Review Article

Elimination of paralogisms of thermodinamics

Abstract

A number of specific examples show that replacing the energy carrier of the thermal form of motion with entropy as a heat transfer coordinate leads to a number of paralogisms, the number of which increases as the scope of application of thermodynamics expands. The epistemological roots of these paralogisms are revealed and a more general measure of the amount of chaotic motion, called a thermal impulse for brevity, is proposed. It is shown how its use instead of entropy eliminates all paralogisms known and discovered by the author, including the prediction of the thermal death of the Universe and the degradation of biological systems. It is concluded that replacing entropy with a thermal impulse opens the way to expanding the capabilities of the thermodynamic method in the study of nonequilibrium systems and non-static processes, to the synthesis of thermodynamics with other fundamental disciplines and to a deeper understanding of the world order.

Keywords: energy and entropy, heat transfer and work, dissipation and irreversibility, biological and cosmological evolution, paradoxes and paralogisms

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Introduction

More than one and a half centuries have passed since the concept of entropy and the principle of its increase in irreversible processes entered natural science.[1] However, disputes about the hidden meaning of this concept and the physical foundations of the mentioned principle,[2] which led to thermodynamics losing its former glory as a theory "whose conclusions will never be refuted by anyone",[3] are still ongoing. In the extensive scientific and pseudo-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 exhaustively proven and the "blatant 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. entropy appeared, which further complicated the interpretation of this multifaceted and difficult-to-intuitive concept.

Against this background, attempts to prove the inadequacy of the concept of entropy to the essence of the matter went unnoticed.[6] On the contrary, a situation like the Gibbs paradox and the theory of heat death has arisen in every area of application of thermodynamics, including radiation, non-thermal and relativistic machines, biological systems and systems with negative absolute temperatures and discrete energy, etc.[7] Entropy has become the "Achilles heel" of thermodynamics and the "scapegoat" for "any and all" irreversibility.[8] The purpose of this article is to show how useful it can be to replace entropy with thermal impulse as a more adequate extensive measure of thermal motion.

The need to redefine the need to redefine or replace thermodynamic entropy

The concept of entropy in the thermodynamics of R. Clausius[1] is inextricably linked with his idea of heat Q and work W as the only two ways of energy exchange between the system and the environment. This follows from his recording of its fundamental law (1st law of thermodynamics) in the form:

$$dU = \delta Q - \delta W = TdS - pdV, \qquad (1)$$

where U is the internal energy of the system; δQ, δW - elementary amounts of heat absorbed by the system and work done by it; T, S – absolute temperature and entropy; p, V - absolute pressure and volume of the system. Meanwhile, before Clausius, there was another idea of heat as a weightless and indestructible fluid called caloric. At the same time, heat was considered on a par with such phenomena as light, electricity, magnetism, etc., i.e., as a function of a state, not a process. This understanding of heat is still preserved in classical thermodynamics in the concept of heat capacity of a system[9] and in the theory of heat transfer, which is defined as the process of exchange of internal thermal energy between bodies.[10] Moreover, this understanding turned out to be the only acceptable one for the thermodynamics of irreversible processes (TIP), which operates with the concept of internal heat sources.[11-14] And R. Clausius himself initially operated with the concept of "total body heat" as the sum of heat supplied from the outside and released inside the body as a result of the "disgregation work" of a dissipative nature.[1] However, such a substitution of the concept of heat became more noticeable with the transition to the study of open systems, where, along with heat exchange and work, there are at least two more types of energy exchange: mass transfer, characterized by a change in the mass of the system while its composition remains unchanged, and diffusion of the kth substance across the boundaries of the system , characterized by a change in the composition of the system while its mass remains unchanged. Moreover, at the boundary where mass transfer or diffusion takes place, "the classical concepts of heat and work lose their meaning".[15] The division of energy exchange into heat exchange and work in complex (multivariant) systems that, in addition to expansion work $\delta W_p = pdV$, perform other types of external work We (mechanical, electrical, etc. forces) has become even more problematic. The elementary quantities of these types of external work dW^e were measured by the product of the vector of the resulting force **F** and the displacement $d\mathbf{r}$ of the object of its application caused by it, and the work itself $dW_i^e = dE = \mathbf{F}_i \cdot d\mathbf{r}_i$ was a quantitative measure of the process of converting external energy E from one (i-th) of its forms E_i to the other (j-th) E_j. Such work did not depend on the path of the process, and its elementary amount dW^e was a complete differential. This also included the work of gas in a flow – Vdp.[16] These types of work were fundamentally different from the work of the comprehensive expansion of pdV, primarily in the direction of the movement process (the vector nature of its

coordinates $\mathbf{r}_i$), as well as its dependence on the path (nature) of the process (the latter is emphasized by the designation of its elementary quantity through δW). This type of work is performed not only during expansion, but also when matter, charge, momentum, and any other energy carrier are introduced into the system. Heat transfer should also be included among them, since it is also associated with a change in the momentum of the chaotic movement of the particles that make up the system.

To distinguish between these two independent categories of work, it is advisable to call them "technical" W^t and "non-technical" W^n, respectively. The lack of understanding that "work and work are different" still prevents us from realizing that the true "watershed line" is not between heat Q and work W, but between ordered W_i^t and disordered W_i^n types of work as quantitative measures of fundamentally different processes of "energy transformation" and "energy transfer".[17] It should be noted that for complex systems in which both processes occur, evidence of the existence of entropy as a coordinate of heat transfer does not exist to date.[18]

There is one more circumstance that forces us to return to the search for a more general extensive measure of heat (its energy carrier) than entropy. It lies in the fact that in mechanics, based on which thermodynamics arose, all processes were considered reversible (going both forward and backward without any residual changes in the environment). This was also the theory of heat engines by S. Carnot,[19] based on the method of cycles he proposed. The very concept of a cycle implied the possibility of returning the working fluid of a heat engine to its original state, i.e., the reversibility of the processes occurring with it, which was fully consistent with the idea of caloric as a carrier of the thermal form of energy. Only the complete collapse of ideas about indestructible and weightless fluids prevented Clausius from seeing this and moving on to treating heat only as a quantitative measure of the heat exchange process. This was facilitated by the property of heat to flow "spontaneously" only in the direction of decreasing temperature, which was the basis for his formulation of the 2nd law of thermodynamics.[1] In any case, understanding heat as "energy in a state of transition," i.e., as a function of a process, required finding the coordinates of this process, i.e., a parameter that necessarily changes during its occurrence and stays unchanged in its absence (in adiabatic systems). R. Clausius found this coordinate by considering the same cycle of an ideal (reversible) heat engine, but he called it "entropy," thereby emphasizing the opposite property of caloric to increase because of the appearance of internal heat sources. This is most clearly manifested in writing the entropy balance equation:[11]

$$dS = d_e S + d_u S, \qquad (2)$$

where improvements in analysis methods, $= \delta_e Q^e/T$ and $d_u S = \delta Q^e/T$ – parts of the entropy change caused, respectively, by external heat exchange Q^e and internal heat sources Q^d.

According to this expression, any irreversible processes cause a change in the same parameter - entropy S. Thus, entropy turned into a "scapegoat" for "any and all irreversibility," although it was originally intended to describe heat transfer. The status of entropy did not change even after internal sources or sinks were discovered for other parameters for the numbers of moles k-x of substances Nk that arise or disappear during chemical reactions. With the expansion of thermodynamics to complex (multivariant) and nonequilibrium (including open, biological, and chemically reacting) systems, as well as to non-thermal and non-cyclic machines, entropy-related paralogisms began to arise in every area of application of thermodynamics.[20] Entropy has become a "cancerous tumor and the

Achilles heel" of thermodynamics.[21] However, the understanding that all these failures are explained by tries to study irreversible processes using equilibrium thermodynamics remained the property of only a few individual scientists.[22] This explains the persistence of this concept and the absence of attempts to construct thermodynamics on an entropy-free basis.

To find a more adequate measure of the amount of chaotic motion, which plays the role of an energy carrier in relation to the internal energy U_q, it is advisable to turn to the concepts of "amount of motion" Mv and "living force" Mv^2, introduced back in the 17th century by R. Descartes[23] and G. Leibniz.[24] Both measures related to internal oscillatory motion. It was the "living force" that was renamed at the suggestion of T. Jung (1807) into "energy", and after the introduction of potential energy - into the internal energy U. This is how the energy of the ether U = Mc2 was decided by G. Schramm (1871); N. N. Umov (1873); J. Thomson (1881); O. Heaviside (1890), A. Poincaré (1898) and F. G. Hasenorl (1904). This energy is twice the kinetic energy of directed motion $Mv^2/2$ at the same value of the average speed v = |$\mathbf{v}$|, which arises in the system because of collective (macroscopic) motion during rotation, diffusion, etc.[14]). Then its resulting impulse $\mathbf{J}$ = M$\mathbf{v}$ can arise, the energy of which becomes external Ekin. As the oscillations decay ($\mathbf{v} \to 0$) and stable structures appear, part of the "living force" turns into internal potential energy U_{pot}. This energy also becomes external E_{pot} if the center of mass of the system changes its position relative to the environment. Thus, internal energy U is by no means always a dissipated part of external energy, as it is represented by the law of conservation of energy in the mechanics of non-conservative systems:

$$(E_{kin} + E_{pot} + U) = \text{const.} \qquad (3)$$

The fact that internal energy is a whole and not a part becomes especially obvious when we consider that for isolated systems the concept of external energy loses all meaning. Thus, it is the internal energy U that is the quantity that is conserved in isolated systems, and only its part minus the ordered components U_{kin} and U_{pot} can be appropriately called internal thermal energy U_q. This corresponds to the law of conservation of species:

$$(U_q + U_{kin} + U_{pot})_{iz} = \text{const.} \qquad (4)$$

This approach helps cut the current situation where "modern physics does not know what energy is".[25] If, in addition, the absolute temperature T (K) is understood as a measure of the intensity of chaotic motion, then the internal thermal energy U_q can be represented by analogy with Helmholtz's "bound energy" TS in the form of the product $U_q = T\Theta_q$, understanding by Θ_q an extensive measure of the amount of this motion:[26]

$$\Theta_q = U_q/T, \ (J \ K\text{-}1) \qquad (5)$$

calling it, for brevity, a "thermal impulse" (i.e., an impulse that has lost its vector nature due to the chaotic nature of its movement). This thermal impulse includes translational, rotational, and oscillatory components of velocity v, which makes it dependent, like heat capacity, on the number of degrees of freedom of the particles of the system. The validity of representing U_q as a product $\Theta_q T$ (J) is confirmed by the fact that in this case its differential.

$$dU_q = Td\Theta_q + \Theta_q dT \qquad (6)$$

correctly reflects the change in internal thermal energy both due to external heat exchange $Td\Theta_q$, and when internal heat sources $\Theta_q dT$ arise due to dissipation. This representation of dU_q, the validity of which will be confirmed below, fully fits within the rules of

differential calculus, which cannot be said about the terms d_eS and d_uS in equation (2). The difference between the internal thermal energy $\dot{U}_q$ and the bound energy TS, which can also be interpreted as the energy associated with thermal motion, is associated with the term $\Theta_q dT$, which vanishes in isothermal processes, for example, in chemical reactions, where $\delta Q = Td\Theta_q = TdS$. In such cases, the concepts of Helmholtz free energy U – TS and Gibbs energy U +pV – TS keep their meaning. However, in other cases this difference manifests itself very clearly, as will be shown below.

Elimination of paralogisms associated with entropy

As shown above, the replacement by R. Clausius of the concept of "body heat" as a quantitative measure of its internal thermal energy U_q with the narrower concept of "process heat" Q as a quantitative measure of the heat exchange process and the introduction of entropy as the coordinate of this process limited thermodynamics to the consideration of equilibrium systems and reversible processes, which do not have internal heat sources. This transformed classical Clausius thermodynamics into thermostatics, which was limited to the study of equilibrium systems and infinitely slow processes. Since with the advent of the mentioned internal heat sources, entropy could only increase, a mistaken conclusion was made about the one-way direction of all processes in the Universe and the "arrow of time", which is not characteristic of the nature of things, was imposed on it. In this regard, the undoubted advantage of the thermal impulse Θ_q over entropy is its ability to both increase in transition of ordered forms of energy into heat, and decrease in the processes of evolution, accompanied by the emergence of "order" of their "chaos".[27] These are precisely the processes of formation of all (microscopic and macroscopic) forms of matter in the Universe.

The existence of a thermal pulse has the degree of evidence that satisfies the concept of phenomenological theory. It obviously exists in systems with a Maxwell-Boltzmann distribution of particle velocity and momentum, which frees us from the need to search for ways to justify the existence of entropy in nonequilibrium systems and its applicability to real processes. Its interpretation does not require the use of molecular-kinetic and statistical-mechanical theories, which makes thermodynamics a completely self-sufficient theory. It stays to show that using thermal impulse instead of entropy eliminates almost all of the paralogisms of thermodynamics mentioned above.

Elimination of inequalities from the mathematical apparatus of thermodynamics

It is known that the combined equation of the 1st and 2nd laws of thermodynamics in the case of irreversible processes takes the form of inequality:

$$TdS > dU + pdV. \qquad (6)$$

The reason for the emergence of inequalities is that in the absence of equilibrium, internal heat sources appear in the system, as a result of which $TdS > \delta Q$. Similar inequalities arise, generally speaking, for other parameters Θ_i, including for its volume V, which can increase when the system expands into empty space without performing work $\delta W_p^n = pdV$. This circumstance is the main obstacle to the application of the thermodynamic research method to other disciplines that study real (non-static) processes.

Meanwhile, a different approach to deriving the basic equation of thermodynamics is possible, initially focused on the study of internally nonequilibrium (inhomogeneous) systems with nonstatic processes

occurring in them. This method is based on the representation of the internal energy Ui of each i-th degree of freedom of a system of constant volume V in the nonequilibrium parameters of the system as a whole Z_i. These parameters can be found from the known density distribution $\rho_i = d\Theta_i/dV$ of their energy carriers Θ_i (mass M, number of moles k-x substances, thermal impulse Θ_q, charge Θ_e, impulse $\mathbf{J} = M\mathbf{v}$, its moment $\mathbf{L}$, etc.) over the volume of the system V. In this case, the heterogeneity of their distribution is expressed by the displacement of the radius vector of their center $\mathbf{R}_i$ from its position in the equilibrium (homogeneous) state $\mathbf{R}_{io}$. The latter are decided in a known manner:[28]

$$\mathbf{R}_i = \Theta_i^{-1}\int\rho_i\,(\mathbf{r}, t)\,\mathbf{r}\,dV; \ \ \mathbf{R}_{io} = \Theta_i^{-1}\int\rho_{io}(t)\,\mathbf{r}\,dV, \qquad (7)$$

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

This implies the existence in inhomogeneous systems of a certain "moment of distribution," which has the meaning of the polarization vector of the system in the most general understanding of this term:

$$\mathbf{Z}_i = \Theta_i(\mathbf{R}_i - \mathbf{R}_{io}) = \int[\rho_i\,(\mathbf{r}, t) - \rho_{io}(t)]\,\mathbf{r}\,dV \qquad (8)$$

with the shoulder $\Delta\mathbf{R}_i = \mathbf{R}_i - \mathbf{R}_{io}$, which we call the "displacement vector."

Since in equilibrium $\mathbf{R}_{io} = 0$, $d\mathbf{Z}_i = \Theta_i d\mathbf{R}_i$, the internal energy of the system as a whole U as the sum of partial energies $_{Ui} = U_i(\mathbf{Z}_i)$ becomes a function of the independent variables Θ_i and $\mathbf{R}_i$: $U = \Sigma_i U_i(\mathbf{Z}_i)$. In this case, its total differential can be represented as an identity:[27]

$$dU \equiv \Sigma_i\Psi_i d\Theta_i + \Sigma_i\mathbf{F}_i\cdot d\mathbf{R}_i, \qquad (9)$$

where $\Psi_i \equiv (\partial U_i/\partial\Theta_i)_\mathbf{R}$ – averaged values of generalized local potentials ψi (absolute temperature T and pressure p, chemical potential of the k-th component μ_k, its electrical φ and gravitational potential ψ_g, etc.); $\mathbf{F}_i \equiv (\partial U_i/\partial\mathbf{R}_i)_\Theta = \nabla U_i$ – forces in their general physical understanding.

The terms of the 1st sum of this identity describe the processes of acquisition or loss of partial energy Ui, regardless of what they are caused by: the transfer of energy carrier Θi across the boundaries of the system or the appearance of its internal sources. The terms of the 2nd sum describe the internal work performed when converting its other forms into the i-th energy U_i, i.e., its internal sources. In homogeneous systems ($d\mathbf{R}_i = 0$), this expression goes into the combined equation of the 1st and 2nd principles of classical thermodynamics of polyvariant systems $dU \equiv \Sigma_i\Psi_i d\Theta_i$.[9]

The main advantage of identity (9) is that it eliminates the uncertainty of the concept of partial energy of any degree of freedom of a nonequilibrium system Ui and gives a unified definition of the concept of force Fi as its gradient. Indeed, the expression $\mathbf{F}_i\cdot d\mathbf{R}_i$ can be easily converted to the form $\Theta_i d\Psi_i$ as an analogue of the gas work in the flow Vdp, or to the expression $\mathbf{X}_i\cdot\mathbf{J}_i\,dt$, if we introduce the concepts of thermodynamic force $\mathbf{X}_i = \mathbf{F}_i/\Theta_i$ and flow $\mathbf{J}_i = d\mathbf{Z}_i/dt = \Theta_i\mathbf{v}_i$, which TIP operates with . In this case, expressions (5) and (6) become a special case of the general expression of the partial energy $U_i = \Psi_i\Theta_i$ of any degree of freedom of the system as the product of its quantitative and qualitative measures, and the thermodynamic forces $\mathbf{X}_i$ and flows $\mathbf{J}_i$ acquire an unambiguous meaning of the tension of the state of the energy carrier and its momentum.

In isolated systems, the change in parameters Θ_i is due exclusively to the emergence of their internal sources $d\Theta_i/dt$, so the law of conservation of energy in them $dU/dt = 0$ takes the simple form:

$$\Sigma_i\Psi_i d\Theta_i/dt + \Sigma_i\mathbf{X}_i\cdot\mathbf{J}_i = 0. \qquad (10)$$

The uniqueness of this law is that it says the presence of sources or sinks of energy carrier $d\Theta i/dt$ not only for entropy, but in the general

case for any degree of freedom of the system. This means not only the possibility of the emergence of new properties in an isolated nonequilibrium system and the disappearance of old ones, i.e., its evolution and involution, and the absence in it of laws of conservation of any of the energy carriers,[29] which modern physics does not allow.

On the other hand, expression (10) makes it possible to study internal processes in isolated systems without dividing them into elementary volumes dV and without thereby increasing the number of their degrees of freedom to infinity. At the same time, the so-called "systemic" properties of the research object that are absent in its individual parts are preserved. Finally, equations (9) and (10) supply a unified definition of the concepts used in thermodynamics, mechanics, electrodynamics and other disciplines. This opens the possibility of their further synthesis.[30]

Removing Component Potential Uncertainty

The application of equilibrium thermodynamics to the study of diffusion processes, chemical and phase transformations associated with changes in the mass and composition of the system under study began with the work of J. Gibbs.[31] He overcame the limitation of classical thermodynamics to homogeneous systems in the most ingenious way, presenting a generally closed system as a set of open homogeneous subsystems, i.e., reducing the internal processes of changing the composition of the system in chemical reactions, processes of dilution, etc. to processes of external selective mass transfer through semi-permeable membranes, imaginary valves, etc. However, some processes in open systems turned out to be so unique that "it is not possible to explain and confirm their patterns on the basis of classical concepts".[32] In particular, along with heat transfer and expansion work, two more types of energy exchange appeared in such systems: ordinary mass transfer (transfer of matter without changing the composition of the system) and selective mass transfer (diffusion of k substances across the boundaries of the system associated with a change in the composition of the system without changing its mass).

In this case, the internal energy of the system U becomes a function of the numbers of moles N_k of all k independent components and phases of the system $U = U(S, V, N_k)$, and the combined equation of the 1st and 2nd principles of equilibrium thermodynamics takes the form of the Gibbs relation:[9]

$$dU = TdS − pdV + \Sigma_k \mu_k dN_k, \qquad (11)$$

where S, V – internal energy, entropy and volume of an open system; $p = -(\partial U/\partial V)_{T,Nk}$, $T = (\partial U/\partial S)_{V,Nk}$ – absolute pressure and temperature; $\mu_k = (\partial U/\partial N_k)_{S,V,Nm}$ – chemical potential of the component, found under conditions of constant S, V and the number of moles N_m of all Writing this expression, Gibbs believed that "the energy U will obviously be a function of S, V and Mk" as independent variables, and the first and second terms of (11) still characterize the heat transfer and work of expansion of the equilibrium system. However, later[20] it turned out that this is far from being the case. The entropy S = sM and volume V = υM of a multicomponent system necessarily changes both with mass transfer (M≠const) and with a change in its composition N_k/N: $S = s_k N_k$, $V = υ_k N_k$ with constant partial molar entropies sky and volumes $υ_k$ of components. This clearly violates the condition of constancy of entropy S and volume V in equation (11), laid down by J. Gibbs when defining the concept of chemical potential μ_k, as a result of which the value of the component potential in the processes of mass transfer, diffusion and osmosis turns out to be different with all the ensuing consequences for thermochemistry.[20]

The situation changes if, instead of entropy as the heat transfer coordinate, the thermal impulse Θq is used as a more general parameter

that changes not only during heat transfer, but also in diffusion and osmosis. In this case, the constancy of Θq guarantees their absence, so that the derivative $\mu_k = dU_k/dN_k$ uniquely specifies the specific energy value of the k-th part introduced into the system. This corresponds to writing the Gibbs relation (11) in a compact form based on the local equilibrium hypothesis:[14]

$$dU = \Sigma_i \psi_i d\Theta_i. \qquad (12)$$

In this case, the free energies of Helmholtz F and Gibbs G keep their meaning and value, since $dU = Td\Theta_q = TdS$.

Elimination of arbitrariness in the choice of driving forces of real processes

When they talk about a revolution in physics of the twentieth century, they usually mean quantum mechanics (QM) and the theory of relativity (STR and GTR). Meanwhile, along with them, in the first third of the same century, another equally fundamental theory arose - the thermodynamics of irreversible processes (TIP). This theory, called the thermodynamics of irreversible processes,[12-14] was based on the pioneering work of the future Nobel laureate L. Onsager,[33] who in 1931 proposed a "quasi-thermodynamic" theory of the rate of irreversible physicochemical processes. This theory for the first time overcame the limitation of thermodynamics to quasi-static processes.[11-14] The main quantities it runs on are the scalar "thermodynamic" forces $\mathbf{X}_i$ and "flows" $\mathbf{J}_i$. These quantities are found in it based on the expression for the rate of entropy occurrence dS/dt as a function of certain parameters αi, characterizing the removal of such systems from equilibrium:

$$dS/dt = \Sigma_i(\partial S/\partial \alpha_i) d\alpha_i/dt = \Sigma_i X_i J_i. \qquad (13)$$

However, the parameters α_i of equilibrium thermodynamics were obviously unknown. Therefore, his theory stayed an empty formalism until another future Nobel laureate I. Prigogine proposed a method for finding these quantities for "stationary" irreversible processes.[9] To do this, he put forward the hypothesis of local equilibrium, according to which there is equilibrium in the elements of the continuum volume dV (despite the occurrence of non-static processes in them), so that their state is characterized by the same set of variables Θ_i as in equilibrium (despite the appearance of additional thermodynamic forces X_i), and all the relations of equilibrium thermodynamics are applicable to them (despite their inevitable transition into inequalities).

Despite its internal inconsistency, this hypothesis made it possible to find vector forces $\mathbf{X}_i$ and flows $\mathbf{J}_i$ using the laws of conservation of mass, momentum, charge, and energy taken from other disciplines. This required the compilation of complex and cumbersome equations for their balance to isolate from dS/dt that part d_uS/dt that characterizes the "production" of entropy due to dissipation. However, even in this case, the "entropy production" can be decomposed into factors X_i and J_i in many ways. This led to a certain arbitrariness in their physical meaning and dimension. Such arbitrariness is completely unacceptable when we are talking not about the dissipation of energy, but about the processes of its transformation since it distorts their dimension and the physical meaning of the factors.[36] This drawback is eliminated if the forces X_i and flows J_i are found directly from relation (10). In this case, there is no need to compile the mentioned balance equations, which is the main difficulty in applying TIP to various systems.[14]

Cutting the "priority" of thermal equilibrium

In the already mentioned work,[31] J. Gibbs, using the minimum internal energy U as an equilibrium condition, found the conditions for thermal, mechanical, and material equilibrium of heterogeneous systems:

T′ = T″; (thermal equilibrium);

p′ = p″; (mechanical equilibrium)   (14)

μ_k′ = μk^-. (material equilibrium),

where one and two strokes show the temperature T, pressure p and chemical potential μk of the kth substance of the multicomponent system.

A different result is obtained when using the principle of maximum entropy S = S (U, V, Nk) =max as an equilibrium criterion, the variation of which δS in energy U, volume V and number of moles N_k leads to equilibrium conditions:[13]

T′ = T″ ; p′/T′ = p″/T″ ; μ_k′/T′ = μ_k″/T″.   (15)

It is easy to notice that the last two equalities require the preliminary fulfillment of the thermal equilibrium condition T′ = T″. From here the conclusion is usually drawn about the special role of thermal equilibrium, without which neither mechanical nor material equilibrium can occur. The discrepancy between this result and experiments in which the cessation of exchange of k substances was seen under conditions of thermal equilibrium disturbance is well known.[13] Meanwhile, the desire of TIP to satisfy conditions (13) leads to the fact that the thermodynamic forces силы $X_i = \Delta\psi_i/T$ in TIP necessarily have temperature, which makes heterogeneous forces interrelated. The latter served as the basis for L. Onsager to postulate the dependence of the speed of any relaxation process Ji on all forces X_i acting in the system, the fallacy of which will be shown below. Thus, replacing energy equilibrium criteria with entropy ones not only distorts the conditions of mechanical and material equilibrium found by Gibbs, but also changes the results of thermodynamic analysis.

Cutting the conflict between TIP and the concept of resultant power

TIP enriched the physical thought of the twentieth century with a number of principles of a general physical nature and established the fundamental possibility of self-organization in systems far from equilibrium. She returned to thermodynamics the concept of force, lost since the time of S. Carnot, and explained many effects that arise when several heterogeneous irreversible processes occur simultaneously in the same regions of space. The contribution of TIP to the paradigm of the twentieth century was appreciated by the award of two Nobel Prizes (L. Onsager, 1968, I. Prigozhin, 1977).

However, TIP is still based on the principle of increasing entropy and a number of hypotheses and postulates, which deprives it of the necessary completeness and rigor. One of these postulates is the linearity principle of L. Onsager, according to which any independent flow J_i (heat, matter, charge, momentum, etc.) linearly depends on all thermodynamic forces X_j acting in the system:[33]

$J_i = \Sigma_j L_{ij} X_j$, (i, j = 1,2,n)   (16)

where L_{ij} are proportionality coefficients, called "phenomenological" by Onsager, like these equations themselves.

The main meaning of these laws was to affirm the universal interconnectedness of real (non-static) processes. The positive sign of all terms of the sum (16) gave rise to the idea of "synergy," i. e., enhancing the effect because of cooperative action. However, these equations diverged from the laws of thermal conductivity (Fourier), diffusion (Fick), electrical conductivity (Ohm), filtration (Darcy), viscous friction (Newton), etc., in which the mentioned flows had a single (resulting) driving force $_{Fi}$, expressed by gradients of temperature, chemical and electrical potential, pressure, speed, etc.

$\mathbf{J}_i = - L_i \mathbf{F}_{i,}$ (17)

The coefficients L_i in these laws were functions of the parameters and structure of the system and were not constant values, so the laws (14) were nonlinear. Therefore, the classification of equations (16) as "phenomenological" (obtained from experience) did not correspond to reality. This also applies to the positive sign of all terms of the matrix form (15), which, as shown by H. Casimir,[12-14] is not true for all forces. In addition, it remained completely unclear how obviously independent flows could be connected.

The reason for this discrepancy can be understood if we proceed not from the idea of "summation" (summation) of entropy sources caused by the action of heterogeneous dissipative forces Xj, but from mechanics, which asserts the existence of the resulting $_{Fi}$ of these forces. In isolated systems, the sum of internal forces $\Sigma_i F_i$ (i = 1, 2…n) is always zero. This means that, in accordance with Newton's third law, any of the applied forces F_i can be expressed as the sum of n-1 reaction forces F_j of a different, j-th kind: $F_i = - \Sigma_{n-1} F_j$. Since $X_i = F_i/\Theta_i$, laws (16) can be represented in a matrix form like (15):

$\mathbf{J}_i = L_i \Sigma_{n-1} (\Theta_j/\Theta_i) \mathbf{X}_j = \Sigma_j L_{ij} \mathbf{X}_j$.   (18)

The coefficients $L_{ij} = L_i \Theta_j/\Theta_i$ in this expression combine kinetic and thermodynamic factors, which explains why their analogues L_{id} in (14) do not make sense for either of them [12]. Thus, it becomes possible to substantiate the matrix form of the transfer laws without resorting to their postulation, and at the same time simplify them by finding the resulting driving force of any independent process and reducing the laws (16) to their "diagonal" form (18).[35]

Elimination of "discrimination" of heat engines

It is taken for granted that the maximum efficiency of any non-thermal machine (mechanical, hydraulic, electrical, etc.) is close to unity, while for thermal engines, to which energy is supplied in the form of heat Q_1, it is limited by the supply temperatures and heat removal and in practice rarely exceeds 40%. This "discrimination" of heat engines is based on the belief that energy supplied to the machine in an ordered form can be completely converted into any other form.[9] Hence the division of all forms of energy into entropic and non-entropic.[36] Echoes of this division can be heard in statements about the inapplicability of the second law of thermodynamics (the principle of an excluded perpetual motion machine of the 2nd kind) to non-thermal machines, as well as in unfounded accusations against thermal power plants for their "waste" of most of the heat of combustion of fuel . At the same time, in scientific and pseudo-scientific literature the voices of those who understand the reason for such discordant opinions are rarely heard. Meanwhile, it lies in the application of the same term efficiency to two fundamentally different types of energy converters with different criteria for their efficiency.

The concept of efficiency was introduced into science and technology at the end of the 19th century, when not only mechanical and electrical machines, but also heat engines already existed. However, their efficiency was determined in different ways. In mechanical and similar machines, for which not only the work W performed by them was known, but also the power N = dW/dt, the efficiency η was determined by the ratio of their output power N″ to the input power N′ or by the ratio of the useful work performed by the machine we to the theoretically possible W^t. In thermodynamics, this kind of efficiency is called relative. Otherwise, the "thermal" efficiency of a heat engine η_t, which belongs to the category of absolute, is determined. In cyclic heat engines, where, along with the heat source Q_1, a heat receiver Q_2 is required, it is determined by the ratio of the useful work we to

heat supplied from the hot source Q1 and depends on the average temperatures of the working fluid of the installation in the process of supplying and removing heat $\overline{T}_1$ and и $\overline{T}_2$:[37]

$$\eta_t \equiv W/Q_1 = 1 - \overline{T}_2/\overline{T}_1 <1, \qquad (19)$$

These efficiencies characterize the degree of convertibility of thermal energy supplied to the heat engine. This kind of absolute efficiency can be determined for any form of energy supplied to the energy converter by the action described by the 1st sum of identity (9). With this approach, the idea naturally arises of the unity of expression for the absolute efficiency of a thermal or non-thermal cyclic machine η_i as the ratio of the useful work W^c performed in the cycle to the energy Ui arriving at the input of the machine. It is convenient to express this efficiency through the average potentials of the energy carrier Θi in the processes of its entry into and exit from the installation $\Psi 1$ and $\Psi 2$ as analogues of the average thermodynamic temperature of heat supply and removal $\overline{T}_1 = \Delta S_1^{-1}\int T_1 dS_1$.and и $\overline{T}_2 = \Delta S_2^{-1}\int T_2 dS_2$. In this case, the expression for the absolute efficiency of any (cyclic and non-cyclic) machine will take the form:[38]

$$\eta_{max} = W_ц/E_1 = 1 - \Psi_2/\Psi_1. \qquad (20)$$

These are, for example, expansion machines (expanders), which expand the gas flow from pressure p_1 to $_{p2} <_{p1}$, magnetohydrodynamic generators operating in an open circuit with plasma enthalpy at the input and output of the generator h_1 and $h_2 < h_1$; wind power plants with input and output wind speeds v1 and $v_2 < v_1$; electrostatic machines that receive charge at potential φ_1 and release it at potential $\varphi_2 < \varphi_1$, etc. For all of them, the absolute efficiency is less than unity, since the absolute values of the energy receiver potential Ψ_2 cannot be equal to zero either theoretically (since in this case interaction with it becomes impossible), much less. This circumstance indicates the unity of the laws of transformation of any forms of energy. In this case, the difference ηmax of converters of various forms of energy is determined not by this form itself, but by the degree of nonequilibrium of the source of the converted energy, i.e., the ratio of the available difference in the generalized potential $\Delta\Psi_i$ to the absolute value of this potential. As an example, consider the absolute efficiency of a hydroelectric power station with a difference in water levels between its, upper and lower pools ΔH = 30 m, if the gravitational potential of the mass M of falling water is determined by the expression Ψ_g = MgH, and its absolute value H_1 is measured from the center of the Earth with a radius R ≅ 6 · 106 m. Then its "absolute" efficiency will be $\eta_g = \Delta H/ H_1 \cong 5\cdot10$-6. Thus, we are extremely far from being able to use "all gravitational energy," so heat engines are by no means the most "wasteful" in terms of using the potential Ψ_1 of the converted form of energy.

The unity of expression for the efficiency of thermal and non-thermal cyclic machines, expressed by relation (20), allows us to substantiate the principles of an excluded perpetual motion machine of the 1st and 2nd kind, without resorting to postulates. If the energy E_1 supplied to the machine is zero, then according to (20) the work of such a machine W^c (first law of thermodynamics) will also be zero. If the medium, which is the source of energy E, is homogeneous, i.e., $_{\Psi 1}$ = Ψ_2, then the efficiency of such a machine is η = 0, as is its work we. This position can be generalized to non-cyclic machines.[39]

Refutation of the theory of "heat death of the Universe"

When substantiating the principle of increasing entropy, R. Clausius was based on the seemingly obvious postulate that the thermal efficiency of any irreversible heat engine ηt =1 – Q2/Q1 is

less than in the reversible Carnot cycle $\eta_t^K = 1 – T_2/T_1$ at the same temperatures heat source T_1 and heat sink T_2 and the amounts of heat supplied Q_1 and removed Q_2. In this case, $dS_2 = \delta Q_2/T_2 > dS_1 = _{\delta Q1}/T_1$, i.e., the entropy of the system, including a heat source, a cyclically operating heat engine and a heat receiver, increases.

Not finding any contradictions in this reasoning, R. Clausius gave this conclusion the status of a general physical "principle of increasing entropy" and laid it as the basis for the "theory of the thermal death of the Universe." This theory predicted the cessation of any macroprocesses in the Universe due to the onset of thermodynamic equilibrium in it, which was tantamount to a statement about its "creativity." This theory has not yet been refuted even though the mentioned "thermal death" did not occur even after the 13–14 billion years allotted to it by this model. Meanwhile, an error crept into Clausius's reasoning, which was not noticed by either his contemporaries or followers. It will become more obvious if we use expression (11), according to which, for the same $\overline{T}_1$ and $\overline{T}_2$, the efficiency of a reversible and irreversible heat engine is the same. Consequently, Clausius's error was to claim that the machines being compared had the same hot and cold spring temperatures.

Other evidence of this principle turns out to be equally untenable.[40] Moreover, it can be shown that, while remaining within the framework of equilibrium thermodynamics, it is generally impossible to prove the principle of entropy increase. To do this, it is enough to consider a system whose internal energy U is determined by the entropy S and volume V, i.e. U = U (S, V). Then, considering entropy in the usual way as an inverse function S = S (U, V), we will necessarily conclude that in isolated systems, where, due to the conservation laws U and V, = const, entropy must also remain unchanged:[41]

$$S_{iz} = S (U, V)_{iz} = const. \qquad (21)$$

A fundamental solution to this issue is provided by the introduction of thermal impulse Θ_q as a true measure of internal thermal energy $U_q = T\Theta_q$. According to this expression, the thermal impulse of the system can decrease not only when the oscillations damp and the thermal energy U_q is converted into the internal potential energy of the same system E_{pot}, but also when it is converted into the kinetic energy of ordered motion E_{kin}. Indeed, as the speed of the system approaches the maximum speed of propagation of disturbances, when it becomes impossible to exceed it in the oscillatory process, this process stops, i.e., thermal (disordered) motion degenerates. It is for this reason that the temperature T of radiation or physical vacuum, in which the speed of light is maximum, is zero. Consequently, the thermal impulse also degenerates during the explosion of "supernovae," accompanied by 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.[27] Thus, replacing entropy with a thermal impulse eliminates the one-way direction of processes in the Universe imposed by Clausius thermodynamics, allowing for the possibility of its unlimited functioning in time and space, bypassing the state of equilibrium.

Eliminating the Gibbs Paradox

Among the paradoxes of physics, there is hardly another one as famous and as mysterious as the "Gibbs paradox" - a statement about the abrupt increase in entropy when mixing non-interacting ideal gases in the absence of any thermal or volumetric effects. In his famous work "On the Equilibrium of Heterogeneous Substances",[42] J. Gibbs extended the methods of thermodynamics of closed systems, presenting them as a set of open systems separated by conditional semi-permeable partitions. Thus, he replaced the internal processes

of changing the composition of the system with processes of external selective mass transfer (diffusion across the boundaries of subsystems). At the same time, he discovered that the difference between the entropy of a mixture of two masses of ideal gases M_1 and M_2, each of which initially occupied half of the total volume of the mixture V, is greater than the sum of the entropies of the same gases before mixing by a constant amount

$$\Delta S = R_{mix} \ln 2, \qquad (22)$$

determined solely by the gas mixture constant R_{mix}.

It is characteristic that Gibbs himself, based on the statistical interpretation of entropy, did not see anything paradoxical in this result, believing that it is "entirely determined by the number of molecules mixed" and depends only on whether we consider them identical or separate. However, as they studied this issue, researchers encountered more and more difficulties, which led to the appearance of the phrase "Gibbs' paradox."

Over the course of a century and a half, this result has repeatedly become the object of study by both physicists and philosophers. It seemed too many of its researchers that they were finally able to explain the strange independence of the entropy jump from the degree and nature of the difference between the gases being mixed, along with the inadmissibility of the mentioned jump when mixing identical gases. However, like the legendary sphinx, this paradox appeared repeatedly on the pages of scientific books and magazines and has not disappeared from them until now. As a result, most researchers of this paradox were inclined to believe that it "cannot be resolved in the plane of classical thermodynamics."[45]

The situation is different if, instead of entropy, which has a configuration component, we use the thermal impulse $_{\Theta q}$, which has a simple physical meaning. Then it becomes obvious that when mixing non-interacting gases with the same temperature and pressure, the thermal impulse does not change, at least due to the law of conservation of momentum of the system. This is more obvious since both gases, even before mixing, were in thermal and pressure equilibrium, which is complete for a system with two degrees of freedom.

Removing the contradiction between thermodynamics and the theory of evolution

There is a well-known "blatant contradiction between thermodynamics and the theory of biological evolution"[27] since the principle of increasing entropy prescribes nature only its degradation. Boltzmann's probabilistic interpretation of entropy did not resolve this contradiction since it gave the Universe only an insignificant chance of avoiding "heat death."

Meanwhile, it is easy to prove that any real processes $d\rho_i/dt \neq 0$ can arise only in nonequilibrium systems (where $\rho_i \neq$), and their speeds in various parts of the system and volume elements dV have the opposite sign. This can be easily verified by representing any extensive parameter of an inhomogeneous system Θ_i (its mass M, the number of moles of k-th substances N_k, entropy S, electric charge Θ_e, impulse **P**, its moment L, etc.) as an integral of its local $\rho_i = d\Theta i/dV$ and average density $\overline{\rho_i} = \Theta_i/V$ by the expression $\Theta_i = \int \rho_i dV = \int \overline{\rho_i} dV$. Then

$$\int [(d (\rho_i - \overline{\rho_i})/dt]\, dV \equiv 0. \qquad (22)$$

It is easy to see that this identity holds only in the case when the processes $d (\rho_i - \overline{\rho_i})/dt$ are oppositely directed. This position, which we called the "principle of counter-directional processes," can be considered as a mathematical expression of the dialectical law of "unity and struggle of opposites." The heuristic value of this principle

as one of the most general laws of natural science lies in the detection of a specific class of processes of "polarization" of a system in the most general understanding of this term as the appearance in it of parts (regions, phases, components) with opposite properties.

This principle eliminates the one-way direction 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 (10), if we represent $F_i \cdot v_i$ as the product of forces and flows $X_i \cdot J_i$, as is customary in nonequilibrium thermodynamics.[11-14] Since in isolated systems the change in parameters Θ_i is due exclusively to the presence of internal sources, the powers $X_i \cdot J_i$ of opposite energy conversion processes also have the opposite sign. This means that, along with dissipation processes in which $X_i \cdot J_i > 0$, processes of "self-organization" of some j degrees of freedom are inevitable in isolated systems, in which the product $X_i \cdot J_i < 0$. These are the processes of "ascending diffusion" (transfer of a substance in the direction of increasing its concentration), the phenomenon of "coupling" of chemical reactions (reactions occurring in the direction of increasing its affinity), "active transport" (accumulation in organs of substances with higher Gibbs energy), etc. Thus, in 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 eliminates the contradiction between thermodynamics and evolution noted above.

Moreover, identity (10) contains thermodynamic forces expressed by potential gradients $X_i = \nabla \psi_i$, the change of which reflects, without additional calculations, not only the approaching or moving away of the system from the equilibrium state for any i-th degree of freedom separately, but also the equilibrium condition of a given kind:

$$d\mathbf{X}_i > 0 (\text{evolution}); d\mathbf{X}_i = 0 \text{ (equilibrium)}; d\mathbf{X}_i < 0 \text{ (involution)}. \qquad (23)$$

This gives researchers a more visual, more "physical" and more informative tool for analyzing evolutionary problems than the non-calculated maximum entropy [44, 45]. At the same time, it turns out that if any processes take place in the system, among them there will certainly be those of an evolutionary nature. Thus, it is argued that nature is characterized not only by destructive, but also creative tendencies. This is observed in living and inanimate nature at all levels of the universe.

Eliminating the paradox of negative absolute temperatures

The concept of negative absolute (spin) 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 a "population inversion" of the energy levels of spin-possessing elementary particles - a state in which the majority of elementary particles are found at the upper energy level.[46] The basis for the introduction of this concept was the same statistical interpretation of the concept of entropy. If statistical entropy is taken to be identical to thermodynamic entropy on the basis that both quantities are additive and reach a maximum in a state of equilibrium (Boltzmann's principle), then, comparing the expression of the derivative $(\partial U/\partial S)$ for the statistically determined internal energy U and entropy S with the known definition of thermodynamic temperature of thermomechanical system

$$T \equiv (\partial U/\partial S)\Theta i, \qquad (24)$$

one can conclude that the system of nuclear spins in a state of inverted population should be assigned a negative absolute temperature

T <0. It is characteristic that with such a "fit to the classics" it was necessary to assume that the states of spin systems with a negative absolute temperature in them lie ... above infinitely high temperatures T = ∞!

It should be noted that the existence of systems with inverted population of levels is now a firmly established fact. The first subsystem that satisfied these requirements was the above-mentioned system of nuclear spins of lithium ions in lithium fluoride (LiF) crystals. If LiF crystals are placed in a magnetic field and then quickly change the direction of the external field (as was the case in the experiments of E. Purcell and R. Pound, 1951), then the nuclear magnets are unable to follow it, and most of them will be in the upper energy state – a population inversion will occur. In installations such as lasers, it is created by "pumping" them with the energy of microwave radiation, due to which a stationary nonequilibrium state of the system is created.

However, inverted population is not yet enough to talk about a negative absolute temperature - it is important that the system remains in internal equilibrium with inverted population. Indeed, according to (24), negative values of thermodynamic temperature can be achieved only in the case when the system, through reversible heat exchange, is transferred to a state with higher internal energy U and lower entropy S. Meanwhile, both known methods of achieving population inversion in a nuclear system spin (inversion of the external magnetic field and exposure to a radio frequency pulse) do not satisfy these conditions. In the first method, the change in the direction of the external magnetic field is conducted, as emphasized by Purcell, so quickly that the nuclear spins do not have time to change their orientation. Consequently, the internal state of the system (including its entropy S) remained unchanged - only the external potential (Zeeman) energy of the spins in the magnetic field, which is included in the Hamiltonian of the system along with the energy of the spin-spin interaction, changed. The internal energy of the system U, which does not depend on the position of the system in external fields, remained unchanged. Otherwise (when U changes), the condition of constancy in expression (16) of the coordinates of all types of work, and not just the volume, would be violated. This also applies to another method of population inversion, achieved using a high-frequency (180-degree) pulse. This effect cannot in any way be classified as heat transfer since it also has a directional nature and corresponds to the adiabatic process of performing external work on the system.

The interpretation of the mentioned experiments changes if instead of entropy in expression (16) the thermal impulse Θ_q appears, which, like the velocity modulus v, does not change sign when the magnetic field is inverted. At the same time, attention is immediately drawn to the violation of the principle of distinguishability of processes. This violation consists in the interpretation of the special, qualitatively distinguishable, and irreducible process of spin-lattice relaxation discovered in the experiment as heat transfer. The fact that there is some connection between the thermal form of motion and the orientation of spins does not yet give grounds to attribute this form to the spin system. It is known, for example, which cooling condensed matter to almost absolute zero temperatures do not lead to the disappearance of the intrinsic angular momentum of the nuclei. In this case, there remains no basis for interpreting temperature T as negative.

These experiments confirmed (with acceptable accuracy) the validity of the law of conservation of angular momentum during spin-spin interaction and showed that the "temperature" of the mixture is determined by the expression:

$$T = (\Sigma_i C_i/T_i)/\Sigma_i C_i, \tag{25}$$

where T_i is the temperature of any part of the spin system; C_i is a weighting coefficient called "spin heat capacity" by experimenters. As follows from expression (23), in it the "spin heat capacity" C_i is associated with the reciprocal of the absolute temperature. Thus, in these experiments we are not talking about thermodynamic temperature at all, but about a certain statistical distribution parameter passed off as it.

Elimination of "inversion" of the second law of thermodynamics

The introduction of the concept of negative absolute temperature, unfortunately, was not limited to the inversion of the temperature scale. The inevitable conclusion followed about the "inversion" in such systems of the very principle of an excluded perpetual motion machine of the 2nd kind.[46] This "inversion" consists in affirming the possibility of complete transformation of heat into work in such systems and the impossibility, on the contrary, of complete transformation of work into heat. Indeed, according to Ramsey, a body with a higher temperature (i.e., with a lower negative temperature in absolute value) should be considered hot in the region T <0. If we now imagine a 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 $\eta_t^K = 1 - T_2/T_1$ will become negative, since the body with the lower absolute value should be considered hot in the region T < 0 negative temperature $(T_2/T_1 > 1)$.[9] This more than "amazing" result means that the work of the Carnot cycle performed in this temperature range will be positive if heat Q_2 is taken from a "cold" source, and the heat sink is a hotter body. Since, with the help 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" one through heat exchange, then in a continuous sequence of cycles the work will be done due to the heat of only one "cold" body without any residual changes in other bodies in violation of the 2nd law of thermodynamics. Thus, not only the concept of thermodynamic temperature as a purely positive quantity, but also the principle of an excluded perpetual motion machine of the 2nd kind underwent an "inversion". It is characteristic that such a conclusion was made based on... the same second principle! In fact, the possibility of complete conversion of heat into work means that the usual expression for efficiency () is not applicable in the region T < 0. But then, obviously, all conclusions based on it lose their validity! There is a "vicious circle"! Nevertheless, the statement about the "inversion" of the principle of an excluded perpetual motion machine of the 2nd kind penetrated the pages of textbooks and began to be reproduced even in the best of them. This is just one of many examples of how the identification of thermodynamic and statistical entropy undermines the former confidence in the infallibility of thermodynamics and the indisputable validity of its consequences.

Eliminating the paradox of relativistic heat engines

In the years following the appearance 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 frames of reference. In the field of thermodynamics, this was first accomplished by M. Planck in 1907.[47] He concluded that the entropy S should remain Lorentz-invariant, since the acceleration of the system is carried out adiabatically, while the internal energy U, heat Q and temperature T should be transformed in accordance with the expressions:

$$U' = U_o/\gamma; \quad Q' = Q\gamma; \quad T' = T\gamma, \tag{26}$$

where Q′, T′ – heat and temperature in the reference system moving relative to the observer with speed v; $\gamma = (1 – v^2/c^2)^{1/2}$ – Lorentz multiplier; c is the speed of light in vacuum.

As a result, he concluded that the efficiency of the relativistic Kano cycle is determined by the expression:

$$\eta_t^K \equiv W_u'/Q_r' = 1 - T_2/T_1\gamma. \tag{27}$$

The relationships found by Planck received the approval of A. Einstein and no one raised doubts until in 1963 H. Ott[48] discovered the absurdity of this result from the point of view of thermodynamics. Indeed, according to Planck, the temperature of a moving source is always lower than that measured in a stationary reference frame, and in accordance with (19) transformations η_t^K is always less than that of a classical one, and for certain γ it can even turn out to be negative. According to Ott, on the contrary, the temperature of a moving source is always higher, and his Carnot machine has a higher efficiency than the classical one:

$$\eta_{t\,(Orr)}^K = 1 - T_2\gamma/T_1. \tag{28}$$

Soon, H. Arzels came to the same conclusion, independently of H. Ott.[49] However, unlike Ott, he considered the formulas for converting energy and momentum to be incorrect. This time the work was noticed, and an avalanche of publications followed, leading to lively discussion at international symposia in Brussels (1968) and Pittsburgh (1969). These discussions revealed such chaos in the field of defining the basic concepts and concepts of thermodynamics that H. Arzels declared a "modern crisis of thermodynamics." And the point here is not only the lack of unity in the relativistic transformations of energy, heat, and work, but the reluctance of researchers to return to the foundations of thermodynamics whenever the need arises to generalize its methods to a more general class of systems. Instead, the authors of numerous works tried to "reconcile" various transformations. It was even agreed that the use of one or another conversion formula depends on the position of the thermometer in space. As a result, the problem of relativistic transformations of thermodynamic quantities was "swept under the rug."

Meanwhile, as we have shown,[20] the relativistic Carnot machine is a combination of a thermal and mechanical machine, which, along with heat Q′ receives kinetic energy $\Delta E_{kin} = Q'\,(1/\gamma_r - 1)$, necessary to maintain its speed. The efficiency of such a machine should be determined by the ratio of the total work to the total amount of thermal Q′ and mechanical E_{kin} energy supplied to it. This efficiency takes on an intermediate value between a purely thermal and a purely mechanical machine and passes into the classical expressions of their absolute efficiencies as their share in the productivity of the combined machine changes. However, this does not solve the problem of relativistic transformations of thermodynamic quantities. Here the concept of thermal impulse as a function of momentum comes to the rescue again. Unlike entropy, it changes with speed, while the internal thermal energy U_q, on the contrary, remains unchanged by definition. Then their efficiency remains invariant with respect to any transformations of entropy and absolute temperature.[20]

Conclusion

The loss of thermodynamics the status of a theory whose consequences were immutable truths is due to the use of entropy in its unusual role as a carrier of the thermal form of energy. Having been mistakenly introduced by R. Clausius as a heat transfer coordinate, entropy gave rise to a number of non-obvious contradictions, the number of which multiplied as the area of its application expanded. As shown in the article, these paralogisms can be eliminated from thermodynamics only by replacing entropy with a more adequate, general, and physically transparent concept of thermal impulse. This allows not only to eliminate the known and newly discovered paralogisms of thermodynamics and return it to its former status as a non-hypothesis theory, but also opens up the possibility of combining equilibrium and nonequilibrium thermodynamics and their synthesis with other fundamental disciplines on a single conceptual and conceptual basis, taking into account the irreversibility of real processes. At the same time, the "blatant contradiction" of thermodynamics with the theory of biological and cosmological evolution is eliminated and the teaching of this discipline is significantly simplified by improving methods of analysis, eliminating thermodynamic inequalities, strictly proving all its provisions, refusing to present thermodynamics on the basis of postulated "principles," etc.[50]

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None.

Conflicts of interest

None.

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