



World Scientific News

An International Scientific Journal

WSN 132 (2019) 187-205

EISSN 2392-2192

Rethinking the Concept of Entropy

V. A. Etkin

Scientific Research Center of Togliatti State University, Togliatti, Russian Federation

E-mail address: etkin.v@mail.ru

ABSTRACT

It is shown that the construction of thermodynamics with a focus directly on nonequivalent systems leads to the understanding of entropy as a “thermoimpulse” — the impulse of internal motion that has lost its vector nature due to its chaos. Unlike entropy, thermoimpulse allows its diminution in adiabatic processes, which eliminates the contradiction of the principle of its increase to the laws of evolution, the threat of the “thermal death of the Universe”, Gibbs paradoxes, absolute temperatures, relativistic heat engines, etc., leaving it unshakable experimentally established laws.

Keywords: thermodynamic and statistical entropy, inequalities, irreversibility, dissipation, evolution, thermal death of the Universe, thermodynamics paralogism

1. INTRODUCTION

More than 150 years have passed since the concept of entropy and the principle of its growth in irreversible processes were included in natural science. However, disputes about the content of this concept and the foundations of the principle that led to the conclusion that the “thermal death of the Universe” [1] and the “glaring contradiction of thermodynamics with the theory of biological evolution” [2] do not cease. In the extensive scientific and pseudoscientific literature this question was discussed from various points of view. Hundreds of books and thousands of articles are devoted to him. However, this did not make the meaning of entropy more comprehensible. On the contrary, entropy has become even more “multifaceted.” Along

with thermodynamic entropy, entropy appeared statistical, informational, mathematical, linguistic, intellectual, etc. [3]. The original meaning of this concept and the reasons that prompted the founder of thermodynamics, R. Clausius, completely disappeared in this choir of opinions with different voices. Therefore, at least a brief insight into history is necessary.

By the middle of the XIX century, it became finally clear that the law of conservation of mechanical energy, which asserts the constancy of the sum of kinetic EC and potential EP energy, is not fulfilled in connection with the transformation of ordered forms of energy into an unordered, getting the name of internal energy U. This triggered the creation of thermodynamics as a new discipline, whose task is to study the above-mentioned processes and properties of internal energy. One of the founders of thermodynamics, R. Clausius, introduced the law of conservation of internal energy in the form [4]:

$$dU = \bar{d}Q - \bar{d}W, \quad (1)$$

where $\bar{d}Q$, $\bar{d}W$ ¹⁾ the elementary quantities of heat supplied to the system from the outside and the work done by the system on the environment.

In this regard, it became necessary to express the heat Q through the state parameters of the system under study. In modern terms, it was necessary to find the coordinate of the heat exchange process, i.e. a value that necessarily changes in this process and remains unchanged in its absence. For this, we had to confine ourselves to so-called “reversible” (equilibrium, quasi-static) processes, because otherwise, the system would have “heat of dissipation” Q^d , not associated with heat transfer. R. Clausius found such a coordinate by considering the arbitrary cycle of the heat engine, showing that in it the circular integral of the heating element $\bar{d}Q$ divided by the absolute temperature T vanishes [3]. This meant that the integrand $\bar{d}Q/T$ represents the total differential of some state function S , which he called entropy:

$$dS = \bar{d}Q/T \text{ or } \bar{d}Q = TdS. \quad (2)$$

In isolated nonequilibrium systems, where $Q = 0$, but $Q^d > 0$, $dS_{iz} = \bar{d}Q^d/T > 0$. This clause was named by Clausius as the principle of increasing entropy, extending it to the entire Universe [3]. Looking back, one can only regret that R. Clausius did not find for the parameter he entered of a different term, closer in meaning to the notion of caloric acid, which served S. Carnot (1824) as a basis for presenting a heat engine as an analogue of a mill wheel. The term “entropy”, translated from Greek, means “turning (way) inward” and emphasizes the property of entropy, which is not inherent in the remaining parameters, to increase in the absence of heat exchange due to the transformation of ordered forms of motion into chaotic. The resulting duality of the concept of entropy as the coordinates of heat exchange, existing due to its reversibility, but becoming uncertain due to irreversibility, has generated numerous discussions about the physical meaning of this parameter. (2)

The resulting numerous paralogisms of thermodynamics [5] make it necessary to search for such a way of building thermodynamics, which would be oriented directly to non-equilibrium systems with non-static (irreversible) processes occurring in them, but unlike the

¹⁾ The sign of incomplete differential \bar{d} in this expression emphasizes the fact that elementary heat transfer $\bar{d}Q$ and elementary work $\bar{d}W$ are not full differentials, and the ratio between them depends on the path of the energy exchange process.

existing non-equilibrium thermodynamics [6], the reversible (useful) component of real processes. For brevity, we called such a theory "thermokinetic" [7]. This theory provides a justification for all the provisions of non-equilibrium thermodynamics (TIP) [6] on a strictly deterministic basis and generalizes it to energy conversion processes in non-thermal and non-cyclic machines. Such an approach allows one to describe thermodynamics "from scratch" and get rid of numerous delusions historically arising in the process of learning the fundamental laws of nature. (2)

2. DYNAMIC ENERGY CONSERVATION LAW

We will proceed from the most general form of the energy conservation law proposed by N. Umov in 1873 and valid for any region V of the nonequilibrium continuum [8]:

$$dU/dt = - \int \mathbf{j}_e \cdot \mathbf{n} df = - \int \nabla \cdot \mathbf{j}_e dV. \quad (3)$$

where U is the internal energy of the system; \mathbf{j}_e is the energy flux density through the vector element df of the closed surface of the system in the direction of the outward normal \mathbf{n} (Figure 1).

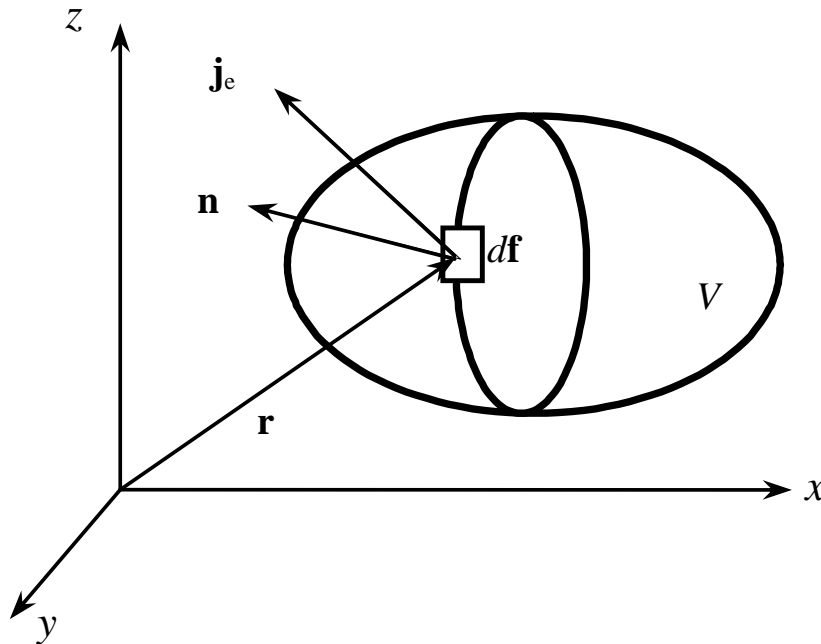


Figure 1. The flow of energy across system boundaries.

In the general case of complex (polyvariant) systems, the flow \mathbf{j}_e includes the extent to which the components j_{ei} correspond to the number $i = 1, 2, \dots, n$ forms of energy ($\mathbf{j}_e = \sum_i j_{ei}$). Moreover, each of them is expressed by the product of a certain potential ψ_i (absolute temperature T and pressure p , chemical μ_k , electric φ_k potential of the k th substance), its velocity

v_k , and so on) by the flux density \mathbf{j}_i of the potential ψ_i associated with this potential playing the role of carrier of this form of energy ($d\Theta_i/dt = -\int \mathbf{j}_i \cdot d\mathbf{f}$):

$$\mathbf{j}_e = \sum_i \psi_i \mathbf{j}_i, \quad (4)$$

where $\mathbf{j}_i = \rho_i \mathbf{v}_i$ is the energy flux density; \mathbf{v}_i , ρ_i is speed and density of the energy carrier Θ_i .

Representing the divergence $\nabla \cdot \mathbf{j}_e = \sum_i \nabla \cdot (\psi_i \mathbf{j}_i)$ as a sum of two terms $\sum_i \psi_i \nabla \cdot \mathbf{j}_i + \sum_i \mathbf{j}_i \nabla \psi_i$, we find:

$$dU/dt = -\sum_i \int \psi_i \nabla \cdot \mathbf{j}_i dV - \sum_i \int \mathbf{x}_i \cdot \mathbf{j}_i dV, \quad (5)$$

where $\mathbf{x}_i \equiv \nabla \psi_i$ is the gradient of the potential ψ_i , which characterizes the strength of its field.

If we now take out the sign of the integral some average values Ψ_i and \mathbf{X}_i of the potential of potential ψ_i and gradient $\nabla \psi_i$, expression (3) can be given the form of the basic thermodynamic equation of nonequilibrium systems as the *law of conservation and transformation of energy* [10]:

$$dU/dt = \sum_i \Psi_i d\Theta_i/dt - \sum_i \mathbf{X}_i \cdot \mathbf{J}_i, \quad (6)$$

where $d\Theta_i/dt = -\int \nabla \cdot \mathbf{j}_i dV$ is the scalar flow of energy carrier Θ_i (mass M , number of moles of the k -th substance N_k , charge Θ_e , amount of movement \mathbf{P} , etc.) across the system boundaries; $\mathbf{J}_i = \int \mathbf{j}_i dV = \Theta_i \bar{\mathbf{v}}_i$ is the vectorial flow of the energy carrier Θ_i within the system; $\bar{\mathbf{v}}_i$ - its average speed; $\mathbf{X}_i \cdot \mathbf{J}_i$ – power of the process of transformation of the i -th form of energy into others¹⁾.

The first sum of the expression (6) characterizes the processes that do not violate the distribution of energy carriers Θ_i over the system volume and are caused solely by their flows \mathbf{J}_i across the system boundaries. The first sum in (6) characterizes the processes that do not violate the distribution of energy carriers Θ_i in the system volume and are caused solely by their flows \mathbf{J}_i across the system boundaries. These include heat transfer, mass transfer, diffusion of the k -th substances, volumetric deformation of the system, etc. i.e. energy transfer processes in the i -th form without converting it into any other forms. Moreover, by replacing ψ_i with Ψ_i , relation (6) preserves the form of equality in the transition to irreversible processes, which eliminates the well-known problem of thermodynamic inequalities [4].

The processes described by members of the 2nd sum (4) have a different character. These processes are non-equilibrium, even being quasi-static since they preserve the nonuniformity of the potential field ψ_i . Such processes are caused by the redistribution of the energy carrier Θ_i over the volume of the system V and the displacement of the center of this quantity \mathbf{R}_i by some distance $\Delta \mathbf{R}_i$ with the average velocity $\bar{\mathbf{v}}_i = d\mathbf{R}_i/dt$. They generate internal flows of energy \mathbf{J}_i , not beyond the boundaries of the system. In this case, there are “moments of distribution” of energy carriers $\mathbf{Z}_i = \Theta_i \Delta \mathbf{R}_i$ with a shoulder $\Delta \mathbf{R}_i$, which characterize the removal of the system as a whole from the equilibrium state.

¹⁾ In equation (6) the rule of signs for heat and work accepted in thermodynamics is preserved: the heat brought to the system and the work done by it are positive.

One of the important consequences of the basic law of thermokinetics (4) is the ability to find energy carrier flows $\mathbf{J}_i = \Theta_i \bar{\mathbf{v}}_i$ directly as time derivatives $d\mathbf{Z}_i/dt$ of the moments \mathbf{Z}_i , and strengths \mathbf{X}_i as derivatives of the system energy U according to the parameters \mathbf{Z}_i

$$\mathbf{X}_i = - (\partial U / \partial \mathbf{Z}_i), \quad (7)$$

Thus, the law (4) allows one to find the basic quantities with which the TIP operates, without requiring for this the compilation of cumbersome balance equations of entropy, energy, mass, charge, momentum, etc. [6]. Since the derivative $(\partial U / \partial \mathbf{Z}_i)$ is in the conditions $\Theta_i = \text{const}$, the expression (6) gives the concept of thermodynamic force \mathbf{X}_i the general physical meaning of the force $\mathbf{F}_i = - (\partial U / \partial \mathbf{R}_i)$, referred to the unit of energy carrier quantity $\mathbf{X}_i = \mathbf{F}_i / \Theta_i$, that is, the field strengths of the potential ψ_i of the system. Although the work remains orderly (W_i^{or}) and is defined in the same way as in mechanics:

$$dW_i^{or} = \mathbf{F}_i \cdot d\mathbf{R}_i = \mathbf{X}_i \cdot d\mathbf{Z}_i, \quad (8)$$

it becomes internal and dependent on the process path, i.e. loses the property of full differential¹⁾.

It is easy to see that for internally equilibrium systems ($\mathbf{X}_i = 0$; $\Psi_i = \psi_i$), equation (4) goes into the combined equation of the 1st and 2nd principles of classical thermodynamics in the form of a generalized Gibbs relation [3, 4]:

$$dU = \sum_i \psi_i d\Theta_i. \quad (9)$$

Heat transfer dQ and any type of work dW_i in this equation are expressed in a different way than in (6) and are determined by multiplying the generalized scalar potential ψ_i (pressure p , chemical μ_k , electric ϕ , etc.) by changing the internal parameter i (volume V , the number of moles of the k th substance N_k , the charge Θ_e , etc.). This reveals the artificiality of the division of all impacts on heat and work by Clausius and makes it possible to attribute all such effects to the work of introducing energy carrier Θ_i . The elementary quantities of this work $dW_i^{ee} = \psi_i d\Theta_i$ are also not full differentials, but they are not related to overcoming the forces \mathbf{F}_i . This reveals the fundamental difference between the works of the input dW_i^{ee} and dW_i^{or} , indicating that the true “dividing line” runs between them, and not between Q and dW_i^{ee} .

So, equation (6) differs from (9) by explicitly taking into account the disequilibrium of the systems under study and the nonstaticity (nonequilibrium) of the actual processes occurring in them using the parameters \mathbf{X}_i and \mathbf{J}_i . At the same time, it becomes obvious that even without speed decomposition into translational and rotational components, the internal energy of a nonequilibrium system becomes a function of double the number of arguments $U = U(\Theta_i, \mathbf{R}_i)$. The latter testifies to the inconsistency of the local equilibrium hypothesis, according to which the elements of a nonequilibrium continuum are characterized by the same set of variables as in equilibrium (despite the appearance of potential gradients in them).

¹⁾ The sign of incomplete differential d in this expression emphasizes the fact that elementary heat transfer dQ and elementary work dW are not full differentials, and the ratio between them depends on the path of the energy exchange process.

Another important consequence of law (6) is the possibility of representing the internal energy U as the sum of the partial energies of all its forms U_i . This is easiest to verify by integrating (5) taking into account $\int \nabla \cdot \mathbf{j}_e dV = \sum_i \int \nabla(\psi_i \mathbf{j}_i) dV$ under the conditions of equality of the velocities v_i and v_e . Then $\int \rho_e dV = \sum_i \int \psi_i \rho_i dV$, and

$$U = \sum_i U_i = \sum_i \int \psi_i \rho_i dV = \sum_i \Psi_i \Theta_i. \quad (10)$$

In this case, each form of the internal energy U_i is expressed by the product of the intensive Ψ_i and the extensive measure Θ_i , which further greatly facilitates their finding. All this allows thermokinetics to obtain all the consequences of consumer goods without invoking any hypotheses, postulates, and considerations of a statistical and mechanical nature. Moreover, due to the unity of the conceptual system for all forms of energy embedded in equation (6), it allows the thermodynamic method of studying systems to be extended to other fundamental disciplines [10].

3. REPLACING ENTROPE BY THERMOIMPULSE

The deductive approach (from the general to the particular), used above in deriving the basic equation of thermokinetics, eliminates the need to idealize the processes contained in the concepts of "equilibrium", "quasistatic", "reversible", "ideal", etc. The concepts "process" and "equilibrium", strictly speaking, were initially incompatible, since equilibrium is defined in thermodynamics as a state characterized by the cessation of any macro-processes. This contradiction laid on the basis of thermodynamics, gave rise to a lot of conventions that impede its understanding. Indeed, if we consider isolated systems, then for them the concepts of external kinetic E^k and potential E^n energy are meaningless, so writing the energy conservation law for isolated systems in the form

$$(E^k + E^n + U)_{u3} = \text{const} \quad (11)$$

is obviously incorrect.

Further, if the thermodynamics of Clausius was limited to the study of internal equilibrium (homogeneous) systems, then by virtue of the very definition of the concept of equilibrium, the possibility of turning kinetic E^k and potential E^n energy into internal U was excluded. In this case, the principle of increasing entropy thermodynamics.

The difficulties of understanding thermodynamics intensified as a result of the distortion of the original meaning of work W and heat Q . The concept of work W passed into thermodynamics from mechanics (L. Carnot, 1783; Poncelet, 1826), where it was measured by the scalar product of the vector of the resulting force \mathbf{F} by the displacement $\Delta \mathbf{R}$ caused by its center of body mass \mathbf{R} ($dW_i = \mathbf{F}_i \cdot d\mathbf{R}_i$) [1]. Subsequently, depending on nature, mechanical, electrical, magnetic, chemical, nuclear, etc. forces were distinguished. However, the work of W always remained in mechanics a quantitative measure of the process of transformation of external energy E from one (i -th) form to another (j -th). In addition, the operation of any forces \mathbf{F}_i in mechanics did not affect the internal energy and therefore did not depend on the process path, so its elementary quantity was expressed by the full differential dW_i . However, equilibrium thermodynamics refused to use the concept of force, since the resultant \mathbf{F} of internal

forces is always zero. In thermodynamics, however, all forces are internal, not having the resulting \mathbf{F} . Therefore, the concept of work in it has a different meaning, being a quantitative measure of the process, not related to the transformation of energy.

The difference in the interpretation of heat is even more significant. Historically, heat has been studied along with such phenomena as light, sound, electricity, magnetism, that is, it was considered as a form of movement inherent in bodies. Such an understanding of heat follows from the law of thermal conductivity of Fourier (1822), based on the idea of heat as a kind of indestructible and weightless fluid. It is also preserved in the concept of the heat capacity of the body. The meaning of heat as a form of energy is also implied in the theory of heat transfer (according to the principle: you can only exchange what your partners have). In non-equilibrium systems, such an understanding of heat is dictated additionally by a number of thermal effects caused by energy dissipation (friction, chemical transformations, high-frequency or induction heating, etc.) and not related to heat exchange. Only in equilibrium systems, where there are no such thermal effects, does heat become an exclusively quantitative measure of the heat exchange process.

It is this understanding of heat that gave rise to the search for the coordinates of heat exchange as a quantity, which necessarily changes in the processes of equilibrium heat exchange, but remains unchanged when performing reversible work W_i (in adiabatically isolated systems). Understanding this circumstance makes the principles of existence and entropy increase incompatible within the framework of equilibrium thermodynamics [11]. Therefore, “the question of the physical bases of the theorem on the monotonic increase of entropy ... remains open [12]. This was the reason for the emergence in thermodynamics of a large number of paralogism, which made the entropy its “Achilles heel” [13].

Meanwhile, the solution to the problem of finding the quantitative measure of the energy carrier $oHoci$ for each i -th form of internal energy $U_i = \psi_i \Theta_i$, including that of thermal energy U_q , is already contained in expression (8). According to him, there is an internal heat energy U_q , which has extensive Θ_q and intensive measure ψ_i . The role of the latter is always a value that takes the same value in all systems that are in equilibrium. In systems with a thermal degree of freedom, this value is the absolute temperature T , which is nonzero as long as thermal equilibrium exists. The quotient of U_q divided by the potential $\psi_i \equiv T$ determines an extensive measure of thermal motion $\Theta_q = U_q/T$. It is easy to see that in classical thermodynamics, the analogs of U_q and Θ_q are the “bound energy” of the Helmholtz TS and the entropy S as the quotient from the division of this energy by the absolute temperature T .

Hence, the physical meaning of Θ_q as a state parameter. If we compare the changes in the internal thermal dU_q and kinetic dE^k energy of a homogeneous system

$$dU_q = Td\Theta_q; dE^k = \mathbf{v} \cdot d\mathbf{P}, \quad (12)$$

and take into account that the temperature T plays the same role in the process of establishing thermal equilibrium as the speed \mathbf{v} - in the process of exchanging the impulse \mathbf{P} of an orderly movement, it becomes clear that the parameter Θ_q is a “thermal impulse”, i.e. *the impulse of the thermal movement of particles*, which has lost its vector nature due to the randomness of thermal motion. Such an understanding of it is consistent with the molecular - kinetic interpretation of temperature as a measure of the intensity of the chaotic motion of the particles of the system.

In the more general case of inhomogeneous systems, the parameter i has the meaning of the average integral temperature of the system. Then in accordance with (6)

$$\bar{d}Q = dU_q = \bar{T} d\Theta_q. \quad (13)$$

Note that this expression also preserves the form of equality for irreversible processes when $TdS > dU + \bar{d}W$, which removes the well-known problem of thermodynamic inequalities [3]. This is another argument in favor of building thermodynamics of real processes according to the principle “from the general to the particular”. Yes, and in the etymological sense, the term “thermoimpulse” more closely matches the essence of the matter, since the parameter Θ_q explicitly exists in a thermally inhomogeneous system regardless of the presence or absence of its heat exchange process with the environment. This frees us from the search for evidence of the existence of entropy in polyvariant systems, which turns out to be very difficult even for the simplest thermomechanical systems [14].

An equally important conclusion from equation (4) is the possibility of interconverting not only any forms U_i of the internal energy $U = \sum_i U_i$, but also their energy carriers Θ_i . Indeed, for isolated systems ($dU/dt = 0$; $\sum_i \Psi_i d\Theta_i/dt = 0$), from (6) in view of (10) it follows:

$$dU_i/dt = d(\Psi_i \Theta_i)/dt = 0. \quad (14)$$

Thus, thermokinetics reveals the possibility of not only increasing but also decreasing thermoimpulse during these transformations. This in no way followed from classical thermodynamics, according to which, in adiabatic processes, entropy could only increase. In this case, the entropy of the universe could only increase, and, therefore, could never be revived after its "heat death". Thermokinetics, on the other hand, allows the emergence of a thermoimpulse in the process of formation of the visible (baryonic) matter of the Universe, which is the main difference between the thermo-impulse and Clausius entropy. It is of interest to consider what this difference leads to.

4. THE GROWTH OF A THERNOIMPULSE IN RELAXATION PROCESSES

At the time of R. Clausius, the only energy carrier not obeying the conservation laws, that is, having internal sources, was entropy S . Therefore, the use of entropy as a criterion reflecting spontaneous changes in the state of the systems under study was completely natural for that time. However, with the application of thermodynamics to chemical reactions, it was found that the numbers of moles k -th of substances N_k also have the same properties, which also change due to the diffusion of k -th substances across system boundaries and due to spontaneous chemical reactions in it.

Moreover, in the future, it was also found that in the processes of metal cutting, the so-called "heat release coefficient", i.e. the ratio of the amount of heat dissipated to the total Q^H/W^T work expended is usually less than one. This means that part of the work of destruction of metals turns into potential energy of chips, and not into heat. This circumstance is even more pronounced in the processes of crushing materials, under which not only the temperature and entropy increase, but also the surface energy of the material particles. Thus, experience confirms that entropy is by no means the only parameter that changes in relaxation processes.

However, according to (14), $dU_q/dt = d(\bar{T} \Theta_q)/dt$, that is, the thermal impulse changes due to the occurrence of only those processes that are accompanied by a change in the thermal form of energy. In the general case, this happens both as a result of heat supply from outside and as a result of the dissipation Q^d :

$$dU_q = \bar{d}Q + \bar{d}Q^d = \bar{T} d\Theta_q + \Theta_q d\bar{T}. \quad (15)$$

This makes the entropy balance equation proposed by Prigogine superfluous:

$$\bar{d}Q + \bar{d}Q^d = T d_e S + T d_i S, \quad (16)$$

where $d_e S = \bar{d}Q/T$ and $d_i S = \bar{d}Q^d/T$, i.e. quantities that are not components of the total entropy differential dS and therefore go beyond the theory of differential calculus (in contrast to $\bar{T} d\Theta_q$ and $\Theta_q d\bar{T}$ as components of $dU_q = T\Theta_q$).

Comparing (15) and (16) with the expression of the dissipative function of $T d_i S$ in the thermodynamics of irreversible processes (TIP) [6, 15]:

$$T d_i S/dt = \sum_i \mathbf{X}_i \cdot \mathbf{J}_i > 0, \quad (17)$$

we find that this theory, like classical thermodynamics, makes entropy a scapegoat for "any and all" irreversibility. In addition, according to (16), the entropy increases only as a result of the transformation of ordered forms of motion into chaotic. In fact, the entropy increases in the process of thermal relaxation of the very thermal energy U_q which is considered to be purely chaotic.

A clear confirmation of this circumstance can serve as a heat exchange process between the Q' source and the Q'' heat receiver with constant temperatures T_1 and $T_2 < T_1$. Since this process is not accompanied by the transformation of heat energy into some other form, then for it $dU_q = dU_q = dU_{q'} + dU_{q''} = 0$. Then $dS' = dU_{q'}/T_1$ and $dS'' = dU_{q''}/T_2$, so

$$dS' + dS'' = dU_{q''}(1/T_2 - 1/T_1) > 0. \quad (18)$$

This means that thermal energy also has a well-defined "ordered" part, which is lost in heat conduction processes. It was not by chance that C. Carnot understood by irreversibility "any decrease in temperature not related to the performance of work" [3].

Direct experimental confirmation of the validity of expression (15), and not (16), were experiments to study the process of thermal relaxation in roll materials [16]. They contained a resistance thermometer conductor along the entire length of a tightly packed roll of paper, cardboard, rubber tape, and other sheet materials, which made it possible to measure the average integral temperature of the system. Then the roll was subjected to non-uniform heating from an external heat source, after which the resistance of such a "dispersed" thermometer was recorded in it during the thermal relaxation of the sample. It remains to show that the replacement of entropy by a thermoimpulse makes it possible to eliminate a number of paralogisms arising in thermodynamics when trying to generalize it to nonthermal forms of energy and to nonstatic processes in polyvariant systems [5]. The most paradoxical in these experiments was the fact that all tested materials initially experienced a significant (up to 17%) rise in temperature, which

lasted for tens of minutes, until a decrease in temperature due to cooling of an insufficiently insulated roll began to prevail.

This phenomenon, which the author called the “growth effect of the measured heat content,” was not satisfactorily explained, since, under conditions of constant isobaric and isochoric heat capacity, the temperature rise violates the law of energy conservation. At the same time, this phenomenon directly follows from relation (17) as a result of the dissipation of the ordered part of the internal thermal energy U_q under the conditions $\bar{T} d\Theta_q = 0$. It also follows that in the reverse process of “concentration” of thermal energy, the entropy should decrease. However, classical thermodynamics excludes this.

The situation is different from the standpoint of thermokinetics, which allows for the interconversion of various forms of energy. In this case, it becomes clear that when the internal reversible work против W_i “against equilibrium” is performed in an adiabatically isolated system ($dU_q = 0$), the thermo-impulse can decrease. This happens, for example, during phase transitions under conditions $\bar{T} = \text{const}$, accompanied by heat removal ($\bar{T} d\Theta_q < 0$) with $\Theta_q d\bar{T} = 0$. This circumstance brings together the notion of a thermal pulse with statistical (Boltzmann) entropy, which can also decrease during “order” [17]. At the same time, the thermopulse as a completely deterministic and phenomenological concept does not need to be interpreted from the standpoint of statistical thermodynamics.

It remains to show that the replacement of entropy by a thermoimpulse makes it possible to eliminate a number of paralogsms arising in thermodynamics when trying to generalize it to nonthermal forms of energy and to nonstatic processes in polyvariant systems [5].

5. THERNOIMPULSE AND "THERMAL DEATH OF THE UNIVERSE"

At the time of R. Clausius, irreversibility was understood only as of the impossibility of restoring the “motive force of heat”. Therefore, in his famous discourse on the operation of two coupled heat engines, R. Clausius takes it 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 the heat source T_1 and the heat sink T_2 [1]. Then in an arbitrary cycle with elementary quantities of the summed dQ_1 and the abstracted dQ_2 heat

$$\eta_t = 1 - dQ_2/dQ_1 < \eta_t^K = 1 - T_2/T_1 \quad (19)$$

It follows that $dS_2 = dQ_2/T_2 > dS_1 = dQ_1/T_1$, i.e., the entropy in the irreversible process of doing work increases. Not seeing limitations to his postulate, R. Clausius gives this conclusion the status of a general physical "principle of increasing entropy" and puts it in the basis of the "theory of the thermal death of the Universe." This conclusion, signifying essentially “co-solubility” of the Universe, is still the basis for cosmological theories of the “Big Bang” type. Meanwhile, it can be shown that remaining within the framework of classical thermodynamics and without introducing additional non-equilibrium parameters Z_i , it is generally impossible to substantiate the principle of entropy increase.

Consider for this purpose the general case of a polyvariant system, whose internal energy U is characterized by entropy S , volume V , charge Θ_e , polarization \mathbf{D} , magnetization \mathbf{M} , momentum \mathbf{P}_k of the internal (diffusion) motion of the k -th components of the system and their moments \mathbf{L}_k , i.e. $U = U(S, V, \Theta_e, \mathbf{D}, \mathbf{M}, \mathbf{P}_k, \mathbf{L}_k)$. Considering the entropy S as an inverse function

of these variables $S = S(U, V, \Theta_e, \mathbf{D}, \mathbf{M}, \mathbf{P}_k, \mathbf{L}_k)$, we find that, by the laws of conservation of these arguments in isolated systems, the entropy of such a system S_{iz} remains unchanged [13]:

$$S_{из} = S(U, V, \Theta_e, \mathbf{D}, \mathbf{M}, \mathbf{P}_k, \mathbf{L}_k) = \text{const.} \quad (20)$$

From a physical point of view, this conclusion is quite obvious: if the state of the system is equilibrium, then, in accordance with the general principle of thermodynamics, no spontaneous processes can arise in it, leading to an increase in entropy. It is a different matter if the entropy S is replaced by the thermoimpulse Θ_q and, along with the above variables, the "heterogeneity parameters" \mathbf{Z}_i are taken into account. Then $U = U(\Theta_q, V, \Theta_e, \mathbf{D}, \mathbf{M}, \mathbf{P}_k, \mathbf{L}_k, \mathbf{Z}_i)$, and in isolated systems $\Theta_q = \Theta_q(U, V, \Theta_e, \mathbf{D}, \mathbf{M}, \mathbf{P}_k, \mathbf{L}_k, \mathbf{Z}_i)$. In this case, it becomes obvious that the thermal pulse Θ_q can vary in both directions depending on the behavior of the parameters \mathbf{Z}_i . This is what happens in the Universe in the processes of "supernova explosion", when baryonic matter, possessing a chaotic form of energy, returns to its original form, turning into the non-barionic (unstructured) matter, possessing the only gravitational form of energy [18].

Here lies the answer to the question why "in classical and later studies on thermodynamics we do not find an impeccably rigorous proof of the entropy increase theorem that is not subordinate to statistics" [19]. The point is simply that the law of increasing entropy, which imposes a one-sided line of behavior on nature, simply does not exist. This conclusion is confirmed by the fact that the thermal equilibrium in the Universe has not come for a period of at least 14 billion years, which the "Big Bang" theory has diverted to it.

Gnoseologically, it is extremely important that the thermal impulse, in contrast to the Clausius entropy, can decrease in adiabatic processes. An example of such a process is the usual acceleration of the system, accompanied by the ordering of chaotic motion and the degeneration of the thermal momentum to zero as it approaches the ultimate speed of light and the transformation of matter into radiation. This brings the thermoimpulse closer to the Boltzmann statistical entropy introduced by him with the aim of giving the Universe at least a chance to avoid the "thermal death". The introduction of a thermopulse frees one from the need to resort to phenomenological thermodynamics to probabilistic considerations.

6. THERNOIMPULSE AND PROCESSES OF EVOLUTION

The "glaring contradiction of thermodynamics with the theory of biological evolution" [2] is well known. It is due to the fact that the principle of increasing entropy prescribes nature only its degradation. Meanwhile, it is known that nature is characterized not only by destructive but also creative tendencies.

Attempts to resolve this contradiction by the spontaneous emergence of "order" from "chaos" [15] are unsatisfactory if only because they contradict the principle of increasing entropy, without making attempts to prove its inconsistency. Replacing entropy with a thermal pulse allows us to resolve this contradiction. Like the Boltzmann statistical entropy, the thermoimpulse can decrease in the system's ordering processes, and this will remove the mentioned contradiction of the theory of evolution not only with the statistical but also the phenomenological thermodynamics. Moreover, it becomes possible to use the inhomogeneity parameters of the systems themselves \mathbf{X}_i as criteria for evolution. Such parameters are the

moments of the distribution $\mathbf{Z}_i = \Theta_i \Delta \mathbf{R}_i$ [20], or the averaged potential gradients associated with them as a measure of the stress state of the system. The latter is most convenient, since their change in the most obvious way reflects not only the approximation or distance of the system from the equilibrium state in any of the degrees of freedom of the system separately, but also sets forth the condition for this equilibrium:

$$\mathbf{X}_i > 0 \text{ (evolution); } \mathbf{X}_i = 0 \text{ (equilibrium); } \mathbf{X}_i < 0 \text{ (involution)}. \quad (21)$$

Thus, thermokinetics returns to the equilibrium condition its initial forceful character, as it was in mechanics. This character is also reflected in the etymology of the term “equilibrium”, which retains its meaning after the expulsion of the concept of force from equilibrium thermodynamics. The return of power gives a more visual, than entropy, more “physical” and more informative tool for analyzing the problems of evolution into the hands of researchers [20].

The proposed thermokinetics generalization of the energy conservation law in the form (6) directly indicates the possibility of the occurrence of oppositely directed processes in isolated non-equilibrium systems, in which

$$(dU/dt)_{iz} = - \sum_i \mathbf{X}_i \cdot \mathbf{J}_i = 0. \quad (22)$$

This means that, along with dissipation processes, in which $\mathbf{X}_i \cdot \mathbf{J}_i > 0$, in isolated systems, there are also possible processes of “self-organization” of certain degrees of freedom, in which the product $\mathbf{X}_i \cdot \mathbf{J}_i < 0$. These are, in particular, “ascending diffusion” processes (substance transfer in the direction of increasing its concentration), the phenomenon of “conjugation” of chemical reactions (reactions in the direction of increasing its affinity), “active transport” (accumulation in the organs of substances with greater Gibbs energy), etc. Therefore, thermokinetics are able to reflect not only oscillatory processes in natural and technical systems, in which the product $\mathbf{X}_i \cdot \mathbf{J}_i$ periodically changes its sign, but also “counter-directed” processes, when one degree of freedom of the system approaches equilibrium, while the other moves away from it. All this eliminates the above-mentioned contradiction between thermodynamics and evolution.

7. ELIMINATE THE PARALOGISM OF "GIBBS PARADOX"

Among the paradoxes of physics, there is hardly another one as well known and as mysterious as the “Gibbs Paradox” - the statement about the stepwise increase in entropy when mixing non-interacting ideal gases in the absence of any thermal or volume effects [5]. In his famous work “On the Equilibrium of Heterogeneous Substances” (1876), J. Gibbs found that the difference between the entropy of a mixture of two masses of ideal gases M_1 and M_2 , each of which occupied at first half of the total volume, is greater than the sum of the entropies of the same gases before mixing. value:

$$S - [M_1 R_1 \ln(V/2) + M_2 R_2 \ln(V/2)] = R_c \ln 2, \quad (23)$$

where $R_c = M_1 R_1 + M_2 R_2$ is the gas constant of the mixture.

It is characteristic that Gibbs himself, who adhered to the probabilistic interpretation of entropy, did not see anything paradoxical in this result, believing that he was “entirely determined by the number of molecules being mixed”. However, as this issue was studied from a phenomenological standpoint, researchers encountered more and more difficulties, which led to the appearance of the phrase “Gibbs paradox” [21].

For a century and a half, this paradox has more than once become the object of study for both physicists and philosophers. Many of his researchers thought that they were able to finally explain the strange independence of the entropy jump on the degree and nature of the difference of the mixed gases and at the same time the inapplicability of the expression (26) to the particular case of identical gases. However, like the legendary Sphynx, this paradox appeared again and again in the pages of scientific books and magazines and did not descend from them right up to the present. It is not by chance that the majority of researchers of this paradox inclined to the opinion that it “is not solvable in the plane of classical thermodynamics” [19, 21].

Indeed, a closed system of two arbitrary gases, separated by a movable partition that is impenetrable for them, has from the standpoint of classical thermodynamics only two degrees of freedom (thermal and mechanical). Even before mixing, such a system was in complete (thermal and mechanical) equilibrium, so the elimination of the partition between them could not cause any macro-process, since neither the temperature T , nor the pressure p , nor the composition of the system was also changed. In this case, the entropy jump can be caused only by a shift in the origin of the entropy. But then this jump contradicts the 3rd beginning of thermodynamics, according to which “the entropy of any equilibrium system, as it approaches absolute zero temperatures ceases to depend on any thermodynamic state parameters and in the limit $T = 0$ takes the same value for all systems, which can be set to zero” [4]. In this case, the Gibbs paradox appears as a paralogism, caused by the arbitrariness in choosing the origin of the entropy of open systems, that is, a violation of the third law of thermodynamics [21]. In other words, in classical thermodynamics, the Gibbs paradox has no right to exist, no matter what content we put into it.

The situation is different from the standpoint of thermokinetics, in which the state of a heterogeneous system is characterized by moments of concentration distribution of components Z_k and their thermoimpulse Z_q . Then it becomes obvious that the process of mixing gases is associated with the approach of the inhomogeneous system to equilibrium, in which these moments vanish. However, this change occurs monotonously and depends on the affinity of the mixed gases, decreasing to zero along with it. This gives a consistent solution to the mentioned paradox [5].

8. ELIMINATE THE PARALOGISM OF "NEGATIVE ABSOLUTE TEMPERATURES"

The concept of negative absolute temperature arose in the second half of the twentieth century after the discovery of spin systems in which, by reversing the sign of a magnetic field or a high-frequency pulse, it was possible to create an “inversion of populations” of energy levels of elementary particles with spin. It is understood as a state in which the majority of elementary particles are at the upper energy level [23]. The basis for the introduction of this concept was all the same statistical interpretation of the concept of entropy. If the

thermodynamic probability of a state is assumed to be identical entropy on the grounds that both quantities are additive and reach a maximum in the equilibrium state (the Boltzmann principle), then comparing the derivative expression $(\partial U/\partial S)$ for the statistically determined internal energy U and entropy S with the known definition thermodynamic temperature of thermomechanical systems

$$T \equiv (\partial U/\partial S)_V, \quad (23)$$

then we can conclude that the system of nuclear spins in the state of the inverse population should be attributed to a negative absolute temperature $T < 0$. It is characteristic that with this interpretation of entropy it was necessary to assume that the states of spin systems with negative absolute temperature lie above infinitely high temperatures $T = \infty$!

However, the troubles with physics were not limited to this, and there followed an inevitable conclusion about the “inversion” in such systems of the very principle of the excluded perpetual motion machine of the 2nd kind [24]. This "inversion" consists in asserting the possibility of the complete transformation of heat into work in such systems and the impossibility, on the contrary, of completely transforming work into heat. If we imagine the Carnot cycle, carried out at negative temperatures of hot and cold bodies T_1 and T_2 , then the thermal efficiency of a reversible Carnot machine

$$\eta_r^K = 1 - Q_2/Q_1 = 1 - T_2/T_1 \quad (24)$$

will become negative, since in the region $T < 0$, a body with a lower absolute negative temperature ($T_2/T_1 > 1$) should be considered hot. This more than “paradoxical” result means that the work done in this temperature region in the Carnot cycle will be positive if heat Q_2 is taken from the “cold” source, and the heat sink is a hotter body. Since, by means of thermal contact between the heat source and the heat sink, all the heat Q_1 transferred to the “hot” source can be returned to the “cold” by heat exchange, in a continuous sequence of cycles, the work will be carried out due to the heat of only one “cold” body without any residual changes in other bodies in violation of the 2nd law of thermodynamics. This means "inversion" not only of the concept of thermodynamic temperature as a value of a strictly positive, but also of the very principle of the excluded perpetual motion machine of the 2nd kind.

Paradoxically, this conclusion was made on the basis of the same second start! In fact, the possibility of the complete transformation of heat into work means that the expression (24) is not applicable in the region $T < 0$. But then all the conclusions based on it are no longer valid! Despite the obviousness of this "vicious circle", the statement about the "inversion" of the principle of the excluded perpetual motion machine of the 2nd kind penetrated the pages of textbooks and began to be reproduced even in the best of them [4]. This is just one of many examples when the identification of thermodynamic and statistical entropy has undermined the former confidence in the infallibility of thermodynamics and the indisputable justice of its consequences [10].

The solution to this problem is the replacement of entropy by the thermal pulse Θ_q . In contrast to the moment of its distribution, Paradoxically, this conclusion was made on the basis of the same second start! In fact, the possibility of the complete transformation of heat into work means that the expression (24) is not applicable in the region $T < 0$. But then all the conclusions based on it are no longer valid! Despite the obviousness of this "vicious circle", the

statement about the "inversion" of the principle of the excluded perpetual motion machine of the 2nd kind penetrated the pages of textbooks and began to be reproduced even in the best of them [4]. This is just one of many examples where the unreasonable transfer of concepts and methods of equilibrium thermodynamics to non-equilibrium systems leads to the loss of its main advantage of the thermodynamic method - the immutable justice of its consequences [5].

The solution to this problem is the replacement of entropy by the thermopulse Θ_q . In contrast to the moment of its distribution $\mathbf{Z}_q = \Theta_q \Delta \mathbf{R}_q$, the thermo-impulse does not change the sign of either energy or thermo-impulse in the expression

$$T \equiv dU_q/d\Theta_q. \quad (25)$$

The principle of the excluded perpetual motion remains unshakable.

9. ELIMINATE THE PARALOGISM OF RELATIVISTIC HEAT ENGINES

In the years following the emergence of the fundamental work of A. Einstein (1905), which contained the formulation of the special theory of relativity (STR), physicists sought to give the classical laws a form that would be invariant in all inertial reference systems. In the field of thermodynamics, this was first accomplished by M. Planck in 1907 [25], and A. Einstein agreed with his transformations. And then there was a rare case when, after half a century, physicists discovered that Planck's transformations lead to an absurd result [26,27]. The stormy discussions that followed revealed such inconsistencies in the definitions and interpretations of the fundamental concepts of thermodynamics (energy, heat, work, entropy, etc.) that their participants were forced to admit the loss of former thermodynamics glory.

The differences that arose concerned the principle of the excluded perpetual motion machine of the 2nd kind. Planck's transformations did not leave an invariant expression for the efficiency η_r^K of the relativistic Carnot cycle (with a fast-moving heat source). According to Planck, the efficiency of the Carnot relativistic cycle turned out to be less than that of the classical one. Moreover, at certain values of the Lorentz multiplier, this efficiency turned out to be even negative. Meanwhile, its expression through temperature was one of the mathematical formulations of the second law of thermodynamics and, therefore, the requirement of invariance extended to it.

A detailed analysis of this circumstance showed that the cause of the differences is the same statistical interpretation of entropy [5]. They are also removed when entropy is replaced by a thermal pulse. The fact is that M. Planck and his followers considered entropy an invariant quantity. In contrast, the thermopulse in fast-moving bodies does not remain unchanged when they are accelerated. Indeed, the speed of any particle is the sum of the speeds of its relative and figurative movement and cannot exceed the limiting magnitude of the speed of light. Consequently, as the moving speed approaches its own limit, the relative (chaotic) movement, characterized by the magnitude of the thermal pulse, should attenuate: the substance "turns" into radiation.

Moreover, all arguments about relativistic transformations of thermodynamic quantities should be stopped if the definition of the concept of internal energy in thermodynamics is adhered to like that part of the total energy that does not depend on the position or movement

of the system relative to the external environment. This is a consistent solution to the paradox under consideration [5].

10. ELIMINATE OF ARBITRARINESS IN THE CHISE OF FORSES AND FLOWS

In 1931, the future Nobel laureate L. Onzager proposed a theory of the speed of irreversible physicochemical processes, rightly called by him “quasi-thermodynamics” [6] in view of the wide use of statistical and mechanical considerations. The main quantities with which this theory operates are the thermodynamic forces \mathbf{X}_i as the causes of the i -th scalar relaxation process, and the flows \mathbf{J}_i as their generalized velocities. These values are determined on the basis of the expression for the rate of occurrence (“production”) of the entropy dS/dt as a function of the parameters α_i , which characterize the removal of an adiabatically isolated system from the equilibrium:

$$dS/dt = \sum_i (\partial S / \partial \alpha_i) d\alpha_i / dt = \sum_i X_i J_i \quad (26)$$

L. Onzager does not specify what these parameters are and where they come from in equilibrium thermodynamics - this becomes clear only from the standpoint of thermokinetics and energodynamics [7, 10]. Therefore, in the theory of stationary irreversible processes (TIP) [4,6,29], built on the basis of quasi-thermodynamics, the main problem is to find the vector flows \mathbf{J}_i and the driving forces \mathbf{X}_i of processes of different nature. This problem is aggravated by the fact that the “entropy production” in expression (29) can be decomposed into factors \mathbf{X}_i and \mathbf{J}_i in many ways. In particular, only for the diffusion processes of the k th substance in multicomponent heterogeneous systems, the TIP allows the choice of \mathbf{X}_i as the driving forces for the concentration gradients of this substance ∇c_k , its enthalpy ∇h_k , and chemical potential $\nabla \mu_k$; differences of these potentials Δc_k , Δh_k and $\Delta \mu_k$, also their functions $\nabla(c_k/T)$, $\nabla(h_k/T)$, $\nabla(\mu_k/T)$ or $\Delta(c_k/T)$, $\Delta(h_k/T)$ and $\Delta(\mu_k/T)$.

Another disadvantage of TIP is the need to involve other fundamental disciplines in finding the parameters X_i and J_i . For this, in addition to a thorough knowledge of these disciplines, it is necessary to compile bulky equations of energy, mass, charge, impulse, its momentum, in order to separate the terms related to the expression (30) from them. The latter, however, is not quite easy to do, since these disciplines consider conservative systems and do not take into account irreversibility.

Another disadvantage of TIP is that it excludes from consideration a reversible part of real processes, which does not contribute to the “production” of the entropy dS/dt . This causes the boundedness of the TIP purely dissipative processes such as thermal conductivity, electrical conductivity, diffusion, and viscous friction. In this regard, it is the antipode of the “pseudo-thermostatics” of V. Thomson, which excluded from consideration the irreversible part of the phenomenon under study [3].

Thermokinetic is free from all these disadvantages. In it, the thermodynamic forces \mathbf{X}_i and the fluxes \mathbf{J}_i are found directly from the law of conservation and transformation of energy (4) as the average gradients of the potentials ψ_i and the impulses of energy carriers Θ_i . At the same time, they acquire a very specific and unambiguous meaning, which is then preserved in other fundamental disciplines. In addition, in thermokinetics, consideration does not exclude any (reversible or irreversible) part of real processes. This allows the thermodynamic method

to be extended to systems that perform useful work, which is primarily interested in thermodynamics [10]. Finally, it does not require the involvement of any hypotheses, postulates, model representations, or probabilistic considerations in the basis of the theory, which makes it possible to preserve in it the best features of classical thermodynamics. All this, taken together, confirms the correctness of A.I. Veinik, who for the first time proposed to expel entropy from thermodynamics and replace it with a measure of thermal energy that is more adequate to the essence of the matter [30].

11. CONCLUSIONS

1) The deductive construction of thermokinetics as a further generalization of nonequilibrium thermodynamics to the transformation processes of various forms of energy dictates the need to introduce additional parameters for the heterogeneity of the systems under study - the moments of the distribution of carriers of various forms of energy and the potential gradients associated with them. The nonequilibrium parameters describe the specific class of transformations of various components of the internal energy of the nonequilibrium system and shed new light on the principles of the existence and increase of entropy.

2) Generalization of thermodynamics to non-equilibrium processes of energy conversion reveals the need to replace entropy with a “thermoimpulse” — the impulse of internal motion of particles of matter, which has lost its vector nature due to the randomness of thermal motion. The difference between thermoimpulse as an extensive measure of thermal motion and thermodynamic entropy as the coordinates of heat exchange lies in its ability to decrease in the processes of transformation of thermal energy into its other forms, which brings the thermoimpulse closer to statistical entropy.

3) The derivation of the basic thermokinetic equation on the basis of the law of energy conservation in flow allows us to obtain a more general analytical expression for it, covering the processes of energy conversion and not turning into inequality in irreversible processes. This solves the problem of thermodynamic inequalities, reveals the possibility of interconversion of carriers of various forms of energy and opens up the possibility of extending the thermodynamic method of research to other fundamental disciplines.

4) One of the consequences of the law of conservation and transformation of energy is the presence of internal sources not only for entropy (thermoimpulse) but also for any other energy carriers. This deprives the entropy of the properties of the universal measure of “any and all” irreversibility and makes it necessary to introduce non-entropic criteria of evolution and equilibrium. The criteria proposed in the article in the form of thermodynamic forces make it possible to follow the behavior of each degree of freedom of the system separately and reflect not only the degradation of the system but also its evolution, thereby eliminating the “glaring contradiction” of evolution with thermodynamics.

5) Replacing entropy with a thermal impulse capable of both increasing and decreasing in real adiabatic processes makes it possible to eliminate not only thermodynamic inequalities and arbitrariness in the choice of flows and forces in the TNP, but also the paralogism of the theory of “thermal death of the Universe”, negative absolute temperatures, relativistic thermal machines, the Gibbs paradox, etc. At the same time, this property makes it unnecessary to involve probabilistic concepts in phenomenological thermodynamics.

References

- [1] Klausius R. Die mechanische Wärmetheorie. Braunschweig, Bd.I, 1876.
- [2] Prigogine I. Time, structure and fluctuations (Nobel lecture in chemistry in 1977). // UFN, 131(1980).185 ... 207. (In Russian).
- [3] Gelfer J.M. History and Methodology of Thermodynamics and Statistical Physics. Edn 2.–M.: Vysshaya shkola, 1981 (In Russian).
- [4] Bazarov I.P. Thermodynamics. Edn 4. M.: Vysshaya shkola, 1991. (In Russian).
- [5] Etkin V.A. Paralogism of thermodynamics - Saarbrücken, Palmarium Ac. Publ., 2015. (in Russian).
- [6] De Groot S.R., Mazur R. Non-Equilibrium Thermodynamics:– Amsterdam, 1962
- [7] Etkin V. Thermokinetics (Synthesis of Heat Engineering Theoretical Grounds).- Haifa, 2010.
- [8] Umov A. I. Selected Works. M.L., 1950. p. 203.(Умов А. И. Избранные сочинения. М. Л., 1950. С. 203).
- [9] Etkin V.A. Synthesis and new applications of the energy transfer and energy conversion theories. (Summary of thesis for doct. techn. sciences. //Moscow: State Techn. Univ. Press, 1998.- 35 pp. (in Russian).
- [10] Etkin V. Energodynamics (Thermodynamic Fundamentals of Synergetics).- New York, 2011.(Эткин В.А. Энергодинамика (синтез теорий переноса и преобразования энергии) – СПб., Наука, 2008).
- [11] Gukhman A. A. On the foundations of thermodynamics. M.: Energoatomizdat, 1986. (In Russian).
- [12] Landau L.D., Livshits E.M. Theoretical Physics. V. Statistical Mechanics. Edn 5.– M.: Fizmathlit, 2004. (In Russian).
- [13] Etkin V.A. Achilles heel of thermodynamics. *Problems of Science*, 10(34), 2018, 5-18. (In Russian).
- [14] Caratheodory C. Untersuchungen über die Grundlagen der Thermodynamik. *Math. Ann.* 1909. – XVII. – №3. – P. 355.
- [15] Prigogine I. Order and Chaos, Man's new dialog with Nature. London, 1984.
- [16] Brovkin L.A. On Measurable Heat Content Rise Effect for Solid Materials. // *Ing.-phys. zhurnal*, 1960–№5; 1962–№6 (in Russian).
- [17] Klimantovich Yu. L. Decrease in entropy in the process of self-organization. S – theorem. *Letters to the Journal of Technical Physics*, 8 (1983) 12-14.
- [18] Etkin V. Gravitational repulsive forces and evolution of universe. *IOSR Journal of Applied Physics* 8(6), 2016. 43-49. DOI: 10.9790/4861-0806054349
- [19] Putilov K.A. Thermodynamics. M.: Science, 1971 (in Russian).

- [20] Etkin V.A. New Criteria of Evolution and Involution of the Isolated Systems. *International Journal of Thermodynamics* 2018, 21(2), pp. 120-126, doi: 10.5541/ijot.341037
- [21] Kedrov, B. M. The Gibbs Paradox. M.: Science, 1969. (In Russian).
- [22] Nernst V. Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes. Halle/Saale, Knapp, 1918
- [23] Abragam A., Proctor W. Spin Temperature. *Phys. Rev.* 1958, 109, 1441
- [24] Ramsey N.F. Thermodynamics and Statistical mechanics by Negative Absolute Temperature. *Phys. Rev.* 1956, 103(1), 279.
- [25] Plank M. Thermodynamics. Issue 5. M. L.: GIZ, 1925. (In Russian).
- [26] Ott H. *Zeitshr. Phys.* 1963, 70, 75.
- [27] Arzelies H. La crise actuelle de la thermodynamique theorie. *Nuovo Cimento*, 41 (1966). 61.
- [28] Onsager L. Reciprocal relations in irreversible processes. *Phys. Rev.* 1931, 237(14), 405-426; 238(12), 2265-2279.
- [29] Gyarmati I. Non-Equilibrium Thermodynamics. Field Theory and Variation Principles. – Springer –Verlag, 1970.
- [30] Veinik A.I. Thermodynamics. Ed. 3rd - Minsk: Higher School, 1968. (In Russian).