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Temporal Method of Presenting the Fundamentals of Classical Thermodynamics

Gennadiy V. Averin¹ , Maria V. Shevtsova² , Anna V. Zvyagintseva¹ 
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¹ Donetsk State University,
24 University St., Donetsk, 283001, Russia
averin.gennadiy@gmail.com

² Belgorod National Research University,
85 Pobedy St., Belgorod, 308015, Russia
shevtsova_m@bsu.edu.ru




Abstract. Thermodynamics has a universal theory with great potential for the development of science. This article proposes a new system of presenting the laws of classical thermodynamics using temporal representations of thermodynamic processes, which allows to introduce time into basic laws and ratios of thermodynamics. The study shows the analysis of thermodynamics representation systems. We formulate thermodynamics methodology based on temporal approach. The principle of the existence of entropy and the equation of energy conservation are justified by methods of statistical modeling and differential geometry. We use the principle of equal possibility of thermodynamic states and processes for modeling the statics and dynamics of the perfect gas. So it is possible to apply the Monte Carlo method for the forming of states and for the estimation of their posterior probabilities. For real gases the principle of equal probability of states does not hold, therefore at statistical modeling it is necessary to take into account the laws of distribution of variables that will be associated with the empirical state equations - the Van der Waals equation, the virial equation, etc. The study presents the new temporal ratios which are important for the development of the theory, such as connection between time and entropy, correlation between entropy and process length, etc. Here we discuss the directions of research related to the disclosure of the physical and mathematical meanings of entropy.

Keywords: Thermodynamics, Fundamentals of Theory, Presentation Systems, Temporal Method

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Оригинальное исследование

Темпоральный метод изложения основ классической термодинамики

Аверин Г. В.¹ , Шевцова М. В.² , Звягинцева А. В.¹ 
(Статья представлена членом редакционной коллегии С. В. Блажевичем)

¹ Донецкий государственный университет,
Россия, 283001, г. Донецк, ул. Университетская, 24
averin.gennadiy@gmail.com

² Белгородский государственный национальный исследовательский университет,
Россия, 308015, г. Белгород, ул. Победы, 85
shevtsova_m@bsu.edu.ru

Аннотация. Термодинамика обладает универсальной теорией с большим потенциалом для развития науки. В данной статье предлагается новая система изложения основ классической термодинамики с использованием темпоральных представлений о термодинамических процессах, что позволяет ввести время в основные законы и соотношения термодинамики. Дается анализ систем изложения термодинамики, формулируется методология термодинамики на основе темпорального подхода. Методами статистического моделирования и дифференциальной геометрии обосновываются законы идеального газа, принцип существования энтропии и уравнение сохранения энергии. При моделировании статики и динамики идеального газа использован принцип равновозможности термодинамических состояний и процессов. Это позволило использовать метод Монте-Карло при формировании состояний и оценке их апостериорных вероятностей. Для реальных газов принцип равновозможности состояний не выполняется, поэтому при статистическом моделировании необходимо учитывать законы распределения величин, которые будут связаны с эмпирическими уравнениями состояний – уравнением Ван-дер-Ваальса, вириальным уравнением и т. д. Приводятся новые темпоральные соотношения, имеющие большое значение для развития теории, такие как связь

времени и энтропии, зависимости между энтропией и длиной траектории процесса и т. д. Обсуждаются направления исследований, связанные с раскрытием физических и математических смыслов энтропии.

Ключевые слова: термодинамика, основы теории, системы изложения, темпоральный метод

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1. Introduction. The initial positions of thermodynamics are based on the postulation of system-wide laws and patterns. These features are characteristic of macroscopic physical systems and established by experimental methods. The bases of thermodynamics are distinguished by their logical originality. So it is quite possible to talk about a certain beauty of this science in the context of its theory: it is characterized by integrity, simplicity and universality. However, although solid there are several problems in this science, a solution to which has not been found yet. Thermodynamic theory in its modern form is not complete, many its aspects are inconsistent and confusing, and a number of provisions have no logical clarity. First of all, it is about the concept of entropy and the principle of its increase, ideas of thermodynamic irreversibility, reflection of the fundamentality of time in theory, the problem of correlation between determinism and probability and other thermodynamic paradoxes [1]–[4]. As G. Falk noted 65 years ago, the main problem of the development of thermodynamic's theory is how to find new ways and expand the original concepts [5]. In this regard, the problem of reflecting time in the relations of classical thermodynamics is fundamental. The ways of further development of this science are associated with it [6].

The purpose of this article is to formulate a new system of presentation the fundamentals of classical thermodynamics. For that, we use temporal ideas of thermodynamic processes, which allows to introduce time into the basic laws and relations of thermodynamics.

2. Thermodynamics Presentation Systems. There are several methods for presenting thermodynamic foundations, for example, K.A. Putilov spoke of five such methods [7]. If we take into account the approaches proposed by A.A. Guhman, A. Sommerfeld, M. Born, G. Falk and other authors the number of such methods will be more than ten. Nevertheless, only two of them can be distinguished as integral systems of presentation of thermodynamics. Let's call them conditionally traditional and axiomatic systems.

The traditional system of presentation of thermodynamics is used in many courses of this subject. For presenting the material, basic terms are introduced: body state, state parameters, thermodynamic process, amount of heat, etc. Empirical laws of perfect gas are given. The first postulate of thermodynamics is formulated based on the generalization of experimental facts - on the state of thermodynamic equilibrium, as well as the principle of the existence of temperature (second postulate). Further, the fundamentality of the concept of absolute temperature is substantiated and the relationship between empirical and absolute temperatures is established. The law of conservation and transformation of energy is stated. The equation of the first principle of thermodynamics is written in the form:

$$dQ = du + pdv + \sum_{k=1}^n P_k dz_k,$$

where work $dA = pdv$, and p, v, z_k -- state parameters.

To justify the second principle (law) of thermodynamics the definitions of the heat engine, working fluid, thermodynamic cycle, hot and cold heat sources, thermal efficiency are introduced and an ideas of reversible and non-reversible processes are given. After that we proceed to the justification of the concept of entropy, for which the Carnot cycle and its thermal efficiency are described. The Carnot theorem is proved and the ratio for the reduced heat is established. By defining entropy as the sum of the reduced heat it is shown that the Clausius integral for the any reversible cycle is zero: $\oint dQ/T = 0$. All this makes possible to represent the entropy change in reversible and irreversible processes correspondingly in the form: $ds = dQ/T$ and $ds \geq dQ/T$ and to write the law of conservation of energy in: $Tds \geq du + pdv + \sum_{k=1}^n P_k dz_k$. The presentation of the material is completed by the formulation of the most important differential equations of thermodynamics. After that we move on to the issues of technical thermodynamics.

In the axiomatic system of presentation of thermodynamics at the first stage the semantic content of basic concepts and definitions are also given. To justify the concept of temperature the postulates of thermodynamics are presented. Then we introduce the concepts of heat, work and energy and give the law of conservation and transformation of energy [8]. From here the fundamental differences in the content of material are already observed, because they adhere to the approach proposed by K. Karatheodori [9].

At the next stage it is shown that for many parameters the energy conservation equation is represented by the differential Pfaff form: $dQ = P_1(z_1, \dots, z_n)dz_1 + \dots + P_n(z_1, \dots, z_n)dz_n$. After that, an analysis of the holonomicity and non-holonomicity of differential forms is given. In the holonomic Pfaff form there exists an integrating divisor $\lambda(z_1, \dots, z_n)$, when $dQ = \sum_{k=1}^n P_k(z_1, \dots, z_n)dz_k = \lambda d\Phi$. Here Φ is a function of parametres z_1, \dots, z_n which is

a common integral. Then the physical sense of the amount of heat concludes the idea that near any point in space $E^n(z_1, \dots, z_n)$ the points that are not achievable from it in the adiabatic process $dQ = 0$ are existed. This property of space is called "adiabatic unreachability". In [9] K. Karatheodori postulated adiabatic unattainability as a universal property of all thermodynamic systems and proved the validity of the theorem: if in the vicinity of a certain point of n-dimensional space there are points that are not achievable without breaking the equation $\sum_{k=1}^n P_k(z_1, \dots, z_n) dz_k = 0$, then for this equation an integrating divisor in the form of absolute temperature $\lambda = T$ is existed. In turn, the common integral $\Phi(z_1, \dots, z_n) = C$ is defined as the entropy of the thermodynamic system $ds = dQ/T$. Due to the fact that the principle of the existence of entropy is justified we can easily proceed to the conclusion of all other theorems and equations of thermodynamics.

The traditional system of presentation is usually criticized for its too close connection with the processes of operation of heat machines, the insufficient expressiveness of mathematical formalism and the contradiction of some provisions. The axiomatic system is criticized for its abstractness and formally mathematical approach to the establishment of concepts, which does not correspond to the style of thermodynamic research and violates the physical clarity and simplicity of the basic provisions. However, when justifying the fundamentality of thermodynamics, the second system is preferable, although we must agree with critics that it misses the physical content of some concepts.

It is especially noted that in both systems of presentation one initial principle is applied, which is based on all subsequent conclusions. The whole system of thermodynamics is built on the universal position - the inviolability of the thermodynamic form of the equation of the law of conservation and transformation of energy [1]. This equation is a fundamental law. Using it the logical integrity of thermodynamics is originally formed.

3. Thermodynamics methodology based on temporal approach. Historically thermodynamics has developed mainly in a phenomenological way from experiment to theory. However, the methods and means of statistical modeling and differential geometry allow to operate with many model states and processes in the state space of thermodynamic system and to establish basic patterns based on data analysis. In this regard, the model of a perfect gas, which has the extremely simple structure, is the basis for the implementation of the temporal approach in thermodynamics.

Based on statistical modeling methods and differential geometry, it is possible to propose a system of presentation of thermodynamic foundations, using probabilistic and geometric models, and to obtain basic empirical laws of thermodynamics.

Ask ourselves the following problematic question: is it possible in thermodynamics of an ideal gas to obtain the Clapeyron equation, the principle of the existence of entropy and the law of conservation of energy in a theoretical way, using ideas about the dependence of processes on time?

One of the important features of the statics and dynamics of an ideal gas is that its states and thermodynamic processes are equally possible. Using this fact, the statistical modeling method can be applied to obtain the laws of ideal gas. The second feature is that all positions and models in this area can be represented in three-dimensional space by geometric objects with the ability to describe all their parameters. Thus, by methods of statistical modeling and differential geometry using ideas about the temporality of processes, it is necessary to establish and justify:

- Clapeyron equation, Charles and Gay-Lussac laws, etc.;
- the principle of existence of entropy and dependences for its definition;
- the law of conservation and transformation of energy in the form of the first principle of thermodynamics;
- new relationships of great importance for the development of the theory.

4. Perfect gas law. Let's hold the following simple statistical experiment, using the Monte Carlo method. Suppose that the state of the system is characterized by two independent parameters x and y . In the definition area of these variables $E^2(0 \leq x \leq x_{max}, 0 \leq y \leq y_{max})$ parameter x changes from zero to x_{max} , and parameter y changes from zero to y_{max} . In this case when modeling we can get a random point, which is a certain state of the system in space E^2 .

It follows from the probability theory that, if a uniformly distributed two-dimensional random variable is given on the plane, then a geometric definition of probability is applicable. The probability of hit of random point in rectangle is determined in the form of ratio of the domain of the rectangle, formed by coordinate lines x and y to point $A(x, y)$, to the domain of the whole rectangular E^2 [10]. Suppose, that the coordinates of the point $A(x, y)$ during statistical experiments can be selected on segments $[0, x_{max}]$ and $[0, y_{max}]$ absolutely by chance, taking into account the uniform distribution of values x and y . Let's define the probability of the point location as

$$\rho = 0 \text{ if } 0 \leq x \text{ or } y \leq 0; \rho = 1 \text{ if } x > x_{max} \text{ and } y > y_{max};$$

$$\rho = \frac{xy}{x_{max}y_{max}} \text{ if } 0 < x \leq x_{max} \text{ and } 0 < y \leq y_{max}.$$

Let's accept a certain reference point $A_0(x_0; y_0)$ in domain E^2 where $\rho = \rho_0$. We will conduct a linear scaling of the geometric probability. For this procedure we assign a value equal to zero, for example, (degrees or grades) to the point $A_0(x_0; y_0)$, and a value equal to 100 (degrees or grades) to the point $A'_0(x_{max}; y_{max})$. Let's construct a linear scale of intervals in the form of an index t [6]:

$$t = 100 \frac{\rho - \rho_0}{1 - \rho_0} = 100 \frac{xy - x_0y_0}{x_{max}y_{max} - x_0y_0}.$$

Further, we will determine the relationship between probability and index using regression methods.

Let's conduct a computational experiment in the available physical data.

Suppose that the parameter x is the specific volume of the gas v and the parameter y is the gas pressure p . Let's take only two test points for random gas, such as helium. It is known that at a pressure of environment equals to $p_0 = 101325 Pa$, and physical conditions, when the water flows into ice, the specific volume of helium is $v_0 = 5.59910 m^3/kg$ (point A_0). At the same pressure and conditions, when the water boils, the specific volume of helium is $v_{100} = 7.64893 m^3/kg$ (point A'_0). We will consider the gas state is a certain joint event for which pairs of values v and p are chosen by chance. Generating a specific volume v value from zero to v_{100} and a pressure value p from zero to p_0 with a uniformly distributed random number generator, we will obtain a set of helium states for the domain E^2 .

Statistical processing of the data gives a practically functional dependence of the index t on the probability ρ for helium (correlation coefficient 0.999):

$$t = a + b\rho = -273.1496 + 373.1496\rho. \quad (1)$$

Taking the experimental data for hydrogen ($v_0 = 11.12720 m^3/kg$, $v_{100} = 15.20087 m^3/kg$) allows to receive the equation (1) in a look:

$$t = -273.1493 + 373.1493\rho.$$

Similarly we can found, for oxygen:

$$t = -273.1492 + 373.1492\rho;$$

for nitrogen:

$$t = -273.1527 + 373.1527\rho;$$

for neon:

$$t = -273.1519 + 373.1519\rho.$$

Let's introduce, taking into account (1) the concept of an absolute index $T = T_0 + t$, where $T_0 = -a$. Then we have a simple linear relationship of this index with the geometric probability in the form $T = b\rho$. It can be shown that the coefficient T_0 is related to the probability ρ_0 at the reference point A_0 and is equal to

$$T_0 = \frac{100\rho_0}{1 - \rho_0} = 273.1496,$$

while the constants a and b in the equation (1) are practically independent of the choice of the reference point on the straight line $p_0 = 101325 Pa$, i.e. do not depend on the value of the specific volume. The main thing is that the condition $\rho_0 = \frac{v_0}{v_{100}} = 0.732011$, which is determined by the experimental data of heating of perfect gas at low pressure, must be fulfilled on this straight line. Consequently, the obtained results are universal in nature and are not attached to the physical properties of specific gases.

Thus, on the basis of statistical experiments, the absolute zero value was found and it equals to $t_z = -273.1496$ grades on the scale t . From the given results it is obvious the analogies with the processes of constructing temperature scales - the Celsius scale and the Kelvin scale. Everything described above allows to make the following outputs:

- when measuring temperatures on the Kelvin scale inside the scale $0 < T \leq 373.15$, the geometric probability of the state of any abstract thermodynamic system, which is called ideal, is determined. The main feature of such ideal system is the equal choice of values of gas parameters at low pressures;
- the absolute zero value on the Kelvin scale ($T = 0K$, $t_z = 273.1496^\circ C$) is determined exclusively by the selected reference state (normal conditions: $p_0 = 101325 Pa$ and $t_0 = 0^\circ C$), the absolute zero temperature is found from conditions $\rho_0 = \frac{v_0}{v_{100}}$; $T_0 = \frac{100\rho_0}{1 - \rho_0}$. In this case, it is conditionally accepted that $1^\circ C = 1K$. It follows from the equation $T = b\rho$ that the Kelvin scale is a positive scale, since the geometric probability $\rho \geq 0$;
- The Clapeyron equation follows as a consequence from equation (1):

$$T = 373.1496\rho = 373.1496 \frac{pv}{p_0v_{100}} = \frac{373.1496}{1.3661} \frac{pv}{p_0v_0}.$$

So we get the Clapeyron equation in the form:

$$pv = R_i T,$$

here the individual gas constant is equal to $R_i = 0.003661p_0v_0$, which fully corresponds to the experimental data. Similarly, the Monte Carlo method justifies the validity of the laws of Charles and Gay-Lussac [6].

Thus, the thermometry procedures, used in the construction of the absolute temperature scale, are based on the principle of linear scaling of geometric probability. Moreover, the perfect gas model assumes that its parameters are subordinated to a uniform probability distribution, which is not characteristic of real systems.

5. Theoretical dependencies. In addition to the Clapeyron equation for the perfect gas, there is an experimental fact that is associated with the existence of concepts of the amount of heat and heat capacities. Since the ratio $dQ = c_l dT$ is true for any thermal process, the following ratios are also true:

$$\frac{\partial Q}{\partial v} = c_p \left(\frac{\partial T}{\partial v} \right) \text{ and } \frac{\partial Q}{\partial p} = c_v \left(\frac{\partial T}{\partial p} \right), \quad (2)$$

where c_p and c_v are the heat capacities of the perfect gas respectively at constant pressure and constant volume. In the most general case, the values c_p and c_v may depend on the parameters v , p or T . In this case, the change of the amount of heat in any process l can be represented as:

$$dQ = \frac{\partial Q}{\partial v} dv + \left(\frac{\partial Q}{\partial p} \right) dp \text{ or } dQ = c_p \frac{\partial T}{\partial v} dv + c_v \left(\frac{\partial T}{\partial p} \right) dp. \quad (3)$$

According to the relations of differential geometry, the Pfaff form (3) corresponds to the first-order partial differential equation. For example, based on the Clapeyron equation, temperature has the form of a second-degree homogeneous function that satisfies the Euler formula [11]:

$$T = \frac{1}{2} \left(v \frac{\partial T}{\partial v} + p \frac{\partial T}{\partial p} \right).$$

This equation, taking into account relations (2), can be represented as a linear non-homogeneous first-order partial differential equation:

$$\frac{v}{2c_p} \frac{\partial Q}{\partial v} + \frac{p}{2c_v} \frac{\partial Q}{\partial p} = T. \quad (4)$$

The solution $Q = Q(v, p)$ of equation (4) in space $E^3(v, p, Q)$ geometrically represents a surface, which is an integral surface and is determined, using a system of ordinary differential equations for characteristics of the form [12]:

$$2c_p \frac{dv}{v} = 2c_v \frac{dp}{p} = \frac{dQ}{T} = ds, \quad (5)$$

where s is a real parameter that can be defined as the arc length varying along the characteristic curve [12]. At once, from the first two equations (5) for the value ds the following dependence is obtained (it is known from thermodynamics for entropy):

$$ds = \frac{dQ}{T} = c_p \frac{dv}{v} + c_v \frac{dp}{p}; \quad s - s_0 = c_p \ln \left(\frac{v}{v_0} \right) + c_v \ln \left(\frac{p}{p_0} \right), \quad (6)$$

and from the last follows the well-known formula $dQ = T ds$. Thus, in geometric representation the entropy can be determined by the arc length of the characteristic curves corresponding to the field of directions, which is determined by the system of equations (5). Based on this, the integral surface $Q = Q(v, p)$ is uniquely connected to the surface $s = s(v, p)$, taking into account the ratio $dQ = T ds$.

Shall we introduce in consideration a value $du = c_v dT$ that we define as the energy of the perfect gas. The value du is a total differential, since the value dT is a total differential by definition, based on the existence of the Clapeyron equation. Let's present a ratio $dQ = T ds$, taking into account (6), in the form of the equation of conservation and transformation of energy:

$$dQ = du_* + pdv, \text{ where } du_* = \frac{c_p - R_i}{R_i} pdv + \frac{c_v}{R_i} v dp. \quad (7)$$

Suppose that du_* is a total differential, then applying the Euler sign, it can be shown that du_* is a total differential under the condition: $c_p - c_v = R_i$. The last relation is the known Mayer equation for the perfect gas, with the validity of which, the value du_* is identically equal to du :

$$du_* = du = \frac{c_v}{R_i} d(pv) = c_v dT.$$

Thus, under the condition $c_p - c_v = R_i$ equation (7) is represented with energy in the form:

$$dQ = du + pdv, \text{ or } dQ = du + dA. \tag{8}$$

If we do not impose strict conditions as the Mayer equation on the relationship of values c_p , c_v and R_i , then du_* will not be a total differential. Here the important result is can be expressed in the form: the possibility of representing the law of conservation of energy in the form (8) is a consequence of the existence of the Clapeyron equation $pv = R_iT$, which we have determined on the basis of statistical experiments, as well as dependence on the amount of heat $dQ = Tds$. Moreover, this law in the form (8) is a consequence arising from the principle of the existence of entropy and the dependencies of the form (5).

6. Justification of the law of energy conservation based on computational experiments. Now on the basis of statistical modeling we will justify the law of energy conservation for perfect gas in a form (8). Using the Monte Carlo method, we will conduct a statistical experiment that allows us to generate many processes for changing the states of a perfect gas. To do this, we will randomly create the points of the beginning and the end of each thermodynamic process, after which we will connect them to each other. This procedure we will be carried out several times for various gases.

For example, for helium, generating a specific volume value v from zero to v_{100} and a pressure value p from zero to p_0 by a uniformly distributed random number generator, we get 1000 states that will determine the beginning of the process (point $A_1(v_1, p_1)$). Similarly, we create another 1000 states that will determine the end of the process (point $A_2(v_2, p_2)$). Connecting points A_1 and A_2 by straight lines, we get 1000 linear processes of changing helium states. Now let's check the validity of the law of energy conservation in the form (8). Integrating (8) over the curve of each process from point A_1 to point A_2 , using dependence

$$dQ = Tds = \frac{c_p}{R_i}pdv + \frac{c_v}{R_i}vdp,$$

we find:

$$\Delta Q = \frac{c_p}{R_i}(p_1 - kv_1)(v_2 - v_1) + k\frac{c_p + c_v}{2R_i}(v_2^2 - v_1^2), \quad k = \frac{p_2 - p_1}{v_2 - v_1},$$

where the curve of each process is defined by the equation

$$\frac{p - p_1}{p_2 - p_1} = \frac{v - v_1}{v_2 - v_1}.$$

Similarly,

$$\Delta u = c_v(T_2 - T_1); \Delta A = (p_1 - kv_1)(v_2 - v_1) + \frac{k}{2}(v_2^2 - v_1^2).$$

The data processing results of the computational experiment for 1000 linear helium state change processes are shown in Figure 1.

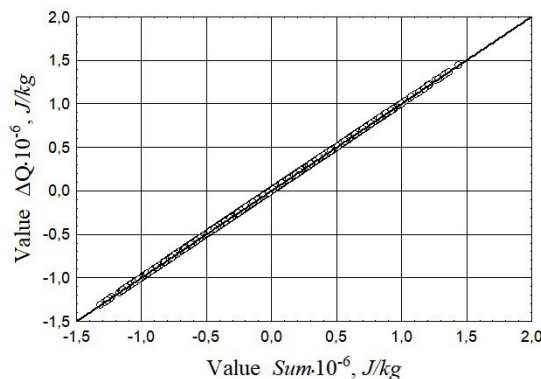


Fig. 1. The equation for conservation of energy (8) for helium state change processes, $Sum = \Delta u + \Delta A$ (number of statistical experiments - 1000)

Рис. 1. Уравнение сохранения энергии (8) для процессов изменения состояний гелия, $Sum = \Delta u + \Delta A$ (число статистических экспериментов – 1000)

As can be seen from the figure 1, the equation (8) holds exactly at least for linear thermodynamic processes. Similar results were obtained for other perfect gases (hydrogen, oxygen, nitrogen, neon, etc.).

Thus, the law of energy conservation for a perfect gas is a mathematical model and can be justified by conducting statistical experiments.

7. Temporal patterns. By the temporal method we can study both linear and nonlinear processes and assess the degree of influence of time τ during processing:

$$v = v_l(\tau); p = p_l(\tau); T = T_l(\tau). \quad (9)$$

We will assume that each process is done in a definitely given time τ_0 and the initial moments of time equal to zero are correspond to the points $A_1(v_1, p_1)$. Since the process paths have different lengths of segments and the time intervals for each process are also different, the speeds of the processes will be different. Let's construct a linear scale of absolute temperature between points $O(v = 0; p = 0; T = 0)$ and $A_0(v_0; p_0; T_0)$, then the scale equation will be:

$$\frac{T}{T_0} = \frac{v}{v_0} = \frac{p}{p_0} = \frac{\tau}{\tau_0}.$$

This scale belongs to the equation of the state $pv = R_i T$. The linear segment between the points O and A_0 can be divided into 273.15 parts, and each degree corresponds to a certain length of the segment δ . For the temporological estimate of processes we will introduce the concept of the amount of impact - a mathematical value that determines the intensity and duration of the processes of changing the state of a perfect gas, based on the external and internal conditions of the impact [1]. The amount of impact Q_* will mathematically characterize the thermodynamic process l , unlike the amount of heat Q gives a physical characteristic of the process, based on experimental data and is defined as $dQ = T ds = \frac{c_p}{R_i} p dv + \frac{c_v}{R_i} v dp$. We will use the amount of impact as a criterion for the similarity of processes to each other:

$$\Delta Q_* = \frac{1}{\delta} \int_l T_l(\epsilon) d\epsilon. \quad (10)$$

where $d\epsilon$ is the arc differential of the curve l . Here the value T will characterize the states during the process l , and the length of the curve will characterize the duration of this process. To determine the values Q_* and δ we shall lead curvilinear integrals the definite integrals over time.

For all generated thermodynamic processes let's determine the amount of impact according to the ratio (10). By specifying the unit of measurement δ as a fraction $1/273.15$ of changing of the amount of impact for the process OA_0 and determining the line integral (10) for an arbitrary linear process $l = A_1A_2$, we shall get the value ΔQ_* in a dimensionless form:

$$\Delta Q_* = \frac{1}{\sqrt{2}} \left(T_1 + T_2 + \frac{p_1 v_2 + p_2 v_1}{2R_i} \right) \sqrt{\left(\frac{p_2 - p_1}{p_0} \right)^2 + \left(\frac{v_2 - v_1}{v_0} \right)^2}. \quad (11)$$

We'll determine the line integrals and the length of the path of each process on the basis of parametric setting of linear processes with respect to the time τ :

$$\frac{T - T_1}{T_2 - T_1} = \frac{v - v_1}{v_2 - v_1} = \frac{p - p_1}{p_2 - p_1} = \frac{\tau}{\tau_0}.$$

According to equation (11) the changing of the amount of impact is always a positive number. In [6] it has been shown that if any value, for example Q_* , characterizes the dynamic process of changing properties of an object and is additive with respect to the curve of this process, then the changing of this value can be represented as $dQ_* = \theta ds_*$, where θ - the interaction potential, which depends only on the parameters of the properties, ds_* - the change of the state coordinate and $ds_* = \Phi(\tau) d\tau$. According to this, we introduce the concept of dynamic entropy ds_* as a temporal characteristic of any process in the form of a function of time. At the same time the method of determining (measuring) this value is directly related to the amount of impact $ds_* = dQ_*/T$.

The general solution of the equation (4) is a family of integral solutions in a space $E^3(v, p, Q)$, that are associated with the characteristics (5) of this equation. Each solution in the state space corresponds to a certain state change process $l(\tau)$, which is characterized by properties of parameters, changing in time (9). Only one characteristic curve (5) passes through each point of the process curve [12].

Based on this, dynamic entropy value can be assigned for each point of any process curve $l(\tau)$. In other words, the length of the curve $l(\tau)$ is uniquely related to the value Δs_* and the length of the curve $l(\tau)$ may be measured in units of this value and vice versa. Thus, the entropy differential ds_* will be proportional to the differential of the arc of the process curve $l(\tau)$, which in a dimensionless form is determined according to the relationship:

$$d\epsilon = \sqrt{\left(\frac{v_l(\tau)}{v_0} \right)^2 + \left(\frac{p_l(\tau)}{p_0} \right)^2} d\tau,$$

where the parameters are given by equations (9). Since in any process the value $\Delta\epsilon$ always increases over time, the rise of dynamic entropy is determined by the irreversible course of time.

8. Justification of established temporal patterns. Using the obtained patterns, we will compare the modeling results with experimental data. Based on known values ΔQ_* for each process, we'll find changes of the values of dynamic entropy Δs_* and establish the relationship between the values ΔQ and ΔQ_* . Figure 2 shows the dependence of the change of the amount of heat on the change of the amount of impact, which is expressed by almost straight lines. There are four processes l_1, l_2, l_3, l_4 here with the following parameters:

- $l_1 = A_1A_2: v_1 = 7.50 \text{ m}^3/\text{kg}, v_2 = 2.70 \text{ m}^3/\text{kg}, p_1 = 42300 \text{ Pa}, p_2 = 12200 \text{ Pa};$
- $l_2 = A_1A_2: v_1 = 2.00 \text{ m}^3/\text{kg}, v_2 = 6.50 \text{ m}^3/\text{kg}, p_1 = 1500 \text{ Pa}, p_2 = 100000 \text{ Pa};$
- $l_3 = A_1A_2: v_1 = 7.00 \text{ m}^3/\text{kg}, v_2 = 3.00 \text{ m}^3/\text{kg}, p_1 = 85000 \text{ Pa}, p_2 = 25000 \text{ Pa};$
- $l_4 = A_1A_2: v_1 = 1.50 \text{ m}^3/\text{kg}, v_2 = 7.50 \text{ m}^3/\text{kg}, p_1 = 30000 \text{ Pa}, p_2 = 70000 \text{ Pa}.$

The dependence of thermodynamic entropy Δs on dynamic entropy Δs_* for each process has a weakly expressed nonlinear character (Figure 3). Entropy increments Δs in processes can increase or decrease, be both positive and negative, and changes of the dynamic entropy are strictly positive and always increase. In this case the value Δs_* is determined by the equation $\Delta s_* = \Delta Q_*/T$ and the entropy of the state Δs – according to (6).

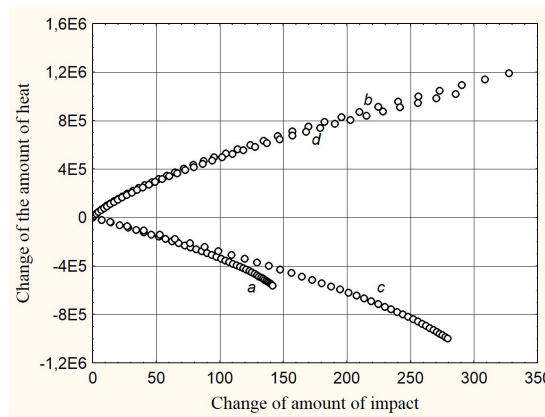


Fig. 2. Dependencies of amount of heat ΔQ on amount of impact ΔQ_* for helium state change processes: a) process l_1 ; b) process l_2 ; c) process l_3 ; d) process l_4

Рис. 2. Зависимости количества теплоты ΔQ от количества воздействия ΔQ_* для процессов изменения состояний гелия: а) процесс l_1 ; б) процесс l_2 ; в) процесс l_3 ; д) процесс l_4

The relationship of dynamic entropy with the length of the process path is shown in Figure 4. An important statement follows from this: in any thermodynamic process the change of dynamic entropy uniquely depends on the length of path of this process and, as a result, on time τ . Since changes in entropy Δs are closely related to changes in value Δs_* (Fig. 3), then thermodynamic entropy Δs also uniquely depends on the length of the process path $\Delta \epsilon$ and, of course, on time τ .

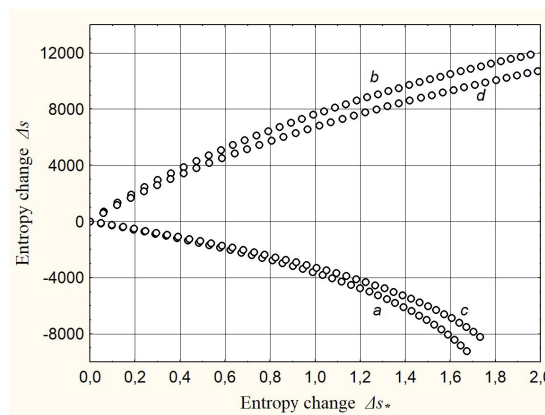


Fig. 3. Dependencies of thermodynamic entropy Δs on dynamic entropy Δs_* for helium state change processes: a) process l_1 ; b) process l_2 ; c) process l_3 ; d) process l_4

Рис. 3. Зависимости термодинамической энтропии Δs от динамической энтропии Δs_* для процессов изменения состояний гелия: а) процесс l_1 ; б) процесс l_2 ; в) процесс l_3 ; д) процесс l_4

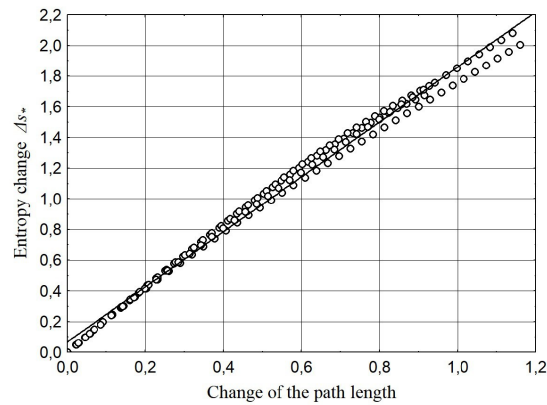


Fig. 4. Dependencies of dynamic entropy Δs_* on the length of the process path $\Delta \epsilon$ for helium state change processes:
a) process l_1 ; b) process l_2 ; c) process l_3 ; d) process l_4

Рис. 4. Зависимости динамической энтропии Δs_* от длины траектории процессов $\Delta \epsilon$ при изменении состояний гелия: а) процесс l_1 ; б) процесс l_2 ; в) процесс l_3 ; г) процесс l_4

Thus, the relationship between changes of the amount of heat and the amount of exposure, between thermodynamic and dynamic entropies can be established. As well as relationships between entropy and the path length of the process have occurred. It was done on the basis of experimental data in the thermodynamic process of changing of the perfect gas states.

8. Discussion of results and conclusions. Thermodynamic temperature is a fundamental concept in thermodynamics. However, as can be seen from the results obtained, this value is a mathematical model since a reference point A_0 for the constructing of a temperature scale is taken randomly. The domain E^2 is also freely selected, which allows you to set a second reference point A'_0 . Based on the obtained equation $T = 100\rho_0/(1 - \rho_0)$, the absolute zero value will change in the Celsius scale in the model by setting the value $\rho_0 = v_0/v_{100}$. But experimental data for all perfect gases give the same amount 0.732011 for this value. That is why the model of thermodynamic temperature is fundamental in thermodynamics, since it is of a system-wide nature.

It should be noted that for real gases outside the domain of ideal thermodynamic states, the principle of equal probability of states will no longer be fulfilled. In this case, it will be necessary to take into account the existing laws of distribution for a two-dimensional random variable, which will be associated with empirically established state equations - the Van der Waals equation, the virial equation, etc. The extension of the proposed method to this case is a separate problem of statistical modeling.

The research results make it possible to propose new methods for determining and measuring entropy when changing of the states of thermodynamic systems. They are based on the established relationships of thermodynamic and dynamic entropy, entropy and the path length of the process, as well as entropy and time. Therefore, further research should be aimed at the practical application of the proposed methods.

In conclusion, we note that the proposed system of presentation of the fundamentals of thermodynamics principally differs from the traditional and axiomatic systems of presentation. The lack of time in classical thermodynamics, as a basic physical theory, is paradoxical. In turn, the temporal approach is based on dynamic process models, where time is fundamental. The method, proposed in the article, allows to solve the problem of introduction of time into classical thermodynamics and reveal the physical and mathematical meaning of entropy. It also permits to exclude the contradictory concept of equilibrium of processes and to formulate adequate ideas about the irreversibility of thermodynamic processes. In turn, generalization of the obtained patterns in multidimensional thermodynamic systems is given in the work [6].

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INFORMATION ABOUT THE AUTHORS

Gennadiy V. Averin – Doctor of Engineering Sciences, Professor, Head of the Department of Computer Technologies Donetsk State University, Donetsk, Russia

Maria V. Shevtsova – Candidate of Physical and Mathematical Sciences, Associate Professor of the Department of Mathematics, Belgorod National Research University, Belgorod, Russia

Anna V. Zvyagintseva – Doctor of Physical and Mathematical Sciences, Head of the Department of Physics, Moscow Technical University of Communications and Informatics, Moscow, Russia

СВЕДЕНИЯ ОБ АВТОРАХ

Аверин Геннадий Викторович – доктор технических наук, профессор, заведующий кафедрой компьютерных наук, Донецкий государственный университет, г. Донецк, Россия

Шевцова Мария Витальевна – кандидат физико-математических наук, доцент кафедры математики, Белгородский государственный национальный исследовательский университет, г. Белгород, Россия

Звягинцева Анна Викторовна – доктор технических наук, профессор, профессор кафедры компьютерных наук, Донецкий государственный университет, г. Донецк, Россия

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