PERIÓDICO TCHÊ QUÍMICA
ARTIGO DE REVISÂO

CÁLCULO DO NÃO-EQUILÍBRIO DE SISTEMAS QUE CONSISTEM NO CONJUNTO DE SUBSISTEMAS DE EQUILÍBRIO LOCAL

CALCULATION OF THE NONEQUILIBRIUM SYSTEMS CONSISTING OF AN AGGREGATE OF LOCALLY-EQUILIBRIUM SUBSYSTEMS

РАСЧЁТ НЕРАВНОВЕСНОСТИ СИСТЕМ, СОСТОЯЩИХ ИЗ СОВОКУПНОСТИ ЛОКАЛЬНО-РАВНОВЕСНЫХ ПОДСИСТЕМ

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

Received 20 June 2019; received in revised form 30 September 2019; accepted 22 October 2019

RESUMO

A segunda lei da termodinâmica (SLT) baseia-se no postulado do não-equilíbrio, segundo o qual existe uma propriedade objetiva da matéria – o "não-equilíbrio", que caracteriza a distribuição desigual da matéria e do movimento no espaço. Uma nova formulação da SLT é dada em relação ao conjunto de subsistemas de equilíbrio local que compõem o sistema de não-equilíbrio: quando ocorrem processos reais (irreversíveis), o não-equilíbrio do sistema isolado (SI) diminui e, nos processos reversíveis, o não-equilíbrio no sistema de subsistemas de equilíbrio local não muda completamente (o incremento de não-equilíbrio de um tipo totalmente compensado por diminuição do não-equilíbrio de qualquer outro tipo). Como característica quantitativa do sistema de não-equilíbrio, consideramos o trabalho máximo que pode ser feito quando o sistema de não-equilíbrio entra em equilíbrio. O artigo fornece uma confirmação calculada das disposições teóricas do conceito de não-equilíbrio e seu aparato matemático por exemplos de determinação da perda de não-equilíbrio de SI durante a operação do motor térmico que executa um ciclo irreversível e o estado de não-equilíbrio do sistema adiabático (SA). Foram dados os esquemas do SI consistindo de um corpo quente, o ambiente e um fluido de trabalho que executa um ciclo de Carnot imperfeito em temperatura, bem como um SA consistindo do ambiente e um fluido de trabalho, cuja expansão dá o trabalho a um receptor externo. Se demonstra que o trabalho externo do sistema adiabático deve ser determinado não pela diminuição do potencial termodinâmico do fluido de trabalho, como geralmente é aceito, mas pela diminuição do potencial de todos os corpos do SA (fluido de trabalho e ambiente). Como resultado, expressões analíticas são obtidas para o cálculo prático do não-equilíbrio e sua redução durante processos reais em sistemas que consistem no conjunto de subsistemas de equilíbrio local, o que é novo em termodinâmica.

Palavras-chave: *segunda lei da termodinâmica, postulado de não-equilíbrio, amount of nonequilibrium, calculation of nonequilibrium.*

ABSTRACT

The basis of SLT is the postulate of nonequilibrium, according to which there is an objective property of matter – “nonequilibrium”, which characterizes the uneven distribution of matter and motion in space. A new formulation of the SLT is given in relation to the set of locally equilibrium subsystems that make up the nonequilibrium system: when real (irreversible) processes occur, the nonequilibrium of the isolated system (IS) decreases, and in reversible processes the nonequilibrium in the system of locally equilibrium subsystems does not change (the increment of one kind of nonequilibrium completely compensated by a decrease in the disequilibrium of some other kind). The maximum work that can be done when the nonequilibrium system goes into equilibrium is considered as a quantitative characteristic of the nonequilibrium system. The article provides a calculated confirmation of the theoretical provisions of the concept of nonequilibrium and its mathematical apparatus by examples of determining the loss of IS disequilibrium during operation of a heat engine performing an irreversible cycle and the nonequilibrium state of an adiabatic system (AS). Schemes of an IS consisting of a hot body, the environment, and a working fluid performing a temperature-imperfect Carnot cycle are given, as well as an AS consisting of the environment and a working fluid, upon expansion of which work is given to an external work receiver. It is shown that the external work of the adiabatic system should be determined not by the decrease in the thermodynamic potential of the working fluid, as is generally accepted, but by the decrease in the potential of all AS bodies (the working fluid and the environment). As a result, analytical expressions are obtained for the practical calculation of nonequilibrium and its reduction during real processes in systems consisting of an aggregate of locally-equilibrium subsystems, which is new in thermodynamics.

Keywords: *second law of thermodynamics, postulate of nonequilibrium, amount of nonequilibrium, calculation of nonequilibrium.*

АННОТАЦИЯ

В основу ВЗТ положен постулат неравновесности, согласно которому существует объективное свойство материи – «неравновесность», характеризующее неодинаковость распределения вещества и движения в пространстве. Даётся новая формулировка ВЗТ применительно к совокупности локально-равновесных подсистем, составляющих неравновесную систему: при протекании реальных (необратимых) процессов неравновесность изолированной системы (ИС) уменьшается, а в обратимых процессах неравновесность в системе локально-равновесных подсистем не изменяется (приращение неравновесности одного вида полностью компенсируется уменьшением неравновесности какого-либо другого вида). В качестве количественной характеристики неравновесности системы рассматривается максимальная работа, которая может быть совершена при переходе неравновесной системы, в равновесное состояние. В статье даётся расчётное подтверждение теоретических положений концепции неравновесности и её математического аппарата на примерах определения потери неравновесности ИС при работе тепловой машины, осуществляющей необратимый цикл, и неравновесности адиабатной системы (АС). Приведены схемы ИС, состоящей из горячего тела, окружающей среды и рабочего тела, совершающего неидеальный по температуре цикл Карно, а также АС, состоящей из окружающей среды и рабочего тела, при расширении которого отдаётся работа внешнему приёмнику работы. Показано, что внешняя работа адиабатной системы должна определяться не по убыли термодинамического потенциала рабочего тела, как общепринято, а по убыли потенциала всех тел АС (рабочего тела и окружающей среды). В результате получены аналитические выражения для расчёта на практике неравновесности и её уменьшения при протекании реальных процессов в системах, состоящих из совокупности локально-равновесных подсистем, что является новым в термодинамике.

Keywords: *второй закон термодинамики, постулат неравновесности, количество неравновесности, расчет неравновесности.*

1. INTRODUCTION

The second law of thermodynamics (SLT) attracts the attention of scientists of many specialties, including philosophers. The analytical expression of the second law of thermodynamics is the inequality of Rudolf Clausius in 1850 (Equation 1).

According to this record, the entropy of a nonequilibrium isolated system $S_{\text{noneq.IS}}$ in irreversible processes increases, while in reversible processes, it remains. The question arises, which property of matter (motion, the form of motion, or other property) is quantitatively preserved in the IS during the course of reversible (ideal) processes. The modern thermodynamics does not have the answer to this question. Ignorance (misunderstanding) of the essence of SLT led to the appearance of various formulations (about twenty formulations of LST (Putilov were proposed) (Putilov, 1971; Freitas *et al.*, 2016) and an abundance of material devoted to clarifying the meaning of these formulations (Reyf, 1972; Wald, 2001; Martyushev and Seleznev, 2006; Rakopoulos and Giakoumis, 2006; Liu and Liu, 2008; Ben-Naim, 2010; Seifert, 2012; Bejan, 2016; D'Alessio *et al.,* 2016; Chen *et al.*, 2017; Altaner, 2017; Martyushev and Celezneff, 2017; de Oliveira, 2019; Marbœuf *et al.,* 2019; Ptaszyński and Esposito, 2019; Sellitto and Di Domenico, 2019; de Blasio, 2019; Borin and Sukhorukov, 2019).

As Moran notes, no wording fully reflects all aspects of the SLT given by other formulations. Many authors (Moran *et al.,* 2014) see the reason for the lack of a uniform formulation of the SLT as the diversity of thematic areas covered by the second law (Guo *et al.,* 2019).

When clarifying the formulations of SLT, contradictions arise both within individual textbooks and between textbooks of different authors: A.I. Andryushchenko (Andryushchenko, 1975), H.D. Baehr (Baehr, 1973), P. Calabrese (Calabrese, 2018), L. Chen and A. Tsutsumi (Chen and Tsutsumi, 2018), E. Fermi (Fermi, 1937), R. Hołyst and A. Poniewierski (Hołyst and Poniewierski, 2012), V.I. Krutov (Krutov *et al.,* 1991); Vukalovich and Novikov (Vukalovich and Novikov, 1968), Novikov (Novikov, 1984), C. Borgnakke, R.E, Sonnag, (Borgnakke and Sonnag, 2009), B. Callen (Callen, 1985), V.A. Kirillin (Kirillin *et al.,* 1983), Ch. Kittel (Kittel, 1993), D. Kondepudi and Prigogine (Kondepudi and Prigogine, 2015), I.R. Krichevsky (Krichevsky, 1970), B.H. Lavenda (Lavenda, 2010), R. Morales-Rodriguez (Morales-Rodriguez, 2016), M.J. Moran (Moran *et al.,* 2014). R.C. Srivastava (Srivastava *et al.,* 2007). These formulations indirectly describe the consequences arising from the SLT or are redundant (for example, the statement about heat removal in the cycle). One single formulation is needed (as is customary in other laws), from which various existing formulations should flow (or be considered redundant) as consequences. If there is a unified formulation of SLT, the need to introduce many formulations will become redundant.

This SLT formulation, based on the postulate "on the existence and change of nonequilibrium", is given by Ryndin V.V.: "The total (complete) nonequilibrium of an isolated system cannot increase – in reversible (ideal) processes it does not change, but in real (irreversible) processes it is reduced." In this paper, instead of the existing concept of equilibrium, which underlies the SLT, the concept of nonequilibrium is introduced. According to this concept, the cause of all processes is nonequilibrium – a property of matter, due to the uneven distribution of the concentration of motion in space.

The following types of nonequilibrium are distinguished: thermal and baric, due respectively to the 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 concept of complete nonequilibrium is introduced as the sum of all types of nonequilibrium of an isolated system (Khantuleva and Shalymov, 2017; Yuan and Yung, 2018; Cao *et al.,* 2019; Patitsas, 2019).

The processes in which the total nonequilibrium of the IS does not change (the growth of the nonequilibrium of one type is completely compensated by the decrease in the nonequilibrium of the other type) will be those reversible processes that are considered in thermodynamics; in irreversible processes, the nonequilibrium of the IS decreases (Saikhanov, 2017). The analytical expression of this formulation is the inequality (Equation 2). Where Λ is nonequilibrium (the amount of nonequilibrium), which is understood as the maximum work obtained in an adiabatic system (AS), or could be obtained in an isolated system during the course of reversible processes that bring the nonequilibrium system to an equilibrium state. Equation 2 is the opposite Clausius Equation 1 – the total entropy of IS cannot decrease. As a result of this generalization, the change in the entropy of the IS dS_{IS} used to record the SLT acquired the meaning of one of the characteristics of the change in the nonequilibrium state of the IS (Chakraborty *et al.,* 2017; Dutt, 2018; Kudinov *et al.,* 2018; Park, 2018; Sobolev, 2018).

2. MATERIALS AND METHODS

2.1. The nonequilibrium of isolated system

In the concept of nonequilibrium, an isolated system is understood to mean a nonequilibrium system consisting of a set of locally-equilibrium (quasi-equilibrium) subsystems (sources and receivers of heat, receivers and sources of work, working fluid, environment, small and finite elements of the flow) that interact with each other, but do not interact with other systems that are not part of the isolated system in question.

Since when real processes take place, IS tends to an equilibrium state, when the system loses its ability to do work (transfer motion in an ordered form), then the maximum work performed by the system upon its transition to an equilibrium state is accepted as a quantitative measure of the system's nonequilibrium Λ (Equation 3).

To calculate the maximum (possible) work in thermodynamics, such values as thermodynamic potentials, heat exergy, and flow exergy are used.

In isolated systems, in the course of real processes, the ordered motion (OM) is transformed into the chaotic motion (CHM), i.e., the dissipation (scattering) of the OM occurs. The equilibrium state in the system occurs when all the OM (work) completely goes into chaotic motion (heat) (Equation 4).

This work is called possible work, lost working capacity, or energy loss. It is estimated through an increase in entropy $\Delta S_{\mathrm{noneq.IS}\rightarrow\mathrm{eq.st}}$ during the transition of IS from a given nonequilibrium state to an equilibrium state, according to the Gouy – Stodola equation Kirillin (1983) (Equation 5). Where TAM is the temperature of the equilibrium ambient medium (AM) (atmosphere or large body of water), which does not change upon the transition of a nonequilibrium system to an equilibrium state (TAM = const).

In the general case, when there is no liquid AM, it takes TCBmin – the variable body temperature with the lowest temperature (cold body temperature) during heat transfer or the temperature of the thermodynamic system when it interacts with work sources (cargo, spring, flywheel, capacitor, battery, etc.), which themselves are not characterized by temperature, and Equation 3 taking into account Equation 5 takes the form (Equation 6).

The change in the IS nonequilibrium (recall: increment (plus sign) (Equation 7), decrease (minus sign) (Equation 8)). (Equation 9) during its transition to the equilibrium state can be represented as the difference between the nonequilibrium values in the final (equilibrium state Λ2, when the nonequilibrium state is zero $\Lambda_{\mathrm{eq.st}} \equiv 0$) and in the initial Λ2 – nonequilibrium state defined by Equation 6 (Equation 10).

Equation 10 for changing IS nonequilibrium in an elementary process, taking into account inequality (1) for changing IS entropy $\mathrm{d}S_{\mathrm{noneq.IS}} \geq 0$, and $T_{\mathrm{CB\,min}} \geq 0$ can be written as (Equation 11). Equation 11 is confirmed by the postulate of nonequilibrium (Equation 2) put forward by the author – the nonequilibrium of an isolated system cannot increase. If to proceed from the primacy of Equation 2, then Clausius Equation 1 follows from Equation 11 $\mathrm{d}S_{\mathrm{IS}} \geq 0$. Equation 10 in differential form for the decrease of the nonequilibrium ($-\mathrm{d}\Lambda$) of the system can be written (Equation 12) and in integral form (Equation 13).

2.2. The nonequilibrium of the adiabatic system

If the thermodynamic potential in the general case is denoted by the symbol Π ("pi" Greek), then the amount of system nonequilibrium will be determined by the potential difference of the system in the nonequilibrium state $\Pi_{\mathrm{noneq.st}}$ and the equilibrium state $\Pi_{\mathrm{eq.st}}$ (let's call it "potential difference" $\Delta\Pi^*$), which is equal to the maximum work of the system when it goes to the equilibrium state (Equation 14). For a final decrease in nonequilibrium, Equation 14 can be written as (Equation 15). In differential form, this equation will take the form (Equation 16). Where $\mathrm{d}\Pi_{\mathrm{eq.st}} \equiv 0$, since during the transition of the system to the equilibrium state, all processes cease and, therefore, changes in all values are equal to zero.

The potential difference of the adiabatic system performing the work decreases in any processes (reversible and irreversible). However, only in reversible (index "o") processes the potential difference decrease, equal to the decrease in the thermodynamic potential, will be equal to the maximum external work of the nonequilibrium system (Equation 17).

In the case of irreversible processes, the external (superscript "e") work of system results in less loss of the potential difference (decrease of the thermodynamic potential) (Equation 18).

Consequently, the general condition for the transition of a system from a more nonequilibrium state to a less nonequilibrium state (more equilibrium) has the form (Equation 19).

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

2.3. Heat exergy and flow exergy as a measure of nonequilibrium change

When heat Q_1 is transferred from a hot body with temperature T_1 to an ambient medium with a constant temperature T_0, thermal nonequilibrium equal to the ideal cycle of Carnot (ICC) is lost (Equation 20).

The value E_Q, equal to the maximum work that can be obtained in an ideal cycle of Carnot due to the supplied heat Q_1, if the cold body is an ambient medium of constant parameters, it is customary to call heat exergy. Thus, heat exergy in accordance with Equation 20 is a quantitative characteristic of the change in the thermal nonequilibrium of the hot body – ambient medium system.

When a unit mass substance flows from a large-capacity tank with pressure p1 and temperature T_1 into the ambient medium with constant parameters p_0 and T_0, nonequilibrium is lost, a measure of which is the work performed by the flow in an ideal turbine. The maximum specific work obtained from a unit mass flow element when it expands in the turbine to the AM parameters is called specific flow exergy (Equation 21) (Krutov *et al.,* 1991).

The exergy of the flow (flow of the substance) will be a measure of the change in the nonequilibrium of the reservoir-AM system during the transfer of a single portion of the substance into the ambient medium of the constant parameters the author (Equation 22).

The following are examples of calculating nonequilibrium and its changes in an isolated and adiabatic system.

3. RESULTS AND DISCUSSION:

3.1. Calculation of the loss of nonequilibrium of an isolated system during operation of a heat engine performing an irreversible cycle

Let a non-equilibrium isolated system consist of a hot body (HB) with a constant temperature T_{HB}, an ambient medium with a constant temperature T_0, a working body that performs an irreversible cycle (for example, Carnot's cycle, nonideal on temperature (CCNT) in which heat is supplied at $T_1 < T_{\mathrm{HB}}$, and heat is removed at $T_2 = T_0$) and the work receiver (WR) (Figure 3). When heat is removed from the HB in the amount of Q_1, the thermal nonequilibrium of the HB-AM system will change (decrease) into the exergy of this heat Equation 20 (Equation 23). As a result of the implementation in the temperature range from T_1 to T_0 irreversible by the temperature of Carnot-cycle, work is performed that is allocated to the work receiver, as a result of which the mechanical nonequilibrium between WR and other IS bodies increases (arises) by the value of W_{CCNT} (Equation 24).

The complete change in the nonequilibrium state of the IS during the operation of the irreversible (real) cycle is determined by the sum of the changes in the thermal (23) and mechanical (24) nonequilibrium systems $(\Delta\Lambda_{\mathrm{WB}} = 0)$ (Equation 25). Decrease (loss) of IS nonequilibrium (Equation 26). From expression (25), it can be concluded that the decrease in the nonequilibrium state of the adiabatic system HB-WR-AM (the maximum work that can be done by the nonequilibrium AS due to the heat Q) is equal to the exergy of heat, which in turn consists of external useful work W_{CCNT} and lost work W_{loss} (see Figure 1) (Equation 27).

Therefore, the external work W^e performed by the nonequilibrium adiabatic system during an irreversible cycle in it is less than the maximum possible work (heat exergy) for the work of losses, which in the general case can be caused by both the finite temperature difference between the working fluid and heat sources, and friction of piston.

Consider the second method for determining the loss of IS nonequilibrium according to Equation 22, after determining the change in the IS entropy. When heat is removed from the HB in the amount (Equation 28), its entropy will decrease by (Equation 29).

This heat is supplied to the heat engine, where it is divided into two parts: one part is converted into work supplied to the WR in the amount (Equation 30), and the other part in the amount (Equation 31) is allocated to the cold body, in which the ambient medium is taken.

As a result of the supply of heat Q_2 to the ambient medium (CB), its entropy will increase by a value (Equation 32). Adding this change in entropy with a change in the entropy of the HB (Equation 29), a complete change in the entropy of a nonequilibrium isolated system during an irreversible cycle is obtained (changes in the entropy of WB and PD during the cycle are zero) (Equation 33).

Replacing Q_2 with Equation 31, the increment (since $T_1 < T_{\Gamma\mathrm{T}}$) of the entropy (Equation 34) is obtained. Loss of IS nonequilibrium (Equation 22), taking into account that (Equations 35-36) (in Figure 1, the lost work is depicted as the area of the rectangle a78ba).

Comparing Equation 36 and Equation 26, it can be concluded that both methods of calculating the decrease in the IS nonequilibrium give the same results. At the same time, the calculation of the total change in the IS nonequilibrium (loss, dissipation of the possible work) as the sum of the change in the thermal and mechanical nonequilibrium according to Equation 25 is more visual than through the change in the entropy of the IS.

3.2. Calculation of the nonequilibrium of the adiabatic system

Let the nonequilibrium adiabatic system (nonequilibrium AS) consist of a working body (WB) located in a cylinder with a movable piston, and a liquid ambient medium (ambient medium, along with the liquid ambient medium (for example, the atmosphere), includes receivers (sources) of work that perceive the work of the adiabatic system; the nonequilibrium adiabatic system (Noneq.AS) together with the sources (receivers) of work form a nonequilibrium isolated system (Noneq.IS)) (AM), with constant parameters p_0 and T_0 (Figure 2).

To ensure the lifting of the load without acceleration (which means that the calculation does not need to take into account the change in the kinetic energy of the load and the piston) with variable gas pressure on the piston and constant mass of the load, a special device is used. The device consists of a gear rack 1, gear 2, and cam 3 and ensures equality of moments relative to the axis of the cam of constant gravity and variable resulting gas pressure and AM forces on the piston by changing the arm length of gravity (Figure 2).

This nonequilibrium AS is capable of performing work, for example, in lifting the load, only until the moment of equilibrium establishment in it. The maximum external work W^e_{max} obtained from this system at the moment of establishing the barometric ($p = p_0$) and thermal ($T = T_0$) equilibrium in it will be the initial amount of nonequilibrium of such a system.

The equation of the first law of thermodynamics (FLT) for the nonequilibrium adiabatic ($\delta Q^e = 0$) system can be written as Equation 37, where Equation 38.

Further, the transformations are reduced to expressing the change in internal energy (IE) of ambient medium (AM) through the WB parameters, which is possible with reversible processes. Unlike nonequilibrium AS, the ambient medium can exchange both heat and work with the working body; therefore, for AM, the FLT equation has the form Equation 39, where Equation 40.

In order to maximize external work, the processes must proceed reversibly inside nonequilibrium AS, i.e., without dissipation (conversion of ordered motion into chaotic motion) of ordered motion both when moving the piston (in the absence of friction between the piston and the cylinder liner), and when heat transfer. The latter is ensured by the use of an ideal heat engine (IHE) in the event of a finite temperature difference between the WB and the AM, or heat exchange during an infinitely small temperature difference between the WB and the AM, when the IHE work can be neglected in comparison with the transferred heat.

Note that here authors consider the reversibility of processes in a purely nonequilibrium system ($p \neq p0$, $T \neq T0$), while the existing concept of reversibility assumes the reversibility of processes in systems close to the equilibrium state (in quasi-equilibrium systems). According to the concept of nonequilibrium in reversible processes, the complete nonequilibrium of an isolated system does not change. In this example, the decrease in the nonequilibrium AS is compensated by the increase in the mechanical nonequilibrium of the receiver of work (load) with respect to the nonequilibrium AS.

Evidence of the reversibility of the processes (lack of dissipation), according to the SLT, is the invariance of entropy (the absence of ordered motion dispersion between the AM molecules) of an isolated or adiabatic system (Equation 41), where (Equation 42). Assuming that the volume of nonequilibrium AS is unchanged Equation 43, Equation 44 follows. Substituting Equation 42 and Equation 44 into Equation 40, authors express the change in the internal energy of the AM through changes in the entropy and volume of the WB (Equation 45).

Substituting Equation 45 into Equation 38, the following expressions for maximum external work are obtained:

a) at a small decrease in the nonequilibrium of the adiabatic system ($-\mathrm{d}\Lambda$) (Equation 46);

b) upon complete transition of the system to the equilibrium state ($\Lambda_{\mathrm{eq.st}} = 0$) (Equation 47), where the value (Equation 48) is uniquely determined by the state parameters of both the WB and the AM, i.e., it is a function of the state of the parameters of this nonequilibrium system.

Since, in accordance with Equation 47, the decrease of the function Z is equal to the external work of nonequilibrium AS, this function can be considered as the potential of a nonequilibrium system consisting of a working body and the ambient medium, whose parameters (AM) do not change as the entire nonequilibrium system transitions to the equilibrium state. The potential function Z is sometimes considered as a generalizing potential for thermodynamic potentials. For example, in the work of A. I. Andryushchenko (1975), it is noted that "in the reactions of systems that maintain a constant volume V and temperature T, the maximum work (Equation 49), where (Equation 50). At $T_0 = T$ there are (Equation 51) and (Equation 52).

These transformations cannot be considered correct for two reasons. First, the transition from the potential function Z (Equation 48) to ZV (Equation 50) is possible not at V = const, but at V = 0; at the same time, with a constant volume (Equation 53). Secondly, the expression for the potential function Z (Equation 50) includes the internal energy and entropy of only the working body (without AM), and the expression for the Helmholtz energy contains the total values of the IE and entropy of the entire nonequilibrium system (WB and AM). Hence (Equation 54).

Consider some specific examples of determining the amount of nonequilibrium of a system consisting of WB and AM. Let the system be in a thermally ($T_1 > T_0$) and barically ($p_1 > p_0$) nonequilibrium state. As reversible processes of the transition of the system to the equilibrium state, first authors take the isentropic process 1–2s (without external heat transfer and friction) of the expansion of the working body to a final temperature $T_{2s} = T_0$, and then the isothermal process 2s – 0 to a final pressure $p_{2T} = p_0$ (Figure 3).

The amount of nonequilibrium of such a system in accordance with Equation 47 will be equal to the decrease in the potential function Z (Equation 55).

To simplify, suppose that the working body is an ideal gas, whose internal energy does not change at a constant temperature. Consequently, a change in IE could only occur in the adiabatic process of 1-2s. In accordance with the FLT, the decrease in the internal energy of the adiabatic system is equal to the external work performed by the system (WB) on the external ambient medium (for the working body, the external ambient medium is a liquid ambient medium and a work receiver) (Equation 56). This work is depicted as the area 12s451 of Figure 3.

Since the change in the entropy of the WB occurs only in the isothermal process, the product $T_0 \Delta S_{\mathrm{WB}}$ gives the heat of the isothermal process, which in the case of an ideal gas is equal to the external work in the isothermal process 2s–2T (depicted as the area 2s2T342s of the Figure 3 (Equation 57). Given that (Equation 58), then the last term in the right-hand side of Equation 55 can be represented as the external work of a liquid AM (for it, the external medium is the working body and the work receiver) (Equation 59).

This work is negative and is depicted as the area 3562_T3 of Figure 3. The total work performed by the nonequilibrium AS upon its transfer to the equilibrium state will be equal to the sum of the works (Equations 56, 57, 59) (Equation 60).

Comparing this expression for works with (Equation 55), it can be concluded that, indeed, a decrease in the potential function Z gives the maximum work of the nonequilibrium adiabatic system, consisting of WB and a liquid AM with constant parameters, upon its transition to the equilibrium state (Equation 61). This work characterizes the nonequilibrium of this system $\Lambda_{\mathrm{noneq.AS}}$ and is depicted as a hatched area of the figure in Figure 3.

The external work of the nonequilibrium AS can also be calculated as the technical work of the piston $W_{\mathrm{tech.piston}}$ (this work is transferred from the piston to the receiver of work through the rod or connecting rod) in the absence of friction in adiabatic and isothermal processes, if to neglect the change in the mechanical energy of the piston (Equation 62).

Consider the case when the system is in a barically nonequilibrium state ($p_1 > p_0$), but in a thermal equilibrium state ($T_1 = T_0$). The amount of baric nonequilibrium of such a system can be determined from (55) and (60), taking into account the fact that the transition of the nonequilibrium AS to the equilibrium state occurs in an isothermal process and, therefore, for an ideal gas $\Delta U_{\mathrm{WB}} = 0$ (Equation 63).

Since the volume and temperature of the entire nonequilibrium AS are constant ($V_{\mathrm{noneq.AS}} = \mathrm{const}$; $T = T_0 = \mathrm{const}$), external work not related to changing the total volume of such a system $W^{*\mathrm{o}}_{V,T}$, until the nonequilibrium is completely lost, will be equal to the decrease in the Helmholtz potential (isochoric-isothermal potential) for throughout nonequilibrium AS (Equation 64). Strictly speaking, the temperature of the AM as a result of heat removal decreases, however, due to its large size, the decrease in the temperature of the ambient medium (atmosphere) is insignificant. Where for an ideal gas in an isothermal process $\Delta U_{\mathrm{WB}} = 0$, and since the process is reversible, the change in the entropy of the nonequilibrium AS is zero ($\Delta S_{\mathrm{noneq.AS}} = 0$).

In accordance with the equation of FLT for the decrease in the IE of the ambient medium can be written (Equation 65), since the heat given off by AM is equal and opposite in sign to the heat received by the working body (Equation 66), in the isothermal process of an ideal gas, all external heat goes to the working heat to perform external work (Equation 67), since the volume of the entire nonequilibrium AS is constant, then (Equation 68).

Substituting Equation 65 for the decrease in the IE of the ambient medium into Equation 64, the expression for external work $W^{*\mathrm{o}}_{V,T}$ is obtainted, that is not related to a change in the total volume of the system, i.e., the maximum work performed by the barically nonequilibrium system WB-AM of constant volume upon its transition to equilibrium state, or – for the amount of baric nonequilibrium of such a system (Equation 69).

As you can see, the maximum external work that can be transferred from the barically nonequilibrium adiabatic system to the consumer of the work is less than the work of changing the volume of the WB in the isothermal process to the work of displacing the ambient medium (performed against the constant pressure of the AM p_0).

If, for the calculation of the work, use Equation 51 for the potential function Z_V or for the Helmholtz potential F_T is used, written for the working body, then (Equation 70) can be obtained.

Consequently, the potential function Z_V and the Helmholtz potential F_T, calculated for a working body in an equilibrium state, are potentials for the work of the volume change performed by the working body in an isothermal process. However, the losses of these potentials are not equal to the external work performed by the nonequilibrium AS in the isothermal process (Equation 69) (Equation 71), which means that they do not characterize the change in the nonequilibrium of any system.

A measure of the nonequilibrium state of the WB-AM system during the course of the isochoric-isothermal process in it in accordance with (Equation 64) is the decrease in the isochoric-isothermal potential $-\Delta F_{\mathrm{V,T}}^{\mathrm{noneq.AS}}$, calculated for the entire nonequilibrium system, and not for one working body.

From here there is a general conclusion, that the potentials of locally-equilibrium systems (for example, the working body in a cylinder) and their decrease that are determined in thermodynamics courses do not characterize the change in any nonequilibrium state and do not give the value of the external work performed by the nonequilibrium system, which includes this locally-equilibrium system. Only a decrease in the thermodynamic potential calculated for the entire set of bodies of a nonequilibrium system is equal to a decrease in the nonequilibrium system, and hence the external work of this system as it transitions to an equilibrium state.

4. CONCLUSIONS:

This article is a continuation of the concept of nonequilibrium, based on the postulate "about nonequilibrium and its change" and the basis of the SLT. It provides calculations of nonequilibrium and its changes for two systems: an isolated system during operation of a heat engine and an adiabatic system. Based on the results of this work, the following conclusions can be drawn:

1) the diagrams of nonequilibrium systems consisting of quasi-equilibrium subsystems are given – adiabatic, consisting of a working body in a cylinder and a liquid AM and an isolated system consisting of an adiabatic system and a receiver of work;

2) the second law of thermodynamics should be used to consider the behavior of just such quasi-equilibrium systems, and not a separate body (working body), as is often practiced;

3) calculations of the nonequilibrium state of the adiabatic system are given by the decrease of the thermodynamic potential recorded for the entire set of bodies of the nonequilibrium system, and by the technical work of the piston in a reversible process;

4) the potentials of locally-equilibrium systems (for example, the working body in the cylinder) determined in thermodynamics courses and their decrease do not characterize the change in any nonequilibrium and do not give the value of the external work performed by the nonequilibrium adiabatic system;

5) a methodology for calculating thermal and baric nonequilibrium is given, and the corresponding expressions for calculating this nonequilibrium were obtained;

6) the above calculations are a practical confirmation of the validity of the postulate of nonequilibrium, introduced by the author on the basis of the second law of thermodynamics.

5. REFERENCES:

1. Altaner, B. *Journal of Physics A: Mathematical and Theoretical*, **2017**, *50*(45), 454001.
2. Andryushchenko, A.I. *Fundamentals of technical thermodynamics of real processes*, Moscow: Vysshaya shkola, **1975**.
3. Baehr, H.D. *Thermodynamics: An Introduction to the Basics and Their Technical Applications*, Berlin-Heidelberg-New York: Springer-Verlag, **1973**.
4. Bejan, A. *Advanced Engineering Thermodynamics*, Durham: Duke University, **2016**.

5. Ben-Naim, A. *Discover Entropy and the Second Law of Thermodynamics: A Playful Way of Discovering a Law of Nature*, Singapore: World Scientific Pub Co Inc, **2010**.
6. Borgnakke, C., Sonnag, R.E. *Fundamentals of Thermodynamics*, Ann Arbor: University of Michigan, **2009**.
7. Borin, A., Sukhorukov, E. *Physical Review B*, **2019**, *99*(8), 085430.
8. Calabrese, P. *Physica A: Statistical Mechanics and its Applications*, **2018**, *504*, 31-44.
9. Callen, B. *Thermodynamics and Introduction to Thermostatics*, New York: John Wiley and Sons, **1985**.
10. Cao, F., Wu, J., Li, Y., Ngai, T. *Langmuir*, **2019**, *35*(27), 8910-8920.
11. Chakraborty, S., Chatterjee, S., Barma, M. *Physical Review E*, **2017**, *96*(2), 022128.
12. Chen, L., Tsutsumi, A. *Chemical Engineering Transactions*, **2018**, *70*, 949-954.
13. Chen, Z.-S., Li, C., Wang, G. *Journal of Engineering Thermophysics*, **2017**, *38*(8), 1589-1596.
14. D'Alessio, L., Kafri, Y., Polkovnikov, A., Rigol, M. *Advances in Physics*, **2016**, *65*(3), 239-362.
15. de Blasio, C. Introduction to entropy and second law. *In: Green Energy and Technology*, Basingstoke: Springer Nature, **2019**.
16. de Oliveira, M.J. *Revista Brasileira de Ensino de Fisica*, **2019**, *41*(1), e20180174.
17. Dutt, A.K. *Journal of Physical Chemistry B*, **2018**, *122*(50), 12049-12059.
18. Fermi, E. *Thermodynamics*, New York: Prentice-Hall, Inc, **1937**.
19. Freitas, R., Asta, M., De Koning, M. *Computational Materials Science,* **2016**, *112*, 333-341.
20. Guo, Y., Jou, D., Wang, M. *Physical Review B*, **2019**, *98*(10), 104304.
21. Hołyst, R., Poniewierski, A. *Thermodynamics for Chemists, Physicists and Engineers*, Dordrecht: Science+Business Media, **2012**.
22. Khantuleva, T.A., Shalymov, D.S. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, **2017**, *375*(2088), 20160220.
23. Kirillin, V.A., Sychev, V.V., Sheyndlin, A. E. *Technical Thermodynamics*, Moscow: Energoatomizdat, **1983**.
24. Kittel, Ch. *Thermal physics*, New York: John Willey and Sons, **1993**.
25. Kondepudi, D., Prigogine, I. *Modern Thermodynamics: From Heat Engines to Dissipative Structurers,* New Delhi: John Wiley and Sons, **2015**.
26. Krichevsky, I.R. *Concepts and foundations of thermodynamics*, Moscow: Chemistry, **1970**.
27. Krutov, V.I., Isayev, S.I., Kozhinov, A.I. *Technical Thermodynamics*, Moscow: Vysshaya shkola, **1991**.
28. Kudinov, V.A., Eremin, A.V., Kudinov, I.V., Zhukov, V.V. *Combustion, Explosion and Shock Waves*, **2018**, *54*(6), 649-653.
29. Lavenda, B.H. *A New Perspective on Thermodynamics*, Berlin: Springer Science+Business Media, **2010**.
30. Liu, Y., Liu, Y.-J. *Separation and Purification Technology*, **2008**, *61*(3), 229-242.
31. Marbœuf, A., Claisse, A., Le Tallec, P. *Journal of Computational Physics*, **2019**, *390*, 66-92.
32. Martyushev, L.M., Celezneff, V. *Entropy*, **2017**, *19*(3), 126.
33. Martyushev, L.M., Seleznev, V.D. *Physics Reports*, **2006**, *426*(1), 1-45.
34. Morales-Rodriguez, R. *Thermodynamics: Fundamentals and Its Application in Science*, Kongens Lyngby: Technical University of Denmark, **2016**.
35. Moran, M.J., Shapiro, H.N., Boettner, D.D., Balley, M.B. *Fundamentals of Engineering 28 Thermodynamics*, New York: John Wiley and Sons, **2014**.
36. Novikov, I.I. *Thermodynamics*, Moscow: Mashinostroenie, **1984**.
37. Park, H. *Journal of the Korean Physical Society*, **2018**, *72*(12), 1413-1420.
38. Patitsas, S.N. *Physical Review E*, **2019**, *100*(2), 022116.

39. Ptaszyński, K., Esposito, M. *Physical Review Letters*, **2019**, *122*(15), 150603.
40. Putilov, K.A. *Thermodynamics*, Moscow: Nauka, **1971**.
41. Rakopoulos, C.D., Giakoumis, E.G. *Progress in Energy and Combustion Science*, **2006**, *32*(1), 2-47.
42. Reyf, F. *Statistical physics: Berkeley physics course*, Berkeley: The University in Berkeley, McGraw; Hill Book Company, **1972**.
43. Saikhanov, M.B. *Theoretical and Mathematical Physics*, **2017**, *191*(1), 572-579.
44. Seifert, U. *Reports on Progress in Physics*, **2012**, *75*(12), 126001.
45. Sellitto, A., Di Domenico, M. *Continuum Mechanics and Thermodynamics*, **2019**, *31*(3), 807-821.
46. Sobolev, S.L. *Physical Review E*, **2018**, *97*(2), 022122.
47. Srivastava, R.C., Subit, K.S., Abhay, K.J. *Thermodynamics: A core course*, New Delhi: Prentice-Hall of India Private Limited, **2007**.
48. Vukalovich, M.P., Novikov, I.I. *Technical Thermodynamics*, Moscow: Energiya, **1968**.
49. Wald, R.M. *Living Reviews in Relativity*, **2001**, *4*, 6.
50. Yuan, H.Y., Yung, M.-H. *Physical Review A*, **2018**, *98*(2), 022125.

$$\mathrm{d}S_{\mathrm{noneq.IS}} \geq 0$$ (Eq. 1)

$$\mathrm{d}\Lambda_{\mathrm{noneq.IS}} \leq 0 \quad \mathrm{d}\Lambda_{\mathrm{noneqIS}} \leq 0$$ (Eq. 2)

$$\Lambda \equiv \Lambda_{\mathrm{noneq.IS}} \equiv W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}}\,.$$ (Eq. 3)

$$W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}} = W^{\mathrm{max}}_{\mathrm{loss}} = Q_{\mathrm{diss}}\,.$$ (Eq. 4)

$$W^{\mathrm{max}}_{\mathrm{diss}} = W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}} = T_{\mathrm{AM}}\Delta S_{\mathrm{noneq.st}\to\mathrm{eq.st}}$$ (Eq. 5)

$$\Delta\Lambda_{\mathrm{noneq.IS}} = W^{\mathrm{max}}_{\mathrm{diss}} = W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}} = T_{\mathrm{CB\,min}}\Delta S_{\mathrm{noneq.IS}\to\mathrm{eq.st}}$$ (Eq. 6)

$$\Delta x = x_2 - x_1$$ (Eq. 7)

$$-\Delta x = x_1 - x_2$$ (Eq. 8)

$$\Delta\Lambda = \Lambda_2 - \Lambda_1$$ (Eq. 9)

$$\Delta\Lambda_{\mathrm{noneq.IS}} = \Lambda_{\mathrm{eq.st}} - \Lambda_{\mathrm{noneq.IS}} = -\Lambda_{\mathrm{noneq.IS}} = -W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}} = -T_{\mathrm{CB\,min}}\,\Delta S_{\mathrm{noneq.IS}\to\mathrm{eq.st}}\,.$$ (Eq. 10)

$$\mathrm{d}\Lambda_{\mathrm{IS}} = -T_{\mathrm{CBmin}}\mathrm{d}S_{\mathrm{IS}} \leq 0$$ (Eq. 11)

$$-\mathrm{d}\Lambda = \delta W_{\mathrm{loss}} = \delta W_{\mathrm{diss}} = T_{\mathrm{CBmin}}\mathrm{d}S_{\mathrm{diss}}$$ (Eq. 12)

$$-\Delta\Lambda = W_{\mathrm{loss}} = W_{\mathrm{diss}} = T_{\mathrm{CBmin}}\Delta S_{\mathrm{diss}}$$ (Eq. 13)

$$\Lambda_{\mathrm{AS}} = \Delta\Pi^{*} = \Pi_{\mathrm{noneq.st}} - \Pi_{\mathrm{eq.st}} = W^{\mathrm{max}}_{\mathrm{noneq.st}\to\mathrm{eq.st}} = W^{\mathrm{e}}_{\mathrm{max}}$$ (Eq. 14)

$$-\Delta\Lambda_{\mathrm{AS}}^{\max} = -\Delta(\Delta\Pi^{*})_{\max} = \Lambda_1 - \Lambda_2 = \Lambda_{\mathrm{noneq.st}} - \Lambda_{\mathrm{eq.st}} = \Lambda_{\mathrm{noneq.st}} = \\ = \Pi_{\mathrm{noneq.st}} - \Pi_{\mathrm{eq.st}} = \Pi_1 - \Pi_2 = -\Delta\Pi_{\max} = W_{\mathrm{noneq.st}\to\mathrm{eq.st}}^{\max} = W_{\max}^{\mathrm{e}}. \tag{Eq. 15}$$

$$-\mathrm{d}\Lambda_{\mathrm{AS}} = -\mathrm{d}(\Delta\Pi^{*}) = -\mathrm{d}\Pi_{\mathrm{noneq.st}} + \mathrm{d}\Pi_{\mathrm{eq.st}} = -\mathrm{d}\Pi_{\mathrm{noneq.st}} \equiv -\mathrm{d}\Pi = \delta W_{\max}^{\mathrm{e}} = \delta W^{\mathrm{e\,o}} \tag{Eq. 16}$$

$$\delta W^{\mathrm{eo}} = \delta W_{\max}^{\mathrm{e}} = -\mathrm{d}(\Delta\Pi^{*}) \tag{Eq. 17}$$

$$\delta W^{\mathrm{e}} < -\mathrm{d}(\Delta\Pi^{*}) = -\mathrm{d}\Pi \tag{Eq. 18}$$

$$\delta W^{\mathrm{e}} \leq -\mathrm{d}(\Delta\Pi^{*}) = -\mathrm{d}\Pi \tag{Eq. 19}$$

$$-\Delta\Lambda_{\mathrm{therm}} = \mathrm{W}_{\mathrm{ICC}} - \mathcal{Q}_1(1 - \mathrm{T}_0/\mathrm{T}_{\mathrm{noneq}}) - \mathrm{E}_{\mathcal{Q}5} \tag{Eq. 20}$$

$$e_{\mathrm{x}} = w_{\text{тур}}^{\max} = h - h_0 + T_0(s_0 - s) \tag{Eq. 21}$$

$$e_{\mathrm{x}1} = h_1 - h_0 + T_0(s_0 - s_1) = w_{\mathrm{tur}}^{\max} = -\Delta\lambda_{\text{reserv-AM}} \tag{Eq. 22}$$

$$\Delta\Lambda_{\mathrm{therm}} = \Delta\Lambda_{\text{HB-AM}} = -E_{\mathrm{Q}_1} = -Q_1(1 - T_0 / T_{\mathrm{HB}}) < 0 \tag{Eq. 23}$$

$$\Delta\Lambda_{\mathrm{mech}} = \Delta\Lambda_{\mathrm{WR}} = W_{\mathrm{CCNT}} = Q_1(1 - T_0 / T_1) > 0 \tag{Eq. 24}$$

$$\Delta\Lambda_{\mathrm{noneq.IS}} = \Delta\Lambda_{\mathrm{therm}} + \Delta\Lambda_{\mathrm{WB}} + \Delta\Lambda_{\mathrm{mech}} = \Delta\Lambda_{\mathrm{noneq.AS}} + \Delta\Lambda_{\mathrm{WR}} = -E_{\mathrm{Q}_1} + W_{\mathrm{CCNT}} = \\ = -Q_1(1 - T_0 / T_{\mathrm{HB}}) + Q_1(1 - T_0 / T_1) = -Q_1 T_0(1 / T_1 - 1 / T_{\mathrm{HB}}) = -W_{\mathrm{loss}}. \tag{Eq. 25}$$

$$-\Delta\Lambda_{\mathrm{noneq.IS}} = W_{\mathrm{loss}} = Q_1 T_0(1 / T_1 - 1 / T_{\mathrm{HB}}). \tag{Eq. 26}$$

$$-\Delta\Lambda_{\mathrm{noneq.AS}} = E_{\mathrm{Q}_1} = W_{\mathrm{CCNT}} + W_{\mathrm{loss}} \equiv W^{\mathrm{e}} + W_{\mathrm{loss}} \tag{Eq. 27}$$

$$Q_{\mathrm{HB}} = -Q_1 < 0 \tag{Eq. 28}$$

$$\Delta S_{\mathrm{HB}} = Q_{\mathrm{HB}}/T_{\mathrm{HB}} = -Q_1/T_{\mathrm{HB}} < 0 \tag{Eq. 29}$$

$$W^{\mathrm{e}} = W_{\mathrm{CCNT}} = Q_1(1 - T_0/T_1) \tag{Eq. 30}$$

$$Q_2 = Q_1 - W_{\mathrm{CCNT}} = Q_1 T_0/T_1 \tag{Eq. 31}$$

$$\Delta S_{\mathrm{CB}} = Q_2/T_0 \tag{Eq. 32}$$

$$\Delta S_{\mathrm{noneq.IS}} = \Delta S_{\mathrm{HB}} + \Delta S_{\mathrm{CB}} = -Q_1/T_{\mathrm{HB}} + Q_2/T_0 \tag{Eq. 33}$$

$$\Delta S_{\mathrm{noneq.IS}} = \Delta S_{\mathrm{diss}} = -Q_1/T_{\mathrm{HB}} + Q_1/T_1 = Q_1(1/T_1 - 1/T_{\mathrm{HB}}) > 0 \tag{Eq. 34}$$

$$T_{\mathrm{CB\,min}} = T_0 \tag{Eq. 35}$$

$$-\Delta\Lambda_{\text{noneq.IS}} = W_{\text{loss}} = T_0 \Delta S_{\text{noneq.IS}} = Q_1 T_0 (1/T_1 - 1/T_{\text{HB}}) \quad \text{(Eq. 36)}$$

$$\mathrm{d}U_{\text{noneq.AS}} + \delta W^{\text{e}}_{\max} = \mathrm{d}U_{\text{WB}} + \mathrm{d}U_{\text{AM}} + \delta W^{\text{e}}_{\max} = 0 \quad \text{(Eq. 37)}$$

$$\delta W^{\text{e}}_{\max} = -\mathrm{d}U_{\text{noneq.AS}} = -\,\mathrm{d}U_{\text{WB}} - \mathrm{d}U_{\text{AM}} \quad \text{(Eq. 38)}$$

$$\delta Q^{\text{e}}_{\text{AM}} = \mathrm{d}U_{\text{AM}} + \delta W^{\text{e}}_{\text{AM}} = \mathrm{d}U_{\text{AM}} + p_0 \mathrm{d}V_{\text{AM}} \quad \text{(Eq. 39)}$$

$$\mathrm{d}U_{\text{AM}} = \delta Q^{\text{e}}_{\text{AM}} - p_0 \mathrm{d}V_{\text{AM}} = T_0 \mathrm{d}S_{\text{AM}} - p_0 \mathrm{d}V_{\text{AM}} \quad \text{(Eq. 40)}$$

$$\mathrm{d}S_{\text{noneq.AS}} = \mathrm{d}S_{\text{WB}} + \mathrm{d}S_{\text{AM}} = 0 \quad \text{(Eq. 41)}$$

$$\mathrm{d}S_{\text{AM}} = -\mathrm{d}S_{\text{WB}} \quad \text{(Eq. 42)}$$

$$\mathrm{d}V_{\text{noneq.AS}} = \mathrm{d}V_{\text{WB}} + \mathrm{d}V_{\text{AM}} = 0 \quad \text{(Eq. 43)}$$

$$\mathrm{d}V_{\text{AM}} = -\mathrm{d}V_{\text{WB}} \quad \text{(Eq. 44)}$$

$$\mathrm{d}U_{\text{AM}} = -T_0 \mathrm{d}S_{\text{WB}} + p_0 \mathrm{d}V_{\text{WB}} \quad \text{(Eq. 45)}$$

$$\begin{aligned} \delta W^{\text{e}}_{\max} &= -\mathrm{d}U_{\text{WB}} + T_0 \mathrm{d}S_{\text{WB}} - p_0 \mathrm{d}V_{\text{WB}} = \\ &= -\mathrm{d}\,(U_{\text{WB}} - T_{\text{AM}} S_{\text{WB}} + p_{\text{AM}} V_{\text{WB}}) = -\mathrm{d}Z = -\mathrm{d}\Lambda; \end{aligned} \quad \text{(Eq. 46)}$$

$$W^{\text{e}}_{\max} = -\Delta Z = Z_1 - Z_2 = -\Delta\Lambda_{\max} = -\,(\Lambda_{\text{eq.st}} - \Lambda_{\text{noneq.st}}) = \Lambda_{\text{noneq.st}} = \Lambda \quad \text{(Eq. 47)}$$

$$Z = U_{\text{WB}} - T_{\text{AM}} S_{\text{WB}} + p_{\text{AM}} V_{\text{WB}} = U - T_0 S + p_0 V \quad \text{(Eq. 48)}$$

$$L_{\max} = Z_{\text{V1}} - Z_{\text{V2}} \quad \text{(Eq. 49)}$$

$$Z_{\text{V}} = U - T_0 S \quad \text{(Eq. 50)}$$

$$Z_{\text{V}} = U - TS = F \quad \text{(Eq. 51)}$$

$$L_{\max} = F_1 - F_2 \quad \text{(Eq. 52)}$$

$$\Delta Z = \Delta Z_{\text{V}}. \quad \text{(Eq. 53)}$$

$$Z_{\text{V}} = U_{\text{WB}} - TS_{\text{WB}} \neq F = U_{\text{WB-AM}} - TS_{\text{WB-AM}} = U_{\text{WB}} + U_{\text{AM}} - T(S_{\text{WB}} + S_{\text{AM}}) \quad \text{(Eq. 54)}$$

$$\begin{aligned} \Lambda_{\text{noneq.AS}} &= Z_1 - Z_{2\text{T}} = Z_1 - Z_0 = U_1 - T_0 S_1 + p_0 V_1 - \\ &- U_0 + T_0 S_0 - p_0 V_0 = -\Delta U_{\text{WB}} + T_0 \Delta S_{\text{WB}} - p_0 \Delta V_{\text{WB}}. \end{aligned} \quad \text{(Eq. 55)}$$

$$W^{\text{e}}_{1-2s} = -\Delta U_{\text{WB}} \quad \text{(Eq. 56)}$$

$$W^{\text{e}}_{\text{T}} = Q_{\text{T}} = T_0 \Delta S_{\text{WB}} \quad \text{(Eq. 57)}$$

$$\Delta V_{\mathrm{WB}} = -\Delta V_{\mathrm{AM}} \tag{Eq. 58}$$

$$W^{\mathrm{e}}_{\mathrm{AM}} = p_0 \Delta V_{\mathrm{AM}} = -p_0 \Delta V_{\mathrm{WB}} < 0 \tag{Eq. 59}$$

$$W^{\mathrm{e}}_{\mathrm{noneq.AS\,max}} = W^{\mathrm{e}}_{1-2s} + W^{\mathrm{e}}_{\mathrm{T}} + W^{\mathrm{e}}_{\mathrm{AM}} = -\Delta U_{\mathrm{WB}} + T_0 \Delta S_{\mathrm{WB}} - p_0 \Delta V_{\mathrm{WB}} \tag{Eq. 60}$$

$$-\Delta Z = W^{\mathrm{e}}_{\mathrm{noneq.AS\,max}} = \Lambda_{\mathrm{noneq.AS}} \tag{Eq. 61}$$

$$\begin{gathered} \Lambda_{\mathrm{noneq.AS}} = W_{\mathrm{tech.piston}} = \int_1^{2\mathrm{T}} (p - p_{\mathrm{AM}})\,\mathrm{d}V = \int_1^{2\mathrm{s}} p\,\mathrm{d}V + \\ + \int_{2\mathrm{s}}^{2\mathrm{T}} p\,\mathrm{d}V - p_{\mathrm{AM}} \Delta V = W^{\mathrm{e}}_{1-2s} + W^{\mathrm{e}}_{\mathrm{T}} + W^{\mathrm{e}}_{\mathrm{AM}} = W^{\mathrm{e}}_{\mathrm{noneq.AS\,max}}. \end{gathered} \tag{Eq. 62}$$

$$\Lambda_{\mathrm{noneq.AS}} = T_0 \Delta S_{\mathrm{WB}} - p_0 \Delta V_{\mathrm{WB}} = W^{\mathrm{e}}_{\mathrm{T}} + W^{\mathrm{e}}_{\mathrm{AM}} = W^{\mathrm{e}}_{\mathrm{noneq.AS\,max}} \tag{Eq. 63}$$

$$\begin{gathered} W^{\mathrm{e}}_{\mathrm{noneq.AS}} = W^{*\mathrm{o}}_{V,T} = -\Delta \Pi^{\mathrm{noneq.AS}}_{V,T} = -\Delta F^{\mathrm{noneq.AS}}_{V,T} = (F_1 - F_2)^{\mathrm{noneq.AS}}_{V,T} = \\ = U_1 - TS_1 - U_2 + TS_2 = -\Delta U_{\mathrm{noneq.AS}} + T\Delta S_{\mathrm{noneq.AS}} = -(\Delta U_{\mathrm{WB}} + \Delta U_{\mathrm{AM}}) + \\ + T(\Delta S_{\mathrm{WB}} + \Delta S_{\mathrm{AM}}) = -\Delta U_{\mathrm{WB}} - \Delta U_{\mathrm{AM}} = -\Delta U_{\mathrm{AM}} = \Lambda_{\mathrm{baric}}, \end{gathered} \tag{Eq. 64}$$

$$-\Delta U_{\mathrm{AM}} = -Q^{\mathrm{e}}_{\mathrm{AM}} + W^{\mathrm{e}}_{\mathrm{AM}} = Q_{\mathrm{T}} + p_{\mathrm{AM}} \Delta V_{\mathrm{AM}} = W^{\mathrm{e}}_{\mathrm{T}} - p_0 \Delta V_{\mathrm{WB}} \tag{Eq. 65}$$

$$Q_{\mathrm{T}} = -Q^{\mathrm{e}}_{\mathrm{AM}} \tag{Eq. 66}$$

$$Q_{\mathrm{T}} = W^{\mathrm{e}}_{\mathrm{T}} \tag{Eq. 67}$$

$$\Delta V_{\mathrm{AM}} = -\Delta V_{\mathrm{WB}} \tag{Eq. 68}$$

$$\begin{gathered} W^{*\mathrm{o}}_{V,T} = W^{\mathrm{e}}_{\mathrm{noneq.AS}} = W^{\mathrm{e}}_{\mathrm{T}} - p_0 \Delta V_{\mathrm{WB}} = \left(\int p\,\mathrm{d}V\right)_{\mathrm{T}} - \\ - \int p_0\,\mathrm{d}V = \int (p - p_{\mathrm{AM}})\,\mathrm{d}V = W_{\mathrm{tech.piston}} = \Lambda_{\mathrm{baric}}. \end{gathered} \tag{Eq. 69}$$

$$\begin{gathered} W^{\mathrm{e}} = -\Delta Z_{\mathrm{V}} = -\Delta F_{\mathrm{T}} = F_{\mathrm{WB}_1} - F_{\mathrm{WB}_2} = U_{\mathrm{WB}_1} - TS_{\mathrm{WB}_1} - U_{\mathrm{WB}_2} + TS_{\mathrm{WB}_2} = \\ = -\Delta U_{\mathrm{WB}} + T_0 \Delta S_{\mathrm{WB}} = T_0 \Delta S_{\mathrm{WB}} = Q_{\mathrm{T}} = W^{\mathrm{e}}_{\mathrm{T}} = W^{\mathrm{e}}_{\mathrm{WB_T}} \neq \Lambda_{\mathrm{baric}} = W^{\mathrm{e}}_{\mathrm{T}} - p_0 \Delta V_{\mathrm{WB}}. \end{gathered} \tag{Eq. 70}$$

$$-\Delta Z_{\mathrm{V}} = -\Delta F_{\mathrm{T}} \neq \Lambda_{\mathrm{baric}} = W^{\mathrm{e}}_{\mathrm{T}} - p_0 \Delta V_{\mathrm{WB}} \tag{Eq. 71}$$

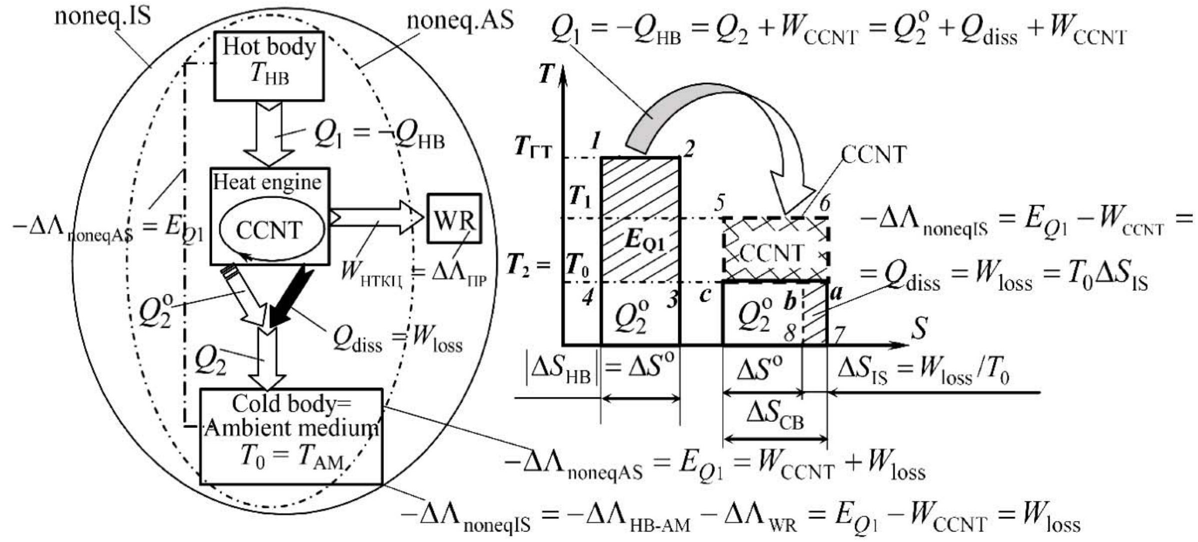

Figure1. *To the calculation of the loss of nonequilibrium of IS during the operation of the heat engine*

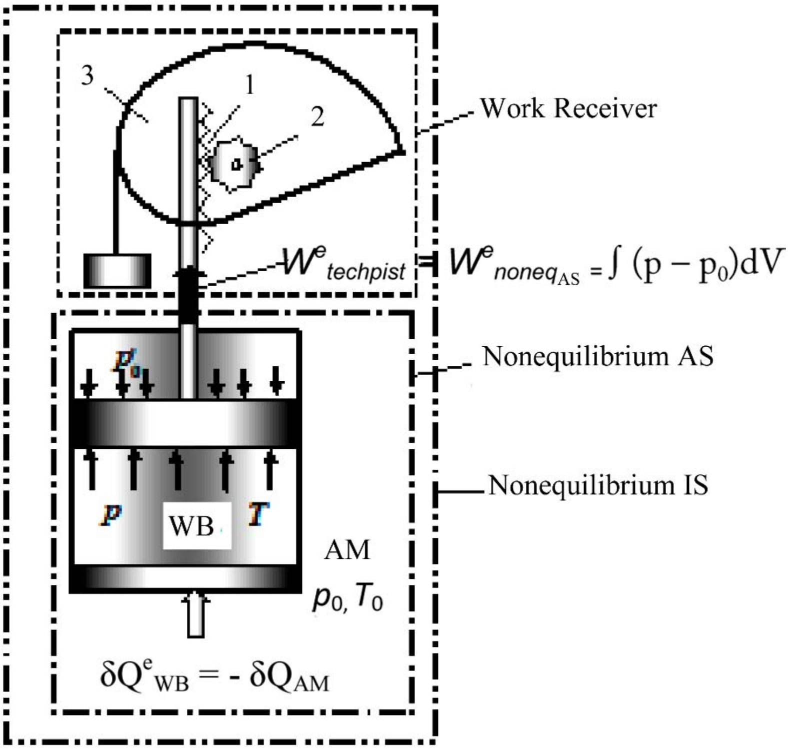

Figure 2. *Scheme and boundary of a nonequilibrium adiabatic system*

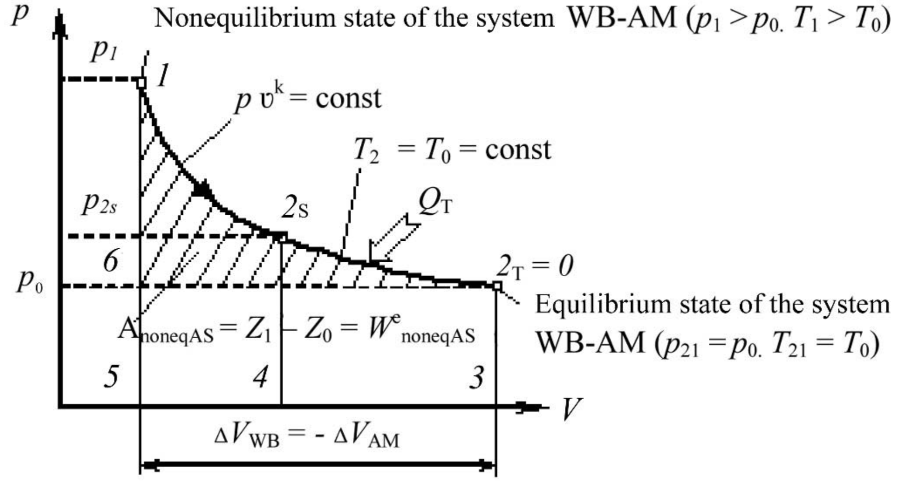

Figure 3. *To the calculation of the nonequilibrium of the adiabatic system*