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DECLARAÇÃO DA SEGUNDA LEI DA TERMODINÂNCIA COM BASE NO POSTULADO DE NÃO-EQUILÍBRIO

STATEMENT OF THE SECOND LAW OF THERMODYNAMICS ON THE BASIS OF THE POSTULATE OF NONEQUILIBRIUM

ИЗЛОЖЕНИЕ ВТОРОГО ЗАКОНА ТЕРМОДИНАМИКИ НА ОСНОВЕ ПОСТУЛАТА НЕРАВНОВЕСНОСТИ

RYNDIN, Vladimir V.[1]*

[1]S. Toraigyrov Pavlodar State University, Department of Mechanics and Oil and Gas Engineering, 64 Lomov Str., zip code 140008, Pavlodar – Republic of Kazakhstan

** Correspondence author*
e-mail: rvladvit@yandex.kz

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RESUMO

A maioria das leis físicas são expressões quantitativas das leis filosóficas da conservação da matéria e de suas propriedades de movimento. A primeira lei da termodinâmica (PLT) é uma expressão analítica da lei da conservação do movimento quando sua forma muda. Quanto à segunda lei da termodinâmica (SLT), ainda não foi esclarecido qual propriedade da matéria não muda durante o curso de processos reversíveis e mudanças durante o curso de processos irreversíveis em um sistema isolado (SI). Assim, um grande número de declarações da SLT e uma abundância de material para esclarecer essas formulações. O autor da SLT baseia-se no “postulado do não-equilíbrio”, segundo o qual existe uma propriedade objetiva da matéria - “não-equilíbrio”, que caracteriza a distribuição desigual da matéria e do movimento no espaço. Todos os processos (reversíveis e irreversíveis) podem prosseguir apenas em sistemas de não-equilíbrio. Isso leva à única formulação da segunda lei da termodinâmica: quando os processos reversíveis (ideais) ocorrem em um sistema isolado, o não-equilíbrio é preservado e, com a ocorrência de processos irreversíveis (reais) - diminui. Quando o sistema atinge um estado de equilíbrio, o não-equilíbrio desaparece e todos os processos cessam. Como medida quantitativa do não-equilíbrio do sistema, consideramos o trabalho máximo que pode ser feito quando um sistema de não-equilíbrio transita para um estado de equilíbrio. As seguintes quantidades são usadas para calcular este trabalho: “diferença de potencial”, “diferença de entropia”, mudança na exergia. Todos esses valores diminuem no curso de processos reais (irreversíveis) no sistema isolado e não mudam no curso de processos reversíveis. Como resultado, uma expressão generalizada do SLT através das características quantitativas do não-equilíbrio do sistema na forma de uma desigualdade, que inclui a desigualdade de R. Claudius para mudar a entropia de um sistema isolado, é obtida.

Palavras-chave: segunda lei da termodinâmica, o postulado do não-equilíbrio, a nova formulação e escrita da segunda lei, a quantidade de não-equilíbrio, entropia.

ABSTRACT

Most physical laws are quantitative expressions of the philosophical laws of the conservation of matter and its properties of motion. The first law of thermodynamics (FLT) is an analytical expression of the law of conservation of motion when its shape changes. As for the second law of thermodynamics (SLT), it has not yet been clarified which property of matter does not change during the course of reversible processes and changes during the course of irreversible processes in an isolated system (IS). Hence, a large number of the SLT statements and an abundance of material to clarify these formulations. The author of the SLT is based on the “postulate of nonequilibrium”, according to which there is an objective property of matter - “nonequilibrium”, which characterizes the unequal distribution of matter and movement in space. All processes (reversible and irreversible) can proceed only in nonequilibrium systems. This leads to the only formulation of the second law of thermodynamics: when the reversible (ideal) processes occur in an isolated system, the nonequilibrium is preserved, and with the occurrence of irreversible (real) processes – decreases. When the system reaches an equilibrium state, the nonequilibrium disappears, and all processes cease. As a quantitative measure of the nonequilibrium of the system, we consider the maximum work that can be done when a nonequilibrium system transitions to an equilibrium state. The following quantities are used to calculate this work: “potential difference”, “entropy difference”, change in exergy. All these values decrease in the course of real (irreversible) processes in the isolated system and do not change in the course of reversible processes. As a result, a generalized expression of the SLT through the quantitative characteristics of the nonequilibrium of the system in the form of an inequality, which includes R. Claudius’s inequality for changing the entropy of an isolated system, is obtained.

Keywords: *second law of thermodynamics, the nonequilibrium postulate, the new formulation and writing of the second law, the amount of nonequilibrium, entropy.*

АННОТАЦИЯ

Большинство физических законов являются количественными выражениями философских законов сохранения материи и её свойства движения. Например, первый закон термодинамики (ПЗТ) является аналитическим выражением закона сохранения движения при изменении его формы. Что касается второго закона термодинамики (ВЗТ), то до настоящего времени не выяснено, какое свойство материи не изменяется при протекании обратимых процессов и изменяется при протекании необратимых процессов в изолированной системе (ИС). Отсюда большое число формулировок ВЗТ и обилие материала по разъяснению этих формулировок. Автором в основу ВЗТ положен «постулат неравновесности», согласно которому существует объективное свойство материи – «неравновесность», характеризующая неодинаковость распределения вещества и движения в пространстве. Все процессы (обратимые и необратимые) могут протекать только в неравновесных системах. Отсюда следует единственная формулировка ВЗТ: при протекании обратимых (идеальных) процессов в изолированной системе неравновесность сохраняется, а при протекании необратимых (реальных) процессов – уменьшается. При достижении системой равновесного состояния неравновесность исчезает, и все процессы прекращаются. В качестве количественной характеристики (меры) неравновесности системы рассматривается максимальная работа, которая может быть совершена при переходе неравновесной системы в равновесное состояние. Для расчёта этой работы используются следующие величины: «потенциальная разность» (разность термодинамических потенциалов в неравновесном и равновесном состояниях системы), «энтропийная разность» (разность энтропии системы в равновесном и исходном неравновесном состояниях), изменение эксергии. Все эти величины при протекании реальных (необратимых) процессов в ИС уменьшаются, а при протекании обратимых процессов не изменяются. В результате получено обобщённое выражение ВЗТ через количественные характеристики неравновесности системы в виде неравенства, включающего в себя неравенство Р. Клаузиуса для изменения энтропии изолированной системы.

Ключевые слова: *второй закон термодинамики, постулат неравновесности, новая формулировка и запись второго закона, количество неравновесности, энтропия.*

1. INTRODUCTION

The thermodynamics is based on some empirical laws irreducible to the fundamental laws of the Newtonian mechanics (Müller, 2019). Therefore, thermodynamics is an empirical science (Straub and Balogh, 2000). Srivastava *et al.* (2007) note that to theoretically substantiate the laws of thermodynamics, it is necessary to involve kinetic theory. Such an approach would not only remove the stigma of "empirical science" from thermodynamics but would logically link kinetics, thermodynamics, and statistical thermodynamics (Ramos *et al.*, 2019).

The main empirical laws of thermodynamics are the first (FL) and the second (SL) laws of thermodynamics (Seifert, 2012; Norton, 2016). From a philosophical point of view, the first law of thermodynamics is an analytical expression of the law of conservation of motion (property of matter) when its form changes in the form of a balance ratio for changing the energy of a system (Einstein, 1965). A detailed analysis of the methods for introducing the equations of the first law of thermodynamics for closed and open systems, as well as for flow, is given in (Khan *et al.,* 2009; Ryndin, 2015).

The analytic expression of the second law is the inequality of Rudolf Clausius (1865) (Equation 1).

According to this record, the entropy of an isolated system in irreversible processes increases, and in reversible processes it unchanged (de Oliveira, 2019). The question arises: what property of matter (motion, form of motion, or other property) is quantitatively preserved in the IS during the course of reversible (ideal) processes (Davidson, 2010;

Faraon *et al.,* 2017; Steinberg, 2005). Modern thermodynamics does not give an answer to this question.

Ignorance (misunderstanding) of the essence of the SLT led to the emergence of different formulations (about 20 formulations of the SLT were proposed (Putilov, 1971)) and an abundance of material devoted to clarifying the meaning of these formulations. In the course of such an explanation, contradictions arise both within individual textbooks and between textbooks of different authors (Wald, 2001; Martyushev and Seleznev, 2006; Rakopoulos and Giakoumis, 2006; Liu and Liu, 2008; Seifert, 2008; Romatschke, 2010; Bejan, 2016; D'Alessio *et al.,* 2016; Marbœuf *et al.,* 2019; Ptaszyński and Esposito, 2019; Sellitto and Di Domenico, 2019). These formulations indirectly describe the consequences arising from the SLT or are superfluous (for example, a statement about heat removal in a cycle) (Thu *et al.,* 2018). One single wording is needed (as is customary in other laws), from which, as a consequence, various existing wording should flow (or be considered redundant). With one formulation of the second law, the need to introduce many formulations will become superfluous.

Certain objections raise statements of the type: “a reversible process can proceed only in fully equilibrium systems,” (Lu *et al.,* 2018) that is, when there are no processes; “The irreversible process cannot be represented graphically,” although the same authors use the corresponding diagrams to depict the change in the state of the gas as it flows with friction in the channel” (Avellaneda *et al.,* 2019); “Heat cannot be completely transformed into work, but work can” (Mishra and Chakraborty, 2019), although it is known that in the isothermal process of expanding an ideal gas, the heat supplied is equal to the work done; “Equilibrium heat transfer in a thermally nonequilibrium system using an ideal heat engine” (Jakhar *et al.,* 2019) and many others.

The “existence” of entropy is proved (postulated) as the first part of the second law. Since entropy is a physical quantity (a named number), it must be derived through basic quantities using the appropriate coupling equations, and not postulated or proven (Loos and Klapp, 2019).

The question arises: is the entropy the only characteristic of an irreversible change in the state of a non-equilibrium isolated system, that is, characterizes the direction of the processes in a non-equilibrium isolated system? Along with the entropy in setting forth the second law of thermodynamics, such quantities as thermodynamic potentials, maximum system work, exergy are introduced (Moran *et al.,* 2014; Pakter and Levin, 2017; Calabrese, 2018; Devine, 2018; Lucia and Grisolia, 2019). These quantities have so far not been united by the general idea of the second law of thermodynamics. There is a need to develop a unified concept of presentation of the second law of thermodynamics, which could combine these quantities into a single theory. Let us consider how modern thermodynamics answers this and other questions.

2. MATERIALS AND METHODS

2.1. Review of the methods of setting forth of the second law of thermodynamics based on the concept of equilibrium

The second law of thermodynamics is perhaps the most complicated and confusing, and in any case, the discussion issue of thermodynamics, to which much attention is paid both in textbooks on thermodynamics and in special articles (Orlov *et al.,* 2003; Ben-Naim, 2010; Pichkur *et al.,* 2015; Amirgaliyev *et al.,* 2017a; Darrigol and Renn, 2017; Sherwood and Dalby, 2018; de Blasio, 2019).

As already noted, there are many different formulations of the SL of thermodynamics, given both by the founders of this law and by the authors of textbooks, leading them in full or incomplete form. Since all formulations are considered equivalent, the authors of the textbooks do not pay enough attention to the accuracy of the statement of these formulations and do not follow the rigor of the proof of their equivalence. From the moment the formulations appeared, their criticism began, and hence, the second law of thermodynamics (Hołyst and Poniewierski, 2012).

The classical formulations of the SLT should include the formulations (postulates) of R. Clausius (1865, 1879-1891), V. Thomson (Kelvin) (1882–1911), M. Planck (1901) and L. Boltzmann (1887). We present the contexts of the SLT from some thermodynamic textbooks.

The formulation (postulate) of R. Clausius (1865) as set forth in the statement by Borgnakke and Sonnag (2009), Kondepudi and Prigogine (2015), Krutov *et al.* (1986), Kirillin *et al.* (1983), Novikov (1984): “Heat cannot by itself pass from a colder body to a warmer one.”

Fermi's statement of the Clausius postulate (1937): “A transformation whose only final result is to transfer heat from a body at a given temperature to a body at a higher temperature is impossible”.

Many authors, voluntarily or involuntarily, in the textbook or in its separate part, associate the SL with this initial formulation of R. Clausius. Thus, in the textbook Vukalovich (1968) it is noted: “Based on one first law of thermodynamics, it is permissible to assume that any conceivable process that does not contradict the law of conservation of energy is fundamentally possible and could take place in nature. It could be assumed, for example, that during heat exchange between two bodies with different temperatures, heat can transfer both from a body with a higher temperature to a body with a lower temperature, and vice versa from a body with a lower temperature to a body with a higher temperature.

The answer to the question of the direction in which the heat transfer between two bodies actually takes place and in other more complicated cases is given by the SLT, according to which heat itself only transfers from a body with a higher temperature to a body with a lower temperature, but never the other way”.

However, as early as 1807, J. Fourier has derived the law (Fourier law), according to which the vector of the surface density of heat flow is directly proportional to the gradient of temperature and opposite to it: $\vec{\varphi} = -\lambda \operatorname{grad} T$ (Landau and Lifshits, 1988). Since the temperature gradient is directed in the direction of increasing temperature, therefore, the heat flux is directed in the opposite direction (indicated by a minus sign), that is, in the direction of decreasing temperature.

Along with the Fourier law, other “gradient” laws of transfer substance and movement (attribute of matter) can be given, according to which the transfer of a substance in space occurs in the direction of decreasing concentration of this substance. For example, according to Fick’s diffusion law, a substance moves in the direction opposite to the direction of the mass concentration gradient, i.e., in the direction of decreasing concentration (Webb and Pruess, 2003; Dubi and Di Ventra, 2009).

As you can see, the gradient laws establish the direction of transfer of heat (Fourier's law) and substance (Fick's law) in space and the use of additional laws (SLT) to indicate the direction of transfer of substance and movement in space is not required (Shahari *et al.,* 2015). Consequently, the essence of the second law of thermodynamics consists of another.

The formulation of the SL "heat cannot by itself pass from a cold body to a hot body", it seems that nothing new would add to the Fourier law (heat transfers from a hot body to a cold one), except for the words “by itself”. Clausius (1879–1891) repeatedly in his articles explained the meaning of the expression “by itself”. Heat in a number of processes can move from a cold body to a warm one, but then simultaneously with this transition from a colder to a warmer body, an opposite process should take place, which should be considered “as compensation for the transfer of heat from a colder body to a warmer one”, and gives a new formulation of the principle: “The transfer of heat from a colder body to a warmer one cannot take place without compensation”. It is in the “compensation” that the Clausius formulation of the second law differs from the formulation of the gradient laws, which, as already noted, are sometimes identified with the second law of thermodynamics. In connection with the above, for a clearer distinction between the SL and of the gradient laws, the textbooks should include the last (extended) Clausius formulation with the words “without compensation”, but not the original, containing the words “by itself”.

With the introduction of the concept of "compensation" by Clausius, all attention was paid to clarifying this concept. Most authors began to understand compensation as the need to remove heat to a cold body (and, consequently, the need for two sources of heat), as well as heat (Q2) transferred to a cold body.

2.2. Postulate of V. Thomson

The postulate of V. Thomson (Lord Kelvin) (1851) as presented by Krutov *et al.*: “The heat of a body cannot be turned into work without producing any other action than cooling this body” (Krutov *et al.,* 1991).

Lavenda (2010): “Clausius claims that heat will not pass from a cold body to a hot body without compensation, but does not tell us what the compensation is. Kelvin says that we cannot get work out of a body by lowering its temperature below that of the surroundings”.

Kelvin's postulate as presented by Fermi (1937): “A transformation whose only final result is to transform into work the heat extracted from a source which is at the same temperature throughout is impossible".

Later, this formulation "corrected" – it is impossible to completely turn the warmth into work, although Clausius did not write this. The corrected formulation of the SLT as submitted by Srivastava *et al.*, (2007): "One hundred percent conversion of heat into work is impossible". The corrected formulation that *Q* cannot be equal to the work does not follow from the Kelvin formulation.

Fermi (1937) is the first to show that in the case of an isothermal process of an ideal gas, heat is equal to the work, since the internal energy of an ideal gas does not depend on the volume: "The internal energy of an ideal gas, which depends only on temperature, in the case of an isothermal process does not change ($\Delta U = 0$), and therefore, according to the FLT, the work L performed during gas expansion is equal to the heat *Q*, which it absorbs from the source; that is, we have the complete transformation of warmth into work".

Further Fermi (1937) explains: "An essential part of Lord Kelvin's postulate is that the transformation of the heat into work be the only final result of the process. Indeed, it is not impossible to transform into work heat taken from a source all at one temperature provided some other change in the state of the system is present at the end of the process".

Regarding the isothermal process, he also notes: "This, however, is not a contradiction of Kelvin's postulate since the transformation of Q into L is not the only final result of the process. At the end of the process, the gas occupies a volume larger than it did at the beginning" (Fermi, 1937).

Thus, Fermi defends the Kelvin formulation but refutes the "corrected" formulation, from which it followed that Q could not equal the work even for an ideal gas in an isothermal process. Fermi has proven that he can.

The following formulations are related to the operation of the engine, making the cycle.

Baehr (1973): "In 1851 Thomson formulated the SLT in the following way: it is impossible to obtain mechanical work from any mass of a substance with an inanimate material agent by cooling it below the temperature of the coldest of surrounding bodies. Planck formulated it even more clearly in 1897: it is impossible to build a periodically operating machine, all functioning of which would be reduced to lifting some weight and cooling the heat source".

Kondepudi and Prigogine (2015): "It is impossible to build an engine that will work in a complete (closed) cycle and convert all the heat that it receives from the reservoir into mechanical work".

Borgnakke and Sonnag (2009): "There are two classical statements of the second law, known as the Kelvin–Planck statement and the Clausius statement. The Kelvin–Planck statement: It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir.

It states that it is impossible to construct a heat engine that operates in a cycle, receives a given amount of heat from a high-temperature body, and does an equal amount of work. The only alternative is that some heat must be transferred from the working fluid at a lower temperature to a low-temperature body.

The Clausius statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body".

Callen (1985) believes that the Kelvin-Planck statement does not exclude the possibility of obtaining work from a single heat source in a separate process. It denies this possibility only if the system goes through a thermodynamic cycle.

The statement that the SLT causes heat removal in a cycle is similar to the statement that the SLT causes spontaneous heat transfer in the direction from a hot body to a cold one. As noted above, heat transfer in the direction of decreasing temperature is described by gradient laws. As for heat removal in a cycle, this is a feature of the cycle itself (a property of the cycle): you cannot get a cycle (circular process) consisting of a set of processes if at least one process would not proceed with heat removal.

Let the cycle 1-2-3-1 consist of three processes (the minimum number of processes of the cycle): the isobaric expansion process 1-2 with the heat input, the adiabatic expansion process 2-3 (without heat exchange) and the polytrophic compression process 3-1 leading the working body into the initial state 1. From the theory of thermodynamic processes (Krutov *et. al.,* 1991; Bertrand, 2005; Birjukov *et al.,* 2008; Cheng and Liang, 2014; Amirgaliyev *et al.,* 2017b; Fitsak *et al.,* 2019) it is known that the compression process proceeding to the left of the adiabat occurs with heat removal, and the expansion process proceeding to the right of the adiabat occur with heat supply. Consequently, the process 3-1 closing the cycle must proceed with heat removal. No matter how we try to build a cycle (a set of processes that return the working body to its original state), at least one process will always be with heat removal. For example, a cycle consisting of an isobaric expansion process with heat supply, isochoric with heat removal and adiabatic compression (Dong *et al.,* 2016; Kojima, 2017; Chen and Tsutsumi, 2018; Glushenkov *et al.,* 2018; Huang *et al.,* 2018). Thus, heat removal in a cycle is a property of the cycle itself, and not a consequence of the SLT, as is commonly believed.

If we assume that the SLT establishes various conditions for reversible and irreversible processes, then the same conditions should be established for cycles. However, heat removal is necessary for both reversible and irreversible cycles. Which also indicates that heat removal in the cycle is not a consequence of the SLT.

2.3. Entropy formulations of the second law

Morales-Rodriguez (2016): “The second law of thermodynamics expresses the existence of a quantity called the entropy *S* and states that for an isolated macroscopic system *S* never decreases, or, alternatively, that perpetual motion machines of the second kind are impossible”.

Holyst and Poniewierski (2012): “There exists an extensive state function, called entropy, *S*, whose change in an adiabatic process satisfies the inequality $\Delta S \geq 0$, where $\Delta S = 0$ only if the process is reversible”.

Along with the above formulations of the classics of thermodynamics, we can note the formulation of Afanasyevoy-Ehrenfest, given as the principle of the existence of entropy: “The second law of thermodynamics consists of two independent propositions, or laws, which are a consequence of independent experimental facts. One of them is called the second law of thermodynamics for reversible processes or the principle of the existence of entropy, the second is the second law of thermodynamics for irreversible processes or the principle of increasing entropy” (Krutov *et al.,* 1991).

Since entropy, as is known, is a physical quantity – a quantitative characteristic of objective reality (named number), and not the objective reality itself, it, like any physical quantity, “exists” only in human consciousness and does not make sense to prove its existence in nature (Chen, 2016; Spinney *et al.,* 2016; Anderson, 2017). It must be introduced through basic physical quantities without involving the second law of thermodynamics (its calculation from 0 K is given in the works of Ryndin (2015), Kirillin *et al.* (1983), Reyf (1972).

2.4. Statistical interpretation of entropy

Along with the formulations of Clausius, Thomson, and Planck, the second law formulation given by L. Boltzmann (1887) occupies a separate place: nature tends to transition from less probable to more probable states, and entropy is a logarithmic measure of the number of microscopic states that correspond to the macroscopic state: $S = k_{\mathrm{B}} \ln W$. Ter Harr (1967) notes that it was Max Planck who introduced k_{B} in the above formula; Planck also determined its numerical value. According to the figurative expression of Kondepudi and Prigogine (2015): “Every process in Nature increases the entropy, thus establishing a distinction between the past and the future. The Second Law establishes an arrow of time: the increase of entropy distinguishes the future from the past”.

According to the Boltzmann (1887) formulation, the second law of thermodynamics is not an exact law of nature, similar to the laws of conservation of momentum or conservation of energy. The second law of thermodynamics is of a statistical nature and therefore is performed only “on average”.

That is, according to this formulation, heat can “by itself” move from a cold body to a hot body, only it is necessary to wait “well”. Will have to wait quite a long time. So, to observe a single unnatural process of transition of a system from an equilibrium state to a non-equilibrium, for example, “spontaneous” (fluctuation) compression of gas (“harmonious” movement of all molecules to a single vessel wall) with a volume of 1 cm^3, resulting in an increase in its density by 1 % , it will take 10^{140} years; Kittel (1993) gives this figure $10^{(10^{10})}\mathrm{c}$ for the spontaneous separation of two gases in a volume of 0.1 liters.

Consequently, in macroscopic systems, the second law of thermodynamics is a reliable law (Leinonen *et al.,* 2015; Tasaki, 2016; Brahma, 2017; Maes and Tasaki, 2017). It has a statistical nature for microscopic systems containing a relatively small number of molecules. For example, if we take the volume of air equal to 0.008 cubic micrometers, then the change in air density in this volume by 1 % will occur very often – about a milliard times per second (Kirillin *et al.,* 1983).

Based on the foregoing, it follows that at present, there is no single theory explaining all the phenomena associated with the second law of thermodynamics. The purpose of this work is to develop an appropriate theory, the task of which is to eliminate contradictions arising from the presentation of the second law of thermodynamics and not solved by the concept of equilibrium.

3. RESULTS AND DISCUSSION:

As already noted, the main provisions defined by the second law of thermodynamics can be expressed in various formulations of this law in the form of postulates. One of these postulates is the postulate of the existence of thermodynamic equilibrium (Roh, 2014, 2015; Mishin, 2015; Skvortsov *et al.,* 2016; Serdyukov, 2018**)**. According to this postulate, any nonequilibrium isolated system over time comes to a state of thermodynamic equilibrium and cannot spontaneously get out of it.

The equilibrium postulate underlies the concept of reversibility, according to which reversible processes can proceed only in fully equilibrium systems when there is "an infinitesimal difference (in the limit is equality) between the temperatures of the machine and the heat source" Krichevsky (1970). After the flow of the inverse equilibrium process, the whole system comes to the former equilibrium state.

In accordance with the concept of equilibrium, the field of application of reversible processes in thermodynamics is limited to considering interactions between systems in almost identical states (with infinitely small pressure and temperature differences between systems), which reduces the practical significance of this concept for real highly nonequilibrium thermal power installation and engines (Chen *et al.,* 2017; Valente, 2019).

Thus, the equilibrium concept existing in thermodynamics does not imply the possibility of reversible processes in nonequilibrium systems. At the same time, in thermodynamics, there are cases of reversible processes, for example, reversible heat transfer with a finite temperature difference between bodies using an ideal heat engine, gas flow in an ideal turbine or compressor with a final pressure drop in a stream, etc (Nili-Ahmadabadi *et al.,* 2018; Guo *et al.,* 2019)

In connection with the difficulties noted above, which arise in presenting the second law on the basis of the existing concepts of equilibrium and reversibility, the postulate "on the existence and change of nonequilibrium" is introduced into thermodynamics.

By nonequilibrium, here we mean the property of matter (matter attribute), due to the uneven distribution of motion and substance in space. Nonequilibrium, in turn, characterizes the ability of a system to do work: work cannot be done in an equilibrium system. Consequently, the measure (quantitative characteristic) of the nonequilibrium will be the maximal work that the system can do when it goes into an equilibrium state.

The following types of nonequilibrium are distinguished: thermal and baric, due, respectively, to a difference in temperature and pressure in space; mechanical (kinetic and potential), electrical, chemical, etc. To assess the nonequilibrium of the entire system consisting of a set of locally equilibrium subsystems, the notion of total nonequilibrium is introduced as the sum of all types of nonequilibrium of an isolated system.

According to the principle of nonequilibrium, the second law of thermodynamics is formulated as follows: *the total (summary) nonequilibrium of an isolated system decreases during the course of real (irreversible) processes and remains constant at the course of ideal (reversible) processes*. It can be said and this way: the nonequilibrium of an isolated system cannot increase: in reversible processes, it does not change (is preserved) and decreases in irreversible ones.

In the case of reversible processes, the loss of the nonequilibrium of one type is fully compensated by the growth of nonequilibrium of another type. The processes during which the total nonequilibrium of the isolated system remains unchanged, and will be those reversible processes that are considered in thermodynamics.

The concept of conservation of nonequilibrium is consistent with the existing definition of a reversible process, according to which an isolated system returns to its original state after the flow of the direct and reverse processes, i. e., to the former nonequilibrium (in an equilibrium system, no processes can occur either in the direct or reverse directions) . It also agrees with the statement of the second law Clausius: heat cannot transfer from a cold body to a hot one without compensation, if, under the compensation of the growth of thermal nonequilibrium during heat transfer from a cold body to a hot body, is understood a reduction of some other nonequilibrium (for example, mechanical) in equivalent amount.

The postulate of nonequilibrium does not contradict the postulate of equilibrium since, with the occurrence of irreversible processes, the isolated system loses its nonequilibrium and ultimately turns into a full equilibrium state (state of equilibrium).

As quantitative characteristics of the system nonequilibrium, the generalized concepts “energy amount of nonequilibrium” and “entropic amount of nonequilibrium” are introduced, combining various thermodynamic quantities (more precisely, their changes): thermodynamic potentials, exergy, and entropy.

The energy amount of nonequilibrium (or abbreviated energy disequilibrium) is understood as the amount of nonequilibrium, defined through the work of various kinds, performed during the transition of the system to an equilibrium state. To calculate the maximum (available) work in thermodynamics, such quantities as thermodynamic potentials, the exergy of heat and flow exergy are used.

If the thermodynamic potential in the general case is denoted by the symbol Π (“pi” Greek), then the amount of nonequilibrium of the system will be determined by “the potential difference” of the system in nonequilibrium state $\Pi_{\text{noneq.st}}$ and equilibrium state $\Pi_{\text{eq.st}}$ (we will call it “potential difference $\Delta\Pi^*$”), equal to the maximum system work when it transitions to an equilibrium state (Equation 2).

The potential difference of the adiabatic system performing the work decreases in any processes (reversible and irreversible). However, only in reversible processes the decrease of potential difference, equal to the decrease of thermodynamic potential, will be equal to the maximum external work of a nonequilibrium system (Equation 3), where $\mathrm{d}\Pi_{\text{eq.st}} \equiv 0$, since the transition of the system to an equilibrium state, all processes cease and, consequently, changes all quantities are zero.

In the case of irreversible processes, the external work of the system W^e is less than the decline of potential difference (a decline of thermodynamic potential):

$$\delta W^{\mathrm{e}} < -\mathrm{d}(\Delta\Pi^*) = -\mathrm{d}\Pi\ .$$

Consequently, the general condition for the transition of a system from a more nonequilibrium state to a less nonequilibrium state (more equilibrium state) has the form

$$\delta W^{\mathrm{e}} \leq -\mathrm{d}(\Delta\Pi^*) = -\mathrm{d}\Pi\ .$$

According to this expression, external work is equal to the decrease of potential difference, or the decrease of thermodynamic potential in reversible processes and less than this decrease in irreversible processes.

To establish a connection between the exergy of heat E_Q and the nonequilibrium of the system, we consider the change in thermal nonequilibrium during heat transfer in the amount $Q_1 = |Q_{HB}|$ from a hot body (HB) with a temperature T_1 to the ambient medium (AM) with a temperature T_0. As a result of heat transfer, the thermal nonequilibrium in the HB-AM system decreases. In order for the heat transfer process to be reversible (without reducing the total nonequilibrium), it is necessary, along with a decrease in thermal nonequilibrium, to increase in an equivalent amount any other nonequilibrium, for example, mechanical.

To create a mechanical nonequilibrium, the ideal heat engine should be added to the HB-AM system, consisting of a working body (WB) performing the cycle and a receiver (source) of work (RW – flywheel, spring, load). In the process of heat transfer, the thermal nonequilibrium in the HB-AM system decreases, but as a result of work done due to a part of this heat, the kinetic or potential energy of the receiver of work increases, that is, the mechanical nonequilibrium increases, and in general, the total nonequilibrium of the isolated system (HB-AM-WB-RW) does not change. In the future, adding an ideal refrigerating machine, such a system can be returned after each cycle to its original nonequilibrium state.

If the amount of the energy nonequilibrium is denoted Λ, then the balance equation for the change in the total nonequilibrium of the IS (HB-AM-WB-RW) in the reversible cycle ($\Delta\Lambda_{\mathrm{WB}} \equiv 0$) is written as $\Delta\Lambda_{\mathrm{IS}} = \Delta\Lambda_{\mathrm{ther}} + \Delta\Lambda_{\mathrm{mech}} = 0$.

From here, the decrease in thermal nonequilibrium will be equal to the increase in the mechanical nonequilibrium of the RW as a result of supplying it with work from the WB, carrying out an ideal Carnot cycle (ICC) in the temperature range HB (T_{HB}) and AM (T_0) (Equation 4), where $|\Delta S_{\mathrm{HB}}| = Q_1 / T_{\mathrm{HB}}$ is the modulus of change in the entropy of a hot body, equal to the increase in the entropy of the ambient medium (cold body – CB) in the reversible process of heat transfer.

The magnitude E_Q equal to the maximum work that can be obtained in the ideal Carnot cycle due to the heat supplied, if the cold body is an ambient medium of constant parameters, it is customary to call exergy of heat. Thus, the exergy of heat in accordance with (2) is a quantitative characteristic of the change in the thermal nonequilibrium of the HB-AM system. The exergy of heat is equal to the work that needs to be expended on the drive of the ideal refrigerator in order to return the cold and hot bodies to its original state (to the previous thermal nonequilibrium $-\Delta\Lambda_{\mathrm{mech}} = \Delta\Lambda_{\mathrm{ther}}$) – to take away Q_2 from the cold body and bring it to the hot body $Q_1 = Q_2 + E_Q$.

For the introduction exergy of flow as a measure of nonequilibrium, the nonequilibrium of a system consisting of a large capacity reservoir with pressure p_1 and temperature T_1 and the ambient medium with constant parameters p_0 and T_0 is considered. In such a system, under the action of a pressure drop, a substance is transferred (flowed) from the reservoir to the ambient medium, as a result of which the nonequilibrium of such a system decreases. To return the same portion of the substance from the ambient medium to the reservoir and, consequently, returning the reservoir-AM system to its former nonequilibrium, it is necessary to compress this portion of the substance to its original pressure and move it with the help of a compressor. The work expended on the drive of an ideal compressor that transfers a portion of a substance from the environment to the reservoir will be a measure of the nonequilibrium lost in the natural process of the flowing substance from the reservoir to the environment.

It is possible to maintain complete nonequilibrium of the IS during the flow of a substance if one obtains work from an element of flow in an ideal turbine and accumulates it in the form of energy (kinetic, potential, electrical) receiver work. That is, it is necessary to consider a nonequilibrium isolated system consisting of a reservoir, the ambient medium, a turbine, and a receiver of work.

Since in a reversible process the complete nonequilibrium of an isolated system consisting of an adiabatic system (a reservoir and ambient medium) and a receiver of work does not change, then for this system it is possible to write Equation 5.

It follows that the decrease in the nonequilibrium of the adiabatic system (AS) is compensated by the increment of the mechanical nonequilibrium between the adiabatic system and the receiver of work as a result of the work in the turbine (Equation 6) or for specific values (Equation 7)

In accordance with Equation 7, the decrease of the specific energy nonequilibrium of the adiabatic system is equal to the specific technical work done in the turbine.

The maximum specific work received from the element of flow during its expansion in the turbine to the AM parameters is called the flow exergy (Krutov *et al.,* 1991) (Equation 8)

If the parameters of the element of flow coincide with the parameters of the reservoir (p_1 and T_1), then the exergy of flow (Eq. 8) in accordance with Equation 7 will be equal to the decrease of the specific nonequilibrium of the reservoir-AM system caused by the transfer of a substance of unit mass from the reservoir to the ambient medium (Equation 9).

According to the second law, an irreversible transition of a nonequilibrium isolated system to an equilibrium state is always accompanied by an increase in the entropy of the IS ($\mathrm{d}S_{\mathrm{IS}} > 0$, or $-\mathrm{d}S_{\mathrm{IS}} < 0$), therefore, the difference between the entropy of the IS in the equilibrium and nonequilibrium states – “the entropic difference” ΔS^* – will also characterize the nonequilibrium of the IS in this state (Equation 10).

The increment of the entropy of the IS $\mathrm{d}S_{\mathrm{IS}}$ will characterize the loss of nonequilibrium of the IS. The relationship between the changes in the entropy of the IS and the entropy difference during the course of irreversible processes can be obtained if we differentiate Equation 10, taking into account that $\mathrm{d}S_{\mathrm{eqIS}} = \mathrm{d}S_{\text{макс}} = 0$ (in the equilibrium state, the entropy of the isolated system is maximum and does not change) (Equation 11).

In accordance with Equation 11, the

occurrence of irreversible processes in IS, the entropic difference, as well as the total nonequilibrium, decreases, and the entropy increases, that is, the decrease in the entropic difference is equal to the increment of the entropy of an isolated system. Consequently, the entropy increment dS_{IS} (namely, the change in entropy dS_{IS}, and not the entropy itself S_{IS}) quantitatively characterizes the decrease in the nonequilibrium of the IS. This is the physical meaning, but not the entropy S itself, but its changes dS_{IS} as one of the quantitative measures of nonequilibrium of an isolated system.

Since in reversible processes the entropy does not change ($\mathrm{d}S^{\mathrm{o}}_{\mathrm{noneqIS}} = 0$), then inequalities (11) in the general case of the flow of reversible and irreversible processes in IS take the following form (Equation 12).

So, based on the postulate of nonequilibrium, a new analytic expression of the second law is obtained – inequality (7/12), the inverse to Clausius inequality (1) $\mathrm{d}S_{\mathrm{IS}} \geq 0$, which implies a new formulation of the second law: *when irreversible processes occur, the entropic difference (as well as the complete nonequilibrium) of the isolated system decreases, and in reversible processes – does not change.*

The entropic difference ΔS^{*} and the entropy change ΔS of an isolated system can be generalized by the concept of “the entropic quantity of the nonequilibrium”.

Inequality (12) with its sign (“less”) directly indicates a decrease in a nonequilibrium (entropic difference) in IS, unlike the well-known inequality $\mathrm{d}S_{\text{ИС}} \geq 0$, the sign of which (“more”) does not explicitly reflect the tendency to decrease the nonequilibrium of an isolated system.

The connection between the entropic difference ΔS* of the IS and the maximum work that this system could do in a reversible process when it goes to an equilibrium state when removing mechanical insulation, i. e., in the case of converting an isolated system to an adiabatic one, can be given by (Equation 13), where $-\Delta(\Delta S^{*})_{\max} = \Delta S^{*}_{\text{initial}} = \Delta S^{*}$ is the maximum decrease in the entropic difference when the system goes to an equilibrium state (in an equilibrium state, the entropic difference is zero $\Delta S^{*}_{\mathrm{PC}} = 0$; it is equal to the entropic difference itself (the initial difference), and in accordance with Equation 11 is equal to the increment of the entropy of an isolated system when it goes into an equilibrium state).

For elementary processes occurring in nonequilibrium systems (isolated or adiabatic) with the loss of possible (available) work $\delta W_{\text{loss}} \equiv \delta W_{\text{poss}}$, in accordance with Equation 13 we can write Equation 14, where $T_{\text{CB min}}$ is the body temperature with the lowest temperature (temperature of the cold body) during heat exchange or the temperature of the thermodynamic system (working body, heat source) when interacting with sources of work (freight, spring, flywheel, electrocondenser, battery, etc.), which they themselves are not characterized by temperature.

If an equilibrium ambient medium is taken as the body with the lowest temperature, the temperature of which does not change when a nonequilibrium system transitions to an equilibrium state (T_{AM} = const), then formula (14) for lost work (it is sometimes called “lost workability” or “energetic loss” (Kirillin *et al.,* 1983) takes the form (Equation 15):

Expression (15) is called the Gui-Stodola equation by the name of the French physicist M. Gui, who derived this equation in 1889, and the Slovak heat engineer A. Stodola, who first applied this equation to solve technical problems.

The relationship between the energetic and entropic amounts of nonequilibrium is established using equations (14) and (15) (Equations 16-17).

Therefore, the total amount of nonequilibrium (AN) should be understood as a generalizing quantity, which includes the energetic and entropic amounts of nonequilibrium: AN $\{\Lambda, \Delta S^{*}, \Delta S\}$. In this case, the energetic amount of nonequilibrium of system, as already noted, should be understood as a generalizing quantity, including such quantities as the maximum work $W^{\max}_{\text{noneq.st}\to\text{eq.st}}$ giving by the system (or dissipated in the system) when it goes to the equilibrium state, potential difference $\Delta\Pi^{*}$, exergy (specific) fluxes substance e_{x} and heat e_{q} (Equation 18).

The energetic amount of nonequilibrium can be used to calculate the change in nonequilibrium of both isolated and adiabatic systems, and the entropic amount of nonequilibrium can be used only for an isolated system, since when the outside work is performed in a reversible process by a nonequilibrium adiabatic system, the nonequilibrium decreases and the entropy does not change.

Analytical expressions of the second law of thermodynamics, according to which the amount of nonequilibrium (nonequilibrium) of an isolated system in irreversible processes decreases and persists in reversible processes, can be represented as the following inequalities (Equation 19).

Ryndin (2015) gives examples of calculating both the nonequilibrium of isolated systems and its reduction during the occurrence of irreversible processes, consistent with an increase in entropy (Equation 1).

4. CONCLUSIONS:

The article puts forward a new postulate of the second law of thermodynamics – the postulate nonequilibrium: there is a property of matter —nonequilibrium characterizing the non-uniform distribution of matter and movement in space. All processes can proceed only in non-equilibrium systems; when the system reaches an equilibrium state, all processes (reversible and irreversible) cease.

The concept of "nonequilibrium" includes:

a) objective reality is a new property of matter;

b) amount characteristics (physical quantities) – measures of nonequilibrium:

1) the maximum work (or possible work) performed (or that could have been done) by a nonequilibrium system when it goes into an equilibrium state;

2) entropic difference;

3) potential difference;

4) exergetic difference.

The nonequilibrium (as an attribute of matter), unlike entropy (physical quantity), really exists, but not for a single equilibrium system, but for a set of locally equilibrium subsystems (heat sources and receivers, receivers and sources of work, working body, ambient medium, small and finite elements of the stream), forming a nonequilibrium system; and it does not "flow" from one body to another (as it is considered for entropy), but changes or remains unchanged.

A new formulation of the second law of thermodynamics is given to the set of locally equilibrium subsystems that make up a nonequilibrium system: when real (irreversible) processes occur, the nonequilibrium of the isolated system decreases, and in reversible processes the nonequilibrium in the system of locally equilibrium subsystems does not change (the increment of nonequilibrium of one species is completely compensated by a decrease in nonequilibrium of any other species).

A new entry of the second law of thermodynamics is given in the form of the inequality $\mathrm{d}\Lambda_{\text{noneq IS}} \leq 0$, according to which the total (full) nonequilibrium of the isolated system Λ cannot increase. This inequality is the opposite of the Clausius inequality $\mathrm{d}S_{\text{noneq IS}} \geq 0$ – the total entropy of the isolated system cannot decrease.

The introduction of the postulate nonequilibrium allows us to give only one formulation of the second law of thermodynamics and thereby reduce the large amount of material associated with clarifying the essence of the second law of thermodynamics, and also to combine, based on the concept of the amount of nonequilibrium, such different physical quantities as thermodynamic potential, exergy and entropy.

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$$\mathrm{d}S_{\text{ИС}} \geq 0 \qquad \text{(Eq. 1)}$$

$$\Delta\Pi^{*} = \Pi_{\text{noneq.st}} - \Pi_{\text{eq.st}} = W^{\max}_{\text{noneq.st}\to\text{eq.st}} \qquad \text{(Eq. 2)}$$

$$\delta W^{\mathrm{e}}_{\max} = -\mathrm{d}(\Delta\Pi^{*}) = -\mathrm{d}\Pi_{\text{noneq.st}} + \mathrm{d}\Pi_{\text{eq.st}} = -\mathrm{d}\Pi_{\text{noneq.st}} \equiv -\mathrm{d}\Pi \qquad \text{(Eq. 3)}$$

$$-\Delta\Lambda_{\text{ther}} = \Delta\Lambda_{\text{mech}} = W_{\text{ICC}} = Q_1(1 - T_0 / T_{\text{HB}}) = Q_1 - T_0\left|\Delta S_{\text{HB}}\right| = Q_1 - T_0\Delta S^{\mathrm{o}}_{\text{AM}} = E_Q \qquad \text{(Eq. 4)}$$

$$\Delta\Lambda_{\text{noneqIS}} = \Delta\Lambda_{\text{reserv-AM}} + \Delta\Lambda_{\text{RW}} = \Delta\Lambda_{\text{noneqAS}} + \Delta\Lambda_{\text{RW}} = 0 \qquad \text{(Eq. 5)}$$

$$-\Delta\Lambda_{\text{noneqAS}} = -\Delta\Lambda_{\text{reserv-AM}} = \Delta\Lambda_{\text{RW}} = \Delta E_{\text{RW}} = W^{\mathrm{o}}_{\text{tur}} \equiv W^{\max}_{\text{tur}} \qquad \text{(Eq. 6)}$$

$$-\Delta\lambda_{\mathrm{noneqAS}} = \Delta\lambda_{\mathrm{RW}} = w_{\mathrm{tur}}^{\max}$$ (Eq. 7)

$$e_{\mathrm{x}} = w_{\mathrm{tur}}^{\max} = h - h_0 + T_0(s_0 - s)$$ (Eq. 8)

$$e_{\mathrm{x1}} = h_1 - h_0 + T_0(s_0 - s_1) = w_{\mathrm{tur}}^{\max} = -\Delta\lambda_{\mathrm{reserv\text{-}AM}}$$ (Eq. 9)

$$\Delta S^* \equiv \Delta S^*_{\mathrm{noneqIS}} = S_{\mathrm{eqIS}} - S_{\mathrm{noneqIS}} = \Delta S_{\mathrm{noneqIS}\rightarrow\mathrm{eq.st}}$$ (Eq. 10)

$\mathrm{d}(\Delta S^*) = \mathrm{d}S_{\mathrm{eqIS}} - \mathrm{d}S_{\mathrm{noneqIS}} = -\mathrm{d}S_{\mathrm{noneqIS}} < 0$, or $-\mathrm{d}(\Delta S^*) = \mathrm{d}S_{\mathrm{noneq\,IS}} > 0$ (Eq. 11)

$$\mathrm{d}(\Delta S^*) \le 0$$ (Eq. 12)

$$-\Delta(\Delta S^*)_{\max} = -(\Delta S^*_{\mathrm{eq.st.}} - \Delta S^*_{\mathrm{noneq.st.}}) = \Delta S^*_{\mathrm{noneq.st.}} = \Delta S^* = \Delta S_{\mathrm{IS}} = W_{\max}^{\mathrm{noneq.AS}} / T_{\mathrm{CB\,min}}$$ (Eq. 13)

$\mathrm{d}S_{\mathrm{noneq.IS}} = \delta W_{\mathrm{loss}} / T_{\mathrm{CB\,min}}$, $\mathrm{d}S_{\mathrm{noneq.AS}} = \delta W_{\mathrm{loss}} / T_{\mathrm{CB\,min}}$, or $\delta W_{\mathrm{loss}} = T_{\mathrm{CB\,min}}\mathrm{d}S_{\mathrm{noneq\,IS\,(noneq\,AS)}}$ (Eq. 14)

$$\delta W_{\mathrm{loss}} = T_{\mathrm{AM}}\mathrm{d}S_{\mathrm{IS}}$$ (Eq. 15)

$$-\mathrm{d}\Lambda_{\mathrm{IS}} = \delta W_{\mathrm{loss}} = T_{\mathrm{CB\,min}}\mathrm{d}S_{\mathrm{IS}} = -T_{\mathrm{CB\,min}}\mathrm{d}\,(\Delta S^*)_{\mathrm{IS}}$$ (Eq. 16)

$$-\mathrm{d}\Lambda_{\mathrm{IS}} = \delta W_{\mathrm{loss}} = T_{\mathrm{AM}}\mathrm{d}S_{\mathrm{IS}} = -T_{\mathrm{AM}}\mathrm{d}\,(\Delta S^*)_{\mathrm{IS}}$$ (Eq. 17)

$$\Lambda\,\{W_{\mathrm{noneq.st}\rightarrow\mathrm{eq.st}}, \Delta\Pi^*, e_{\mathrm{x}}, e_q\}$$ (Eq. 18)

$\mathrm{d}(\mathrm{AN}_{\mathrm{IS}}) \le 0$, $\mathrm{d}\Lambda_{\mathrm{IS}} \le 0$, $\mathrm{d}(\Delta S^*) \le 0$, or $\mathrm{d}S_{\mathrm{IS}} = -\mathrm{d}(\Delta S^*) \ge 0$ (Eq. 19)