, the synthesis of thermodynamics with other fundamental disciplines is carried out.

## 6.2. Disambiguation of the meaning of the driving forces and speeds of various processes

In 1931, the future Nobel laureate L. Onsager proposed a "quasi-thermodynamic" theory of the rate of irreversible physical and chemical processes [11]. The main quantities used by this theory were scalar ("thermodynamic") forces $X_i$ as the causes of the *i*-th scalar relaxation process, and "flows" $J_i$ as their generalized velocities. These quantities were found based on the expression for the rate of entropy occurrence $dS/dt$ as a function of certain parameters $\alpha_i$ characterizing the removal of such systems from equilibrium:

$$dS/dt = \Sigma_i(\partial S/\partial\alpha_i)\, d\alpha_i/dt = \Sigma_i X_i J_i. \tag{17}$$

Finding driving forces $X_i = \partial S/\partial\alpha_i$ and generalized velocities $J_i = d\alpha_i/dt$ of various dissipative processes makes it possible, in principle, to study the kinetics of relaxation processes using thermodynamic methods. The latter would mean a transition from thermostatics, which was classical thermodynamics [12], to thermokinetics as a theory of the rate of real processes [11]. However, the parameters $\alpha_i$ were obviously absent in equilibrium thermodynamics. Therefore, his theory remained essentially an empty formalism until another future Nobel laureate, I. Prigogine, proposed a method for finding vector thermodynamic forces $X_i$ and flows $J_i$ for "stationary" irreversible processes [18]. To do this, he put forward the hypothesis of local equilibrium, according to which there is an equilibrium in the volume elements of the continuum $dV$ (despite the occurrence of non-static processes in them), so that their state is characterized by the same set of variables $\Theta_i$ as in equilibrium (despite the appearance of additional thermodynamic forces Xi ), and all relations of equilibrium thermodynamics are applicable to them (despite their inevitable transition to inequalities).

For all its internal inconsistency, this hypothesis made it possible to apply the laws of conservation of mass, momentum, charge, and energy, taken from other disciplines, to find the forces $X_i$ and flows $J_i$. This required compiling rather cumbersome equations of their balance to

extract from $dS/dt$ that part $d_uS/dt$ that characterizes the "production" of entropy due to dissipation. However, the "entropy production" $d_uS/dt$, like expression (17), can be decomposed into factors $X_i$ and $J_i$ in many ways. This led to a certain arbitrariness in their meaning and dimension.

An even more serious shortcoming of the theory of irreversible processes (TIP), based on the principle of increasing entropy, was that it excluded from consideration the reversible part of real processes, which does not contribute to the "production" of the entropy $dS/dt$. This led to the limitation of TIP to purely dissipative processes such as thermal conductivity, electrical conductivity, diffusion, and viscous friction, while thermodynamics was created as a theory of the transformation of various forms of energy with minimal losses from irreversibility.

Identity (16) frees from these shortcomings. Being written in the form

$$dU/dt \equiv \Sigma_i \Psi_i dP_i/dt + \Sigma_i X_i \cdot J_i, \tag{18}$$

where the thermodynamic forces $X_i \equiv (dU_i/dZ_i) = \Theta_i^{-1}(\partial U/\partial r_i) = F_i/P_i$ have a well-defined meaning of the specific forces $F_i$ in their general physical understanding, it frees from the need to involve other disciplines for their finding and compiling on rather cumbersome entropy balance equations [9, 10]. Thus, it allows generalizing the conceptual system and mathematical apparatus of several engineering disciplines, drastically easing the transition from one of them to others [20].

### 6.3. Refutation of the theory of "heat death of the Universe"

R. Clausius, when substantiating the principle of increasing entropy based on the famous argument about the operation of two conjugate heat engines, takes for granted that the thermal efficiency $\eta_t = 1 - Q_2/Q_1$ of any irreversible heat engine is less than in the reversible Carnot cycle $\eta_t^K = 1 - T_2/T_1$ at the same temperatures of heat source $T_1$ and heat receiver $T_2$ [13]. In this case, $dS_2 = đQ_2/T_2 > dS_1 = đQ_1/T_1$, i.e., the entropy of the system, which includes a heat source, a cyclically operating heat engine and a heat sink, increases.

Not finding any contradictions in this reasoning, R. Clausius gave this conclusion the status of a general physical "principle of entropy increase" and put it at the basis of the "theory of heat death of the Universe". This theory predicted the termination of any macroprocesses in the Universe due to the onset of thermodynamic equilibrium in it, which was tantamount to the assertion of its "creativity". Thus, this theory still serves as the basis for the standard cosmological model of the origin of the Universe through the "Big Bang", even though the mentioned "heat death" did not occur even after 14 billion years of its existence following this model [2].

Meanwhile, an error crept into Clausius's reasoning, which will become more obvious if we represent the thermal efficiency of any cycle of a heat engine, including the Carnot cycle, through the so-called "average integral" temperatures of heat supply and removal $\bar{T}_1 = Q_1/\Delta S_1$ and $\bar{T}_2 = Q_2/\Delta S_2$ [20]:

$$\eta_t = 1 - Q_2/Q_1 = 1 - \bar{T}_2/\bar{T}_1. \tag{19}$$

According to this expression, a decrease in thermal efficiency is inevitably associated with a change in the average temperatures of heat supply and removal $\bar{T}_1$ and $\bar{T}_2$, i.e., with a decrease in the "driving force of heat" $\bar{T}_1 - \bar{T}_2$, as it followed from S. Carnot's theory. This means that the very first assumption of R. Clausius that the irreversible cycle at the same temperatures $T_1$, and $T_2$ as in the reversible Carnot cycle will have a lower efficiency $\eta_t < \eta_t^K$ is invalid.

Other proofs of this principle turn out to be just as untenable [23]. That is why "the question of the physical foundations of the law of monotonic increase in entropy remains ... open" [24]. The cardinal solution to this issue comes with finding the thermoimpulse $P_q$ as a true measure of internal thermal energy $U_q = TP_q$. According to this expression, the thermoimpulse of the system

can both increase and decrease by the value of the internal thermal energy $U_q$. In this case, the thermoimpulse degenerates not only when the oscillations are damped and $U_q$ is converted into the internal (intrinsic) potential energy of the same system $E^r$, but also when it is converted into the kinetic energy of the ordered motion $E^v$. Indeed, as the speed of the system approaches the limiting speed of light, when the deviation of the speed $v$ up or down from it vanishes, the oscillatory motion in matter also degenerates. It is for this reason that the temperature T of the physical vacuum, like any other media free of matter, is equal to zero. From this it follows that the thermoimpulse degenerates during the explosion of "supernovae", accompanied by the so-called "big gap", i.e., the transformation of matter into radiation. This process can serve as an example of the emergence of "order" from "chaos", the possibility of which was substantiated by I. Prigogine [5]. Thus, the replacement of entropy by a thermoimpulse cuts the one-sided orientation of processes in the Universe imposed by Clausius thermodynamics, allowing for the possibility of its functioning unlimited in time and space, bypassing the state of equilibrium.

## 6.4. Elimination of the contradiction between thermodynamics and the theory of evolution

Let us now show that the thermoimpulse eliminates "the blatant contradiction of thermodynamics with the theory of biological evolution", since the principle of increasing entropy prescribes only its degradation to nature [25]. Boltzmann's probabilistic interpretation of entropy did not resolve this contradiction since it gave the Universe only an insignificant chance to avoid "heat death". Meanwhile, identity (16), like (1), asserts the deterministic nature of processes in nonequilibrium systems. It follows from (1) that in systems where some processes take place, i.e., $d\,(\rho_i - \bar{\rho}_i\,)/dt \neq 0)$, integral (1) vanishes only when its terms have the opposite sign and mutually compensate. This means that in any nonequilibrium system there are always subsystems in which processes try in the opposite direction. This provision, which we called the "principle of opposite direction" of processes, has a general physical status, and can be considered a mathematical expression of the dialectical law of "unity and struggle of opposites" [24]. It cuts the one-sided orientation of processes in the Universe imposed by Clausius thermodynamics. We come to the same conclusion based on the law of conservation of energy in an isolated system (dU/dt) from =0 and identity (15), if we stand for $\boldsymbol{F}_i \cdot \boldsymbol{v}_i$ as a product $\boldsymbol{X}_i \cdot \boldsymbol{J}_i$, as is customary in nonequilibrium thermodynamics [10, 12]:

$$(dU/dt)_{\text{is}} = \Sigma_i dU_i/dt = \Sigma_i\,(\Psi_i dP_i/dt + \boldsymbol{X}_i \cdot \boldsymbol{J}_{i)} = 0, \qquad (20)$$

where $\boldsymbol{X}_i \equiv (dU_i/d\boldsymbol{Z}_i) = \Theta_i^{-1}(\partial U/\partial \boldsymbol{r}_i) = \boldsymbol{F}_i/P_i;\ \boldsymbol{J}_i = P_i \boldsymbol{v}_i.$

The vanishing of the sum $\Sigma_i dU_i/dt$ means that the individual terms of this sum have the opposite sign and cancel each other out. Since in isolated systems the acceleration of movement $dP_i/dt$ is due solely to the presence of internal sources in $P_i$, the powers $\boldsymbol{X}_i \cdot \boldsymbol{J}_i$ of opposite processes of energy conversion have the opposite sign. This means that along with dissipation processes in which $\boldsymbol{X}_i \cdot \boldsymbol{J}_i > 0$, processes of "self-organization" of some $j$-th degrees of freedom are inevitable in isolated systems, in which the product $\boldsymbol{X}_i \cdot \boldsymbol{J}_i < 0$. Such are the processes of "ascending diffusion" (transfer of a substance in the direction of increasing its concentration), the phenomenon of "coupling" of chemical reactions (the course of reactions in the direction of increasing its affinity), "active transport" (accumulation in organs of substances with a higher Gibbs energy), etc. Thus, in non-equilibrium systems, counter-directional processes of evolution and involution (degradation) necessarily arise, when one degree of freedom of the system approaches equilibrium, while the other moves away from it. This drops the above contradiction between thermodynamics and evolution [5].

Moreover, identity (15) also holds parameters $\boldsymbol{Z}_i$, which reflect not only the approach or removal of the system from the equilibrium state for any $i$-th degree of its freedom separately, but also the equilibrium condition of this kind [26]:

$$dZ_i, >0 \text{ (evolution)}; \quad dZ_i, =0 \text{ (equilibrium)}; \quad dZ_i, <0 \text{ (involution)}. \qquad (21)$$

Thus, the polarization vectors themselves become more visual and more informative criteria than entropy, which can reflect only the behavior of the system, and, moreover, only its degradation. No less convenient in this role can be thermodynamic forces expressed by potential gradients ($X_i = \nabla\psi_i$):

$$dX_i > 0 \text{ (эволюция)}; \quad dX_i = 0 \text{ (равновесие)}; \quad dX_i < 0 \text{ (инволюция)}. \qquad (22)$$

Thus, thermokinetics returns to the concept of equilibrium its original meaning of the equality of opposing forces (their absence of the resulting force), as it was in mechanics. This gives researchers a more visual, more "physical" and more informative tool for analyzing evolutionary problems than the uncalculable entropy maximum [27]. Non-entropic criteria confirm that nature is characterized not only by destructive, but also by creative tendencies, which are clearly manifested in evolution of animate and inanimate nature occurring at all levels of the universe.

## 7. Conclusion

1. The need to search for an alternative to the concept of entropy is due to the blatant contradiction of its consequences to the observed nature of processes in the Universe and the fact of the evolution of biological systems. This deprived thermodynamics of the status of a theory based on experience, and with its further generalization to open, polyvariant and inhomogeneous systems, it led to several paralogisms that made entropy a "cancerous tumor" of thermodynamics.

2. The reason for the inconsistency of the concept of entropy with the essence of the matter is the mistaken division by R. Clausius of the energy exchange of the system with the environment into heat and work, which became obvious only with the transition to the study of open and polyvariant systems. Then it was discovered that the true "watershed line" runs between technical and non-technical types of work as quantitative measures of fundamentally different processes of energy conversion and energy transfer.

3. The replacement by R. Clausius of the concept of "body heat" as a quantitative measure of its internal thermal energy $U_q$ with the concept of "process heat" $Q$ as a quantitative measure of the heat transfer process limited thermodynamics to consideration of equilibrium systems and reversible processes that do not have internal heat sources. Thus, thermodynamics, barely born, turned into thermostatic, which studies only quasi-static processes.

4. The substitution of the empirical principles of the excluded perpetual motion by the law of entropy increase and led to mistaken conclusions about the transition of thermodynamic equations for real processes into inequalities, about the inevitable "thermal death" of the Universe and to a blatant contradiction of thermodynamics with the theory of biological evolution.

5. The proof by R. Clausius of the principle of entropy increase turns out to be contrary not only to the theory of heat engines by S. Carnot, but also to his own conclusion about the equality of entropy changes in cyclic processes of heat supply and removal. The use of this mistaken principle, which has not yet been rigorously proven, has made entropy a "scapegoat" for "any and all" irreversibility.

6. Replacing entropy with a "thermoimpulse" as an impulse that has lost its vector nature due to the chaotic nature of thermal motion, removes the limitations associated with it in the scope of applicability of thermodynamics, cuts several paralogisms generated by it, and allows us to propose more illustrative and informative criteria for the evolution and balance of living and non-living systems.

7. The use of impulses of the translational, rotational and oscillatory motion of the system as universal carriers of energy of any substance in any of its phase states allows you to return the energy to its simple and clear meaning of the common measure of all (ordered and disordered,

translational, rotational and oscillatory) forms of motion and radically simplifies the system of physical quantities, facilitating the transition from one of them to the other.

8. The introduction of the missing parameters of spatial inhomogeneity removes the limitation of the sphere of applicability of TIP by dissipative processes and systems near equilibrium and makes it possible to give the energy conservation law the form of an identity, which is also valid for irreversible processes.

9. Thermodynamic identity cuts arbitrariness in the choice of thermodynamic forces and flows and predicts the emergence of processes in non-equilibrium systems directed "against equilibrium", which causes the simultaneous flow of evolution and involution (degradation) processes in them.

10. Thermokinetics as an entropy-free theory of the rate of real processes of energy transfer and transformation cuts the above-mentioned contradictions of classical thermodynamics and substantiates the possibility of the functioning of the Universe unlimited by time and space, bypassing the state of equilibrium.

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