APLICAÇÃO DO POSTULADO DE NÃO-EQUILÍBRIO PARA CÁLCULAR O NÃO-EQUILÍBRIO DE SISTEMAS DE VÁRIOS GASES E LÍQUIDOS

APPLICATION OF THE POSTULATE OF NONEQUILIBRIUM TO CALCULATE THE NONEQUILIBRIUM OF SYSTEMS OF DISSIMILAR GASES AND LIQUIDS

ПРИМЕНЕНИЕ ПОСТУЛАТА НЕРАВНОВЕШНОСТИ ДЛЯ РАСЧЁТА НЕРАВНОВЕШНОСТИ СИСТЕМ РАЗЛИЧНЫХ ГАЗОВ И ЖИДКОСТЕЙ

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RESUMO

A segunda lei da termodinâmica é baseada no postulado de não-equilíbrio. De acordo com este postulado, 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 ocorrer apenas em sistemas sem equilíbrio. Como uma característica quantitativa de um sistema sem equilíbrio, considera-se o trabalho máximo que pode ser feito quando o sistema sem equilíbrio entra em equilíbrio. A única formulação da segunda lei é dada: quando ocorrem processos reais (irreversíveis), o não-equilíbrio de um sistema isolado diminui e, quando ocorrem processos reversíveis, o não-equilíbrio no sistema de subsistemas de equilíbrio local não muda (o aumento em um tipo de não-equilíbrio é completamente compensado por diminuição em algum outro tipo de não-equilíbrio). Quando o sistema alcança o equilíbrio, o não-equilíbrio desaparece e todos os processos cessam. O artigo fornece uma confirmação calculada das disposições teóricas do conceito de não-equilíbrio e de seu aparato matemático com os exemplos de determinação da perda de não-equilíbrio do sistema durante a mistura isotérmica de gases diferentes e alterações no estado de não-equilíbrio do sistema “solvente puro – solução” quando uma parte do solvente entra em solução. A mistura dos mesmos gases leva ao paradoxo de Gibbs, que também é considerado neste artigo. O conceito de não-equilíbrio foi desenvolvido e as características quantitativas (medidas) do sistema de não-equilíbrio foram introduzidas, permitindo estudar os sistemas de não-equilíbrio que consistem em subsistemas de equilíbrio local nas seções da termodinâmica clássica tão simplesmente como os sistemas de equilíbrio separados.

Palavras-chave: *segunda lei da termodinâmica, postulado do não-equilíbrio, valor do não-equilíbrio, paradoxo de Gibbs, cálculo do não-equilíbrio.*

ABSTRACT

The postulate of nonequilibrium is at the heart of the second law of thermodynamics. According to this postulate, there is a real property of matter – “nonequilibrium,” which characterizes the uneven distribution of matter and motion in space. All processes (reversible and irreversible) can occur only in nonequilibrium systems. As a quantitative characteristic of the nonequilibrium of the system, the maximum work that can be performed during the transition of the nonequilibrium system to the equilibrium state is considered. The only formulation of the second law is given. 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 one kind of the nonequilibrium entirely compensated by a decrease in the disequilibrium of some other kind). When the system reaches an equilibrium state, the disequilibrium disappears, and all processes cease. 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 the nonequilibrium of system when an isothermal mixing of dissimilar gases, and changes of nonequilibrium of system “pure solvent – solution” in the transition of part of the solvent in the solution. The mixing of the same gases leads to the Gibbs paradox, which is also considered in this paper. The concept of nonequilibrium was developed and the quantitative characteristics (measures) of nonequilibrium of the system were introduced allow to study nonequilibrium systems consisting of locally equilibrium subsystems in the sections of classical thermodynamics as simply as individual

Keywords: *second law of thermodynamics, postulate of nonequilibrium, quantity of nonequilibrium, Gibbs paradox, calculation of nonequilibrium.*

АННОТАЦИЯ

В основе второго закона термодинамики лежит постулат неравновесности. Согласно этому постулату существует объективное свойство вещества – «неравновесность», которое характеризует неравномерное распределение вещества и движения в пространстве. Все процессы (обратимые и необратимые) могут происходить только в неравновесных системах. В качестве количественной характеристики неравновесной системы рассматривается максимальная работа, которую можно выполнить при переходе неравновесной системы в состояние равновесия. Дается единственная формулировка второго закона: когда происходят реальные (необратимые) процессы, неравновесность изолированной системы уменьшается, а в обратимых процессах неравновесность в системе локально равновесных подсистем не изменяется (увеличение одного вида неравновесности полностью компенсируется уменьшением неравновесия какого-либо другого вида). Когда система достигает состояния равновесия, неравновесие исчезает, и все процессы прекращаются. В статье приведено расчётное подтверждение теоретических положений концепции неравновесности и её математического аппарата на примерах определения потери неравновесности системы при изотермическом перемешивании разнородных газов и изменения неравновесности системы «чистый растворитель – раствор» при переходе части растворителя в раствор. Смешивание одних и тех же газов приводит к парадоксу Гиббса, который также рассматривается в данной статье. Была разработана концепция неравновесности и введены количественные характеристики (меры) неравновесности системы, позволяющие изучать неравновесные системы, состоящие из локально равновесных подсистем, в разделах классической термодинамики так же просто, как отдельные равновесные системы.

Ключевые слова: *второй закон термодинамики, постулат неравновесности, количество неравновесности, парадокс Гиббса, расчёт неравновесности.*

1. INTRODUCTION:

All the fundamental laws of physics are based on the philosophical law of conservation of matter and its motion properties. Thus, the first law of thermodynamics (FLT) is an analytical (quantitative) expression of the law of motion conservation when changing its shape. As for the second law of thermodynamics (SLT), it has not been determined so far which property of matter (motion, form of motion or any other property) is quantitatively conserved in the isolated system (IS) when reversible (ideal) processes occur and decreases when irreversible (real) processes occur (Borgnakke and Sonntag, 2009).

Lack of knowledge (misunderstanding) of the SLT essence led to various formulations (about twenty formulations of the SLT were proposed (Putilov, 1971) and an enormous amount of researches on explaining the meaning of these formulations (Reyf, 1972; Bejan, 2016; Ben-Naim, 2010; Chen *et al.*, 2017; Wald, 2001; Martyushev and Seleznev, 2006; Rakopoulos and Giakoumis, 2006; Liu and Liu, 2008; Seifert, 2012; D'Alessio *et al.*, 2016; De Oliveira, 2019; Marboeuf *et al.*, 2019; Ptasiński and Esposito, 2019; Sellitto and Di Domenico, 2019; De Blasio, 2019).

When explaining the SLT formulations,

contradictions arise both within separate textbooks and textbooks of different authors: Andryushchenko (1975); Baehr (1973); Calabrese (2018); Chen and Tsutsumi (2018); Holyst and Poniewierski (2012); Krutov V.I. (Krutov *et al.*, 1991); Vukalovich and Novikov (1968); Novikov (1984); Callen (1985); Fermi (1937); Kirillin V. A. (Kirillin *et al.*, 1983); Kittel (1993); Kondepudi and Prigogine (2015); Krichevsky (1970); Lavenda (2010); Morales-Rodriguez (2016); Moran (Moran *et al.*, 2014); Srivastava (Srivastava *et al.*, 2007).

A single formulation is needed (as in other laws) from which consequently must result (or be deemed redundant) various existing formulations. Such the 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, and in real (irreversible) processes it decreases”. This monograph introduces the concept of nonequilibrium. According to this concept, the cause of all processes is the nonequilibrium, a property of matter caused by the uneven distribution of the concentration of motion in space (Ryndin, 2014).

The following types of nonequilibrium are singled out: thermal and baric, caused by

temperature and pressure difference in space; mechanical (kinetic and potential), electric, chemical, and others. To estimate the nonequilibrium of the whole system consisting of a set of locally equilibrium subsystems, the concept of total nonequilibrium is introduced as a sum of all the types of nonequilibrium of an isolated system (Ryndin, 2014).

Processes in which the total nonequilibrium of IS does not change (the increase in nonequilibrium of one type is fully compensated by the loss of nonequilibrium of other types), and will be those reversible processes that are considered in thermodynamics; in irreversible processes, the nonequilibrium of IS decreases. The analytic expression of the postulate of nonequilibrium (nonequilibrium IS cannot increase) is the following inequality (Ryndin, 2014) (Equation 1), where Λ – nonequilibrium (the amount of nonequilibrium), which means the maximum work obtained by running reversible processes in the adiabatic system (AS) before the full transition of the system to the equilibrium state, or lost work in the IS when the system changes to the equilibrium state.

Whereas the IS can be mentally transformed into an adiabatic system, the loss of the IS nonequilibrium can be defined as the work of the adiabatic system with reversible processes occurring in it, that bring the nonequilibrium system into an equilibrium state. Inequality (Equation 1) is the opposite of Rudolf Clausius inequality (Clausius, 1850) (Equation 2) – total entropy of IS cannot decrease. As a result of this generalization, the dS_{IS} , entropy change used to write the SLT has become one of the characteristics of IS nonequilibrium change.

This article gives the calculated confirmation of the main provisions of the nonequilibrium concept by examples of calculation of the nonequilibrium of systems of dissimilar gases and liquids.

The mixing of homogeneous gases is associated with the Gibbs Paradox. The paradox was formulated by Josiah Willard Gibbs in 1875 at the same time as the version of its explanation (Gibbs, 1982). According to Gibbs, there was nothing paradoxical about the entropy of mixing; the term Gibbs paradox was probably first used by O. Wiedeburg (Wiedeburg, 1894; Gelfer *et al.*, 1975).

Gibbs Paradox is the absence of continuity for entropy when moving from mixing different (dissimilar) gases to mixing identical gases: mixing entropy when moving from ideal gases with an

arbitrarily small degree of difference to identical gases jumps from constant value to zero, which seems unexpected and illogical (Lyuboshits and Podgoretsky, 1971). Sometimes Gibbs paradox is called the apparently nonadditivity of entropy when two volumes of the same ideal gas are combined (Poltorak, 1991; Klimontovich, 1982; Anselm, 1973). To solve the Gibbs paradox means to establish the reasons for the jump in entropy of the ΔS when moving from a mixture of closely similar gases to a mixture of identical gases.

A significant number of various attempts to solve the Gibbs paradox are described in the literature. However, the fact that more and more new paradox solutions are appearing suggests that there is no generally accepted answer to the posed question (Ignatovich, 2010; Haytun, 2010).

2. MATERIALS AND METHODS:

2.1. Nonequilibrium of an isolated system

The concept of nonequilibrium defines an isolated system as a nonequilibrium system consisting of a set of local-equilibrium (quasi-equilibrium) subsystems (heat sources (HS) and heat receivers, work receivers and work sources, work body (WB), ambient medium (AM), finite and small flow elements), that interact with each other but do not interact with other systems that do not belong to the considered isolated system.

Since when real processes take place, the IS tends to the equilibrium state, when the system loses the ability to perform work (to transfer motion in an ordered form), then as a quantitative measure of the nonequilibrium of the system Λ it is accepted the maximum work that could be transferred by the system to the environment when mechanical isolation is removed, i.e. if it is mentally turned into an adiabatic system (Equation 3).

To calculate the maximum (possible) work, values such as thermodynamic potentials, heat exergy and flow exergy are used in thermodynamics. In isolated systems, when real processes take place, there is a transformation of dissipation of ordered motion (OM) into chaotic motion (CHM), i.e. there is dissipation (scattering) of chaotic motion. The equilibrium state in the system occurs when all the OM (work) completely turns into CHM (heat) (Equation 4).

This work is called a possible work, loss of performance, or energy loss. It is estimated through the entropy increase (Equation 5) at the transition of the IS from the nonequilibrium state to

the equilibrium state according to the Gouy-Stodola equation (Equation 6) (Kirillin *et al.*, 1983), where T_{AM} is the temperature of the equilibrium ambient medium (AM) (atmosphere or large waterbody), which does not change at the transition of the nonequilibrium system to the equilibrium state (Equation 7).

In general, when there is no liquid AM, the T_{CBmin} temperature is taken, i.e. the variable body temperature with the lowest temperature (cold body temperature – CB) during the heat exchange or the temperature of the thermodynamic system (WB, HS) during its interaction with the work sources (load, spring, flywheel, capacitor, accumulator, etc.), which alone are not characterized by temperature, and Equation 3 with consideration of Equation 6 becomes as Equation 8.

Change of nonequilibrium (Equation 9) IS (recall: increment (plus sign) (Equation 10), decrease (minus sign) (Equation 11)) at its transition to the equilibrium state it can be represented as the difference between the values of the nonequilibrium in the final state (equilibrium state Λ_2 , where the nonequilibrium is zero (Equation 12) and the initial Λ_1 – nonequilibrium state determined by Equation 8 (Equation 13).

The equation (Equation 13) for changing the IS nonequilibrium in a simple process considering the inequality (Equation 2) for changing the IS entropy (Equation 14) is recorded as follows (Equation 15).

The inequality (Equation 15) confirms the postulate of nonequilibrium (Equation 1) – IS nonequilibrium cannot increase. If we proceed from the primary inequality (Equation 1), then out of (Equation 13) follows the Clausius inequality (Equation 2) (Equation 16). The Equation 13 in differential form for the loss of $(-d\Lambda)$ system nonequilibrium can be recorded as follows (Equation 17) and in integral form (Equation 18).

2.2. The nonequilibrium of the adiabatic system

If in general the thermodynamic potential is indicated by the symbol Π (“pi” Greek), then the amount of the system's nonequilibrium will be determined by the difference between the system's potentials in the nonequilibrium state $\Pi_{noneq.st}$ and the equilibrium state $\Pi_{eq.st}$ (let's call it the “potential difference” $\Delta\Pi^*$), equal to the maximum work of the system during its transition to the equilibrium state (Equation 19).

For the finite loss of nonequilibrium, the

equation (Equation 19) can be recorded as Equation 20. In differential form, this equation will look like Equation 21, where (Equation 22), because all processes stop when the system goes into an equilibrium state and, consequently, changes of all values are equal to zero. The potential difference in the adiabatic system performing the work decreases in any processes (reversible and irreversible). However, only in reversible processes (index “o”) the loss of potential difference equal to the loss of thermodynamic potential will be equal to the maximum external work of the nonequilibrium system (Equation 23).

In the case of irreversible processes, the external (upper index “e”) work of the system results in fewer losses of potential difference (losses of thermodynamic potential) (Equation 24).

Consequently, the general condition of the transition of the system from a more nonequilibrium state to a less nonequilibrium state (more equilibrium) is as follows (Equation 25). According to this formula, the external work is equal to the loss of potential difference, or the loss of thermodynamic potential in reversible processes and less than this loss in irreversible processes.

2.3. Gibbs Paradox

Many specialized works are dedicated to the Gibbs Paradox: Bazarov (1979; 2010), Gelfer (Gelfer *et al.*, 1975); Ignatovich (2010); Lyuboshits and Podgoretsky (1971); Terletsky (1984); Haytun (2010) and others. Let us consider the isothermal mixing of two originally separated ideal gases placed in a box with diathermic (heat-conducting) walls impermeable to the substance and the same partition dividing the box into two parts with different gases; both parts have identical volumes (Equation 26) and contain the same amount of substance (Equation 27) with temperature T and pressure p ; the box is placed in a thermostat with the same temperature T , to achieve equality of gas temperatures during the mixing process, and the partition is equipped with an opening door (flap, crane, valve). Molar heat capacities of gases on both sides of the partition are the same. The assumption of the uniformity of molar heat tanks, volumes of subsystems, and the equality of the substance quantity contained in them is made to simplify the calculations. In the book by Bazarov I.P. a formula for the entropy of mixing is given without using this simplification.

Gibbs has discovered the fact that when identical ideal gases are mixed, there is no change

in entropy, and when dissimilar gases are mixed, there is a jump in entropy (Bazarov, 2010) (Equation 28), where v – substance quantity, mole; R_μ – molar (universal) gas constant, J/(mol.K); k_B – Boltzmann's constant, J/K; N – particle number (atoms, molecules).

This abrupt (discontinuous) behavior of the entropy of mixing ΔS is called the Gibbs Paradox. The paradox here is that when considering the mixing of gases entropy, the mixing of two identical gases cannot be considered as a limiting case of mixing two different gases (the paradox, as we know, is a true statement, which is unusual, contradicts the previously known, and about which it should be said that it cannot be). As noted in the paper (Bazarov, 1979), "the paradox cannot be 'removed' or eliminated, but can be explained or solved". Various solutions to the Gibbs Paradox were proposed.

Solutions that reject the actual existence of the paradox. The reasoning logic of researchers who reject the very existence of the Gibbs paradox is as follows. The paradox comes down to a jump in the behavior of ΔS mixing entropy at a continuous convergence of some parameters characterizing the gases being mixed. If such continuous approximation is contrary to the laws of physics, i.e., if the differences between gases can only change discretely (for example, between the H and He atoms there's no continuous transition), the Gibbs paradox disappears: there's nothing strange about the fact that when gases parameters are changed discretely, their mixtures properties also change discretely (Sommerfeld, 1955; Kedrov, 1969).

Quantum discrete solutions. Today, the discrete quantum solution to the Gibbs Paradox has the most significant number of supporters. It is distinguished from the solutions rejecting the paradox itself by the paradox existence recognition, the discreteness of the mixing entropy is perceived as a natural result of the substance discreteness, the correct dependence of the gas entropy on the number of particles (quantity of substance) follows from the quantum statistics of indistinguishable particles (Haytun, 2010), and the autonomy of the mixing entropy from the properties of gases is considered as an obvious consequence of the assumption of their ideality (Gelfer *et al.*, 1975).

On the experimental discovery of the Gibbs Paradox. Throughout the whole 20th century more and more new approaches have been invented, trying to verify the reality of the Gibbs paradox, and over and over again convincing of the impossibility

of their realization. The Van der Waals hypothesis of the fundamental impossibility of experimentally verifying the existence of the Gibbs Paradox (Waals and Kohnstamm, 1912) remains unproven, but in practice the paradoxical jump of the entropy of mixing still cannot be measured.

3. RESULTS AND DISCUSSION:

3.1. Nonequilibrium of a system of dissimilar gases at the same pressures and temperatures (isothermal mixing – diffusion)

Let's consider two gases divided by partition A into two volumes V' and V'' (Figure 1). Initially (at time t_1) the temperature and pressure of gases are the same (Equation 29). After removing the partition, each gas spreads over the entire volume of (Equation 30) towards each other and at the time t_2 reaches the corresponding pressure (p_2' or p_2''). In the case of ideal gases, the temperature of their T does not change during mixing.

When the gases are mixed, the diffusion (concentration) nonequilibrium is lost, allowing the work to be obtained in the presence of an appropriate device. Such a device can be movable semi-permeable partitions (pistons), each of which is pressurized by only one gas for which the partition is impermeable. Under the appropriate pressures, the pistons-partitions will move from partition A to the end of the cylinder, and the gases will expand while working. So that the temperature of gases when disposing the work from the pistons-partitions to the work receiver (flywheel, spring, load...) does not change, it is necessary to supply heat equal to the work performed, i.e. a heat source (HS) is required.

In such isolated system (HS-WB-WR) when a reversible process is running, the loss of diffusive nonequilibrium in the system "gas–gas" $-\Delta\Lambda_{\text{dif}}$ WB-WB (WB – work body) is compensated for by an increase in the mechanical nonequilibrium of the system working body-work receiver WB-WR $\Delta\Lambda_{\text{mech}}$ (thermal nonequilibrium in all IS does not change (Equation 31), since the process is isothermal and is running at (Equation 32), thus the thermal nonequilibrium of IS does not change (Equation 33).

If the work receivers (WR) are separated from the rest of the system bodies, i.e., consider a non-isolated adiabatic system WB-HS (Figure 1), then in accordance with (Equation 24) the loss of diffusive nonequilibrium AS will be equal to the increase of mechanical nonequilibrium WR, which

in its turn is equal to the external work (Equation 34), performed by AC in a reversible process (index "o") at its transition to an equilibrium state (Equation 35).

The work performed by nonequilibrium AS will consist of the works of isothermal expansion of the 1st W_T and 2nd W''_T gases (Equation 36), where pressures are expressed through volumes using the Clapeyron equation (Equation 37) and (Equation 38), where R (Equation 39) – specific gas constant, J/(kg.K); R_μ – molar gas constant, J/(kg.K); M – molar mass, kg/mole. Since the volume and temperature of the nonequilibrium adiabatic system do not change (isochoric and isothermal process), the maximum operation of such a system at its reversible transition to an equilibrium state will be equal to Helmholtz potential (energy) losses (Equation 20) (Equation 40), where the change in Helmholtz energy of heat source is equal to zero: because it does not perform any external work (Equation 41), then according to the FLT (Equation 42), i. e. (Equation 43).

Specific Helmholtz energy of ideal gas (Equation 44) can be calculated if the expression for entropy is known. In the case of the ideal gas, the expression for specific entropy in the function of temperature T and specific volume is as follows (Kirillin *et al.*, 1983) (Equation 45), where s_o – constant for this gas. By substituting the expression for s in the general formula for Helmholtz specific energy (Equation 44), we'll get Equation 46, where $b(T)$ – the function of only one temperature, since energy expression for the ideal gas depends only on the temperature, i.e. (Equation 47).

By multiplying all the figures (Equation 46) by the mass of the gas and expressing the specific volume of the gas through the complete volume, we obtain the expression for Helmholtz energy in function of temperature, mass, and volume of the ideal gas (Equation 48). By substituting expression (Equation 48) for Helmholtz potential in (Equation 33), given that (Equation 49), we'll get Equation 50.

Comparing expressions (Equation 40) and (Equation 50), we conclude that, indeed, the work of nonequilibrium AS in the case of a reversible isochoric and isothermal process is equal to the Helmholtz energy losses. In the case of a complete transition of nonequilibrium AS to an equilibrium state, it is equal to the diffusive nonequilibrium of such a system (Equation 51).

As there are no such special devices (semi-permeable pistons) in actual practice, all

possible external work at system transition to an equilibrium state is lost, it dissipates inside the system. The entropy increase of an isolated system consisting of two dissimilar gases associated with the loss of concentration nonequilibrium due to diffusion will be determined by the general formula (Equation 8) considering that (Equation 52) and lost work is equal to external work (Equation 50) of adiabatic system (WB-HS) in case of reversible isochoric and isothermal process, i. e. (Equation 53).

For an ideal gas, we can introduce a "body gas constant" (Equation 54), through which specific and molar gas constants are introduced (Equation 55). Considering (Equation 54), the expression (Equation 53) can be recorded as follows (Equation 56).

In the particular case, of equal quantities of gases (Equation 57), remaining before mixing in equal volumes (Equation 58) the ratio (Equation 56) will be as follows (Equation 59), which is similar to the known expression (Equation 28) for entropy jump in the mixing of dissimilar gases. As we can see, calculations of the IS entropy change through lost work (Equation 53) and the entropy values of gases before and after mixing (Equation 28) give the same results, which once again confirms the correctness of formula (Equation 53) for calculating the entropy change of an isolated system.

In the case of a reversible process of equalizing the concentration of gases over the entire cylinder volume in an adiabatic (WB-HS) or isolated system (AS-WR), the change of entropy of these systems is equal to zero, because in the reversible process the heat supplied to WB by HS is equal and opposite in sign to the heat supplied by HS (Equation 60), as well as equal to the temperatures of WB and HS (Equation 61), where the work receiver entropy change ΔS_{WR} is equal to zero, because it does not possess a reserve of chaotic (thermal) motion.

If we take two identical gases at equal pressures and temperatures, separated by a partition, and then remove this partition, the entropy of such a system will not change, although the gas molecules will take up the entire volume. This fact is easily explained by the concept of nonequilibrium. According to the described nonequilibrium concept based on the postulate of nonequilibrium, a change in IS entropy is only possible if the system loses its full (total) nonequilibrium characterized by the lost work. Since there is no nonequilibrium, including concentration (diffusion) nonequilibrium in a

homogeneous gas separated by a partition in two parts at the same pressure and temperature, there can be no lost work (Equation 62) and the entropy increase associated with it: when two portions of the same gas are mixed, the gas-permeable pistons-partitions on both sides will be stationary. Therefore, although technically it is possible to calculate the change of IS entropy, consisting of homogeneous gas, by formula (Equation 28), such calculation does not make sense, because there are no devices working in a full equilibrium system. Since there is no lost work (no change in the nonequilibrium system) when mixing two portions of the same gas, there is no change in entropy (there is no dissipation of ordered motion) of such a system according to (Equation 59).

When two different (dissimilar) ideal gases are mixed with the same molar heat capacity, the system entropy increases by the same value regardless of the degree of difference between the gases. In other words, the mixing entropy during the transition from ideal gases with as little difference as possible to identical gases changes by a jump from a constant value to zero (*paradoxical jump of entropy of mixing*) (Vukalovich and Novikov, 1968). As already mentioned, the autonomy of the entropy of mixing from the nature of gases is considered as an obvious consequence of the assumption of their ideality. Ideal gas is a model of gas, rather than the gas itself, in which there are no interaction forces between the molecules (and in our case with permeable partitions) that could influence the possible mixing work. Therefore, as a special property of an ideal gas (as in the assumption that the internal energy is constant about the gas volume), it should be recognized that the amount of nonequilibrium and entropic difference is constant when mixing dissimilar ideal gases in an isolated system.

3.2. Calculation of change of nonequilibrium of system "pure solvent-solution" at transition of a part of solvent in a solution

Suppose that in a hermetically sealed boiler at a constant temperature T , in two vessels, there is pure solvent and solution of any non-volatile substance (Figure 2).

This system is in an equilibrium state, as the vapor pressure above the solvent p_1 is higher than above the solution p_2 . When a portion of the solvent of a single mass ($m = 1$ kg) evaporates and passes into the solution, the nonequilibrium (specific) of the system decreases by the value of specific external work (Equation 20), which could have been obtained in a reversible process in the

presence of a special device (Equation 63).

Such a device can be a cylinder with a moving piston, which is connected in turn with a special crane to a pure solvent or solution. In the first stage (*a-b*), 1 kg of water evaporates at constant values of pressure (Equation 64) and temperature (Equation 65). To do this, the cylinder is connected by a crane to a vessel containing pure solvent and an isobaric expansion of this steam is performed. As a result of the steam expansion, steam performs a specific work on the piston (Equation 66).

By neglecting the specific volume of water (liquid) compared to the specific volume of steam and considering steam as an ideal gas (Equation 67), we will get Equation 68, where R_{st} – specific gas steam constant, J/(kg.K). In the second stage (*b-c*), there is an isothermal expansion of the steam to the pressure p_2 . In this case, the steam performs a specific work of isothermal expansion over the piston, which is known to be determined by the expression (Equation 69).

In the third stage (*c-d*), there is a condensation of steam, for which the cylinder cavity is connected by a crane to a vessel in which there is a solution at a pressure of p_2 of steam above it, and isobaric compression is performed. As a result, a portion of water weighing 1 kg passes into the solution, with a specific compression work above the steam (the specific volume of condensate – liquid – neglected) (Equation 70).

Since isobaric and isothermal processes are carried out with the supply (removal in compression) of heat, it is necessary to provide for the presence of sources (receivers) of heat exchanging heat with steam (work body) in such a system. Consequently, the nonequilibrium adiabatic system will include the work body (steam in nonequilibrium state in two vessels above both solvent and solution, and in the cylinder – in equilibrium state) and heat sources. To receive the work performed by nonequilibrium AS, it is necessary to provide the work receiver (it can also be used as a source of work during compression). As an AS receiver (source) of work, can be used a special device that provides equality of moments relative to the axis of the cam of constant gravity and variable force of steam pressure on the piston, which ensures the slowness (and thus equilibrium) of the expansion process (Figure 2). The total specific work performed by such nonequilibrium AS, will be equal to the sum of works defined by expressions (Equations 68 – 70), (Equation 71).

Since the volume of nonequilibrium AS in

the process of transition of water solvent in the solution does not change, as well as temperature, such a process will be isochoric and isothermal, and thus the loss of nonequilibrium (specific) system will be equal to the loss of Helmholtz potential (specific), which in its turn is equal to the external specific work of nonequilibrium AS in the reversible process (Equation 72).

As there is no special device for reversible transition of water solvent to solution in actual practice, all possible useful work will be lost (Equation 73). In the case of a natural (irreversible) transition process of solvent into solution, the entropy (specific) of the isolated system consisting only of solvent and solution vessels will increase by the value of (Equation 74).

It is evident from the considered examples that in the presence of special devices reversible processes can take place also in strictly nonequilibrium systems, and not only in the systems close to an equilibrium state as it is generally accepted to count.

4. CONCLUSIONS:

Thus, it was calculated confirmation of the theoretical provisions of the concept of nonequilibrium and its mathematical apparatus by examples of determining the loss of the nonequilibrium of system. The formula for calculating the change in entropy of an isolated system when mixing dissimilar gases, obtained through the lost nonequilibrium (lost work), coincides with the Gibbs formula, which is a practical confirmation of the validity of the postulate of nonequilibrium, which the author used as a basis for the SLT.

When considering the isothermal mixing of two originally separated ideal gases, the following was found: Gibbs Paradox of a jump-like change in the entropy of an isolated system when mixing dissimilar gases is explained by a jump-like loss of nonequilibrium inherent in the ideal gas model, when the interaction forces between gas molecules as well as with the walls are not considered.

Based on the results, the concept of nonequilibrium was developed and introduced quantitative characteristics (measures) of nonequilibrium system allow to investigate nonequilibrium systems consisting of locally equilibrium subsystems in sections of classical thermodynamics as easily as separate equilibrium systems.

This article is a continuation of the author's

concept of nonequilibrium. The above expressions which obtained in the calculations of diffusive nonequilibrium of the dissimilar gases system that is lost as a result of gases isothermal mixing, and also nonequilibrium changes of the "pure solvent – solution" system at transition of a part of solvent to solution can be used in practice.

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$$d\Lambda_{\text{noneq.IS}} \leq 0 \quad (\text{Eq. 1})$$

$$dS_{\text{IS}} = dS_{\text{noneq.IS}} \geq 0 \quad (\text{Eq. 2})$$

$$\Lambda \equiv \Lambda_{\text{noneq.IS}} \equiv W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} \quad (\text{Eq. 3})$$

$$W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} = W_{\text{lost}}^{\text{max}} = Q_{\text{diss}} \quad (\text{Eq. 4})$$

$$\Delta S_{\text{noneq.IS} \rightarrow \text{eq.st}} \quad (\text{Eq. 5})$$

$$W_{\text{diss}}^{\text{max}} = W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} = T_{\text{AM}} \Delta S_{\text{noneq.st} \rightarrow \text{eq.st}} \quad (\text{Eq. 6})$$

$$T_{\text{AM}} = \text{const} \quad (\text{Eq. 7})$$

$$\Lambda_{\text{noneq.IS}} = W_{\text{diss}}^{\text{max}} = W_{\text{lost}} = W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} = T_{\text{CBmin}} \Delta S_{\text{noneq.IS} \rightarrow \text{eq.st}} \quad (\text{Eq. 8})$$

$$\Delta \Lambda = \Lambda_2 - \Lambda_1 \quad (\text{Eq. 9})$$

$$\Delta x = x_2 - x_1 \quad (\text{Eq. 10})$$

$$-\Delta x = x_1 - x_2 \quad (\text{Eq. 11})$$

$$\Lambda_{\text{eq.st}} \equiv 0 \quad (\text{Eq. 12})$$

$$\Delta \Lambda_{\text{noneq.IS}} = \Lambda_{\text{eq.st}} - \Lambda_{\text{noneq.IS}} = -\Lambda_{\text{noneq.IS}} = -W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} = -T_{\text{CBmin}} \Delta S_{\text{noneq.IS} \rightarrow \text{eq.st}} \quad (\text{Eq. 13})$$

$$dS_{\text{noneq.IS}} \geq 0 \quad (\text{Eq. 14})$$

$$d\Lambda_{\text{IS}} = -T_{\text{CBmin}} dS_{\text{IS}} \leq 0 \quad (\text{Eq. 15})$$

$$dS_{\text{IS}} \geq 0 \quad (\text{Eq. 16})$$

$$-d\Lambda = \delta W_{\text{lost}} = \delta W_{\text{diss}} = T_{\text{CBmin}} dS_{\text{diss}} \quad (\text{Eq. 17})$$

$$-\Delta \Lambda = W_{\text{lost}} = W_{\text{diss}} = T_{\text{CBmin}} \Delta S_{\text{diss}} \quad (\text{Eq. 18})$$

$$\Lambda_{\text{AS}} = \Delta \Pi^* = \Pi_{\text{noneq.st}} - \Pi_{\text{eq.st}} = W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\text{max}} = W_{\text{max}}^{\text{e}} \quad (\text{Eq. 19})$$

$$\begin{aligned} -\Delta\Lambda_{AS}^{\max} &= -\Delta(\Delta\Pi^*)_{\max} = \Lambda_1 - \Lambda_2 = \Lambda_{\text{noneq.st}} - \Lambda_{\text{eq.st}} = \Lambda_{\text{noneq.st}} = \\ &= \Pi_{\text{noneq.st}} - \Pi_{\text{eq.st}} = \Pi_1 - \Pi_2 = -\Delta\Pi_{\max} = W_{\text{noneq.st} \rightarrow \text{eq.st}}^{\max} = W_{\max}^e. \end{aligned} \quad (\text{Eq. 20})$$

$$-d\Lambda_{AS} = -d(\Delta\Pi^*) = -d\Pi_{\text{noneq.st}} + d\Pi_{\text{eq.st}} = -d\Pi_{\text{noneq.st}} \equiv -d\Pi = \delta W_{\max}^e = \delta W^{e\circ} \quad (\text{Eq. 21})$$

$$d\Pi_{\text{eq.st}} \equiv 0 \quad (\text{Eq. 22})$$

$$\delta W^{e\circ} = \delta W_{\max}^e = -d(\Delta\Pi^*) \quad (\text{Eq. 23})$$

$$\delta W^e < -d(\Delta\Pi^*) = -d\Pi \quad (\text{Eq. 24})$$

$$\delta W^e \leq -d(\Delta\Pi^*) = -d\Pi \quad (\text{Eq. 25})$$

$$V_1 = V_2 = V \quad (\text{Eq. 26})$$

$$v_1 = v_2 = v \quad (\text{Eq. 27})$$

$$\Delta S = 2vR_{\mu} \ln 2 = 2k_B N \ln 2 \quad (\text{Eq. 28})$$

$$p_1' = p_1'' \quad (\text{Eq. 29})$$

$$V = V_2' = V_2'' = V' + V'' \quad (\text{Eq. 30})$$

$$\Delta\Lambda_{\text{therm}} = 0 \quad (\text{Eq. 31})$$

$$T_{WB} = T_{HS} \quad (\text{Eq. 32})$$

$$\Delta\Lambda_{\text{noneq.IS}} = \Delta\Lambda_{\text{noneq.AS}} + \Delta\Lambda_{WR} = \Delta\Lambda_{\text{therm}} + \Delta\Lambda_{\text{dif}} + \Delta\Lambda_{\text{mech}} = 0 \quad (\text{Eq. 33})$$

$$W_{AS \rightarrow \text{eq.st}}^o \quad (\text{Eq. 34})$$

$$-\Delta\Lambda_{\text{noneq.AS}} = -\Delta\Lambda_{\text{dif}} = \Delta\Lambda_{\text{mech}} = W_{AS \rightarrow \text{eq.st}}^o \quad (\text{Eq. 35})$$

$$\begin{aligned} W_{AS \rightarrow \text{eq.st}}^o &= W_T' + W_T'' = \int_{V'}^V p' dV + \int_{V''}^V p'' dV = m' R' T \int_{V'}^V \frac{dV}{V} + \\ &+ m'' R'' T \int_{V''}^V \frac{dV}{V} = [m' R' \ln(V/V') + m'' R'' \ln(V/V'')] T, \end{aligned} \quad \text{Eq. 36})$$

$$p' = m' R' T / V' \quad (\text{Eq. 37})$$

$$p'' = m'' R'' T / V'' \quad (\text{Eq. 38})$$

$$R = R_{\mu}/M \quad (\text{Eq. 39})$$

$$\begin{aligned} W_{V,T}^{\max} &= W_{AS \rightarrow \text{eq.st}}^o = -\Delta F_{AS} = -\Delta F_{WB} - \Delta F_{HS} = \\ &= -\Delta F_{WB} = F_{WB1} - F_{WB2} = F_1' + F_1'' - F_2' - F_2''. \end{aligned} \quad (\text{Eq. 40})$$

$$W_{\text{HS}} = 0 \quad (\text{Eq. 41})$$

$$Q_{\text{HS}} = \Delta U_{\text{HS}} \quad (\text{Eq. 42})$$

$$-\Delta F_{\text{HS}} = F_{\text{HS}2} - F_{\text{HS}1} = \Delta U_{\text{HS}} - T \Delta S_{\text{HS}} = \Delta U_{\text{HS}} - Q_{\text{HS}} = 0 \quad (\text{Eq. 43})$$

$$f = u - Ts \quad (\text{Eq. 44})$$

$$s(T, v) = c_v \ln T + R \ln v + s_0 \quad (\text{Eq. 45})$$

$$f = u - Ts = u - T(c_v \ln T + R \ln v + s_0) = -RT \ln v + b(T) \quad (\text{Eq. 46})$$

$$b(T) = u - Tc_v \ln T - Ts_0 \quad (\text{Eq. 47})$$

$$F = -mRT \ln v + m b(T) = -mRT \ln(V/m) + B(T) \quad (\text{Eq. 48})$$

$$m'_1 = m'_2 = m', \quad m''_1 = m''_2 = m'', \quad V'_1 = V', \quad V''_1 = V'', \quad V'_2 = V''_2 = V, \quad B'(T) = B''(T) \quad (\text{Eq. 49})$$

$$\begin{aligned} W_{\text{V,T}}^{\text{max}} = W_{\text{AS} \rightarrow \text{eq.st}}^0 = F'_1 + F''_1 - F'_2 - F''_2 = -m' R' T \ln(V'/m') + B'(T) - \\ - m'' R'' T \ln(V''/m'') + B''(T) + m' R' T \ln(V/m') - B'(T) + \\ + m'' R'' T \ln(V/m'') - B''(T) = m' R' T \ln(V/V') + m'' R'' T \ln(V/V''). \end{aligned} \quad (\text{Eq. 50})$$

$$\Lambda_{\text{noneq.AS}} = \Lambda_{\text{dif}} = -\Delta F_{\text{V,T}}^{\text{max}} = W_{\text{AS} \rightarrow \text{eq.st}}^0 \quad (\text{Eq. 51})$$

$$T_{\text{CB}} = T' = T'' = T \quad (\text{Eq. 52})$$

$$\Delta S_{\text{IS}} = W_{\text{lost}}/T = W_{\text{V,T}}^{\text{max}}/T = m' R' \ln(V/V') + m'' R'' \ln(V/V''). \quad (\text{Eq. 53})$$

$$R_{\text{body}} = \frac{pV}{T} = mR = \nu R_{\mu} = \text{const} \quad (\text{Eq. 54})$$

$$R = R_{\text{body}}/m; \quad R_{\mu} = R_{\text{body}}/\nu \quad (\text{Eq. 55})$$

$$\Delta S_{\text{IS}} = W_{\text{lost}}/T = W_{\text{V,T}}^{\text{max}}/T = \nu' R_{\mu} \ln(V/V') + \nu'' R_{\mu} \ln(V/V''). \quad (\text{Eq. 56})$$

$$\nu' = \nu'' = \nu \quad (\text{Eq. 57})$$

$$V' = V'' = V/2 \quad (\text{Eq. 58})$$

$$\Delta S_{\text{IS}} = W_{\text{loss}}/T = W_{\text{V,T}}^{\text{max}}/T = 2\nu R_{\mu} \ln 2 \quad (\text{Eq. 59})$$

$$Q_{\text{WB}} = -Q_{\text{HS}} \quad (\text{Eq. 60})$$

$$\begin{aligned} \Delta S_{\text{IS}} = \Delta S_{\text{WB}} + \Delta S_{\text{HS}} + \Delta S_{\text{WR}} = \Delta S_{\text{AS}} = \Delta S_{\text{WB}} + \Delta S_{\text{HS}} = \\ = Q_{\text{WB}}/T + Q_{\text{HS}}/T = Q_{\text{WB}}/T - Q_{\text{WB}}/T = 0, \end{aligned} \quad (\text{Eq. 61})$$

$$W_{\text{lost}} = 0 \quad (\text{Eq. 62})$$

$$-\Delta\lambda_{\text{noneq.AS}} = w_{\text{noneq.AS}}^{\text{eo}} \quad (\text{Eq. 63})$$

$$p_1 = \text{const} \quad (\text{Eq. 64})$$

$$T = \text{const} \quad (\text{Eq. 65})$$

$$w_{a-b}^p = p_1 (v_{\text{st}} - v_{\text{liq}}) \quad (\text{Eq. 66})$$

$$(p_1 v_{\text{st}} = R_{\text{st}} T) \quad (\text{Eq. 67})$$

$$w_{a-b}^p = p_1 v_{\text{st}} = R_{\text{st}} T \quad (\text{Eq. 68})$$

$$w_{b-c}^T = \int p \, dv = R_{\text{st}} T \ln(v_c / v_b) = R_{\text{st}} T \ln(p_b / p_c) = R_{\text{st}} T \ln(p_1 / p_2) \quad (\text{Eq. 69})$$

$$w_{c-d}^p = p_2 (v_{\text{liq}} - v_{\text{st}}) = -p_2 v_{\text{st}} = -R_{\text{st}} T \quad (\text{Eq. 70})$$

$$w_{\text{noneq.AS}}^{\text{eo}} = w_{a-b}^p + w_{b-c}^T + w_{c-d}^p = R_{\text{st}} T + R_{\text{st}} T \ln(p_1 / p_2) - R_{\text{st}} T = R_{\text{st}} T \ln(p_1 / p_2) \quad (\text{Eq. 71})$$

$$-\Delta\lambda_{\text{noneq.AS}} = -\Delta f_{V,T} = w_{\text{noneq.AS}}^{\text{eo}} = R_{\text{st}} T \ln(p_1 / p_2) \quad (\text{Eq. 72})$$

$$w_{\text{lost}} = w_{\text{noneq.AS}}^{\text{eo}} = R_{\text{st}} T \ln(p_1 / p_2) \quad (\text{Eq. 73})$$

$$\Delta S = w_{\text{lost}} / T = R_{\text{st}} \ln(p_1 / p_2) \quad (\text{Eq. 74})$$

Figure 1. To the calculation of the work of the adiabatic system in transition it to an equilibrium state

Figure 2. To calculation of change of nonequilibrium of system "pure solvent-solution"