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## To the Question of Rigorous Axiomatization of Thermodynamics

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**Abstract.** An attempt is made in the article to rigorously axiomatize thermodynamics, i.e., to construct such a presentation of it in which its entire presentation follows from several axioms. At the same time, it turns out that the classical point of view, which consists in the fact that the entire building of thermodynamics can be built on five principles (the so-called minus first, zero, first, second and third laws of thermodynamics), does not stand up to criticism — the number of axioms is much larger. An attempt to reveal the logical necessity of introducing these axioms into the foundations of thermodynamics and revealing their very physical essence (formulation) is undertaken in this article.

**Keywords:** foundations of thermodynamics, minus the third law of thermodynamics, state of thermodynamic equilibrium, minus the second law of thermodynamics, internal energy of a thermodynamic system, minus the first law of thermodynamics, thermodynamic work.

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Thermodynamics as a science began to emerge at the end of the XVI century, when Galileo invented the first thermometers. Since that time, such prominent scientists as Robert Boyle, Jacques Alexander Cesar Charles, Joseph Louis Gay-Lussac, Robert Hooke, Sadi Carnot, from whose works thermodynamics began to acquire truly scientific features, James Joule, Rudolf Clausius and William Thomson, who introduced thermodynamics the most important concept of entropy, Walter Nernst and Max Planck, who established the third law of thermodynamics and completed that part of thermodynamics that was logically irreducible from the rest of it and was based only on physical experiment, took part in the construction of thermodynamic science.

Despite such a solid contingent of truly outstanding physicists, the question of a strict axiomatic justification of this science still worries the minds of scientists today. Despite the large number of excellent textbooks and articles [1–9] on this discipline, it is the foundations of thermodynamics that are not presented in them logically satisfactorily enough. Namely, each of the axioms presented in these textbooks ultimately contains no more than five axioms (often called minus the first, zero, first, second and third laws of thermodynamics). And these axioms, as convincingly shown in this article, are not enough for a logically rigorous construction of thermodynamics. That is why the question of axiomatization of thermodynamics is relevant today.

In this article, after many years of studying this issue, the author attempts to present the axiomatics of thermodynamics, which was invented by the author himself.

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## 1. Minus the third law of thermodynamics

This postulate is as follows. Let there be a macroscopic system - one or several material bodies, consisting of a large number of particles that make up these bodies. We will call a macroscopic system isolated if it does not exchange matter or energy with the surrounding material bodies. We will call a macroscopic system thermodynamic if it satisfies the principles of thermodynamics. The statement minus the third law of thermodynamics is that isolated thermodynamic systems eventually come to the so-called state of thermodynamic equilibrium, in which they remain for an arbitrarily long time and from which they can never exit spontaneously.

Thus, thermodynamics does not study all macroscopic systems, but only those that satisfy the minus third law. We note right away that there are macroscopic systems that do not come to a state of thermodynamic equilibrium over time (let alone remain in this state for an arbitrarily long time). The Universe is a classic example of such a macroscopic system.

It should be noted that this thermodynamic axiom is often presented as "minus the first law of thermodynamics". Solely due to the fact that this provision of thermodynamic science is obviously fundamental, we introduce it as the very first among other provisions-axioms of thermodynamics. That is why, in the framework of this article, it is called the minus third law of thermodynamics.

## 2. Minus the second law of thermodynamics

### 2.1. Internal energy of a macroscopic system

In this section, remaining within the framework of classical Newtonian mechanics, we will prove that the total mechanical energy of any macroscopic system (not necessarily thermodynamic) can be represented as the sum of two quantities that are essentially different in their physical nature: the so-called internal energy of the system and the energy, which, for reasons of expediency, it is reasonable to call external. We do not provide a proof of this fact within the framework of quantum mechanics in this article.

Any macroscopic system consists of a gigantic number of moving and interacting particles. It is natural to define the energy of a macroscopic system as the sum  $K$  of the kinetic energies of all the particles that make up this system, the potential energy  $\Pi^{(\text{out})}$  of these particles in external fields, and the potential energy of their interaction  $\Pi^{(\text{int})}$  :

$$E = K + \Pi^{(\text{out})} + \Pi^{(\text{int})}. \quad (1)$$

Note that within the framework of the nonrelativistic theory, the independence of the quantities  $\Pi^{(\text{out})}$  and  $\Pi^{(\text{int})}$  from the reference frame relative to which the quantity  $E$  is considered is obvious. The situation is essentially different with the quantity  $K$ .

In the courses of classical mechanics, the so-called Koenig's theorem on the representation of the total kinetic energy of a system of moving particles is proved. According to Koenig's theorem

$$K = K_C + \frac{1}{2} \sum_{i=1}^N m_i \mathbf{v}^2, \quad (2)$$

where  $K_C$  is the kinetic energy of the system in the reference frame of the center of mass,  $m_i$  is the mass of the  $i$ -th particle,  $i \in \{1, 2, \dots, N\}$ ,  $N$  is the number of particles in the system,  $\mathbf{v}$  is

the velocity of the center of mass. Again, according to Koenig's theorem

$$K_C = \frac{1}{2} \sum_{i=1}^N I_i \boldsymbol{\omega}_i^2 + \frac{1}{2} \sum_{i=1}^N m_i \mathbf{v}_{iC}^2, \quad (3)$$

where  $\boldsymbol{\omega}_i$  is the vector of the angular velocity of rotation of the  $i$ -th particle in the frame of reference of the center of mass of this particle itself,  $I_i$  — the moment of inertia of this particle about the axis passing through the center of mass of this particle parallel to the vector  $\boldsymbol{\omega}_i$  (axis of rotation),  $\mathbf{v}_{iC}$  — velocity of the  $i$ -th particle relative to the center of mass of the system. Taking into account that the entire macroscopic system can perform rotational motion with an angular speed  $\boldsymbol{\Omega}$  (around the center of mass) it is advisable to decompose the vector of the velocity of the  $i$ -th particle in the frame of reference of the center of mass  $\mathbf{v}_{iC}$  into two components — the linear speed of rotation about the axis passing through the center of mass of the system parallel to the vector  $\boldsymbol{\Omega}$ , and the speed  $\mathbf{u}_i$  relative to the rotating system:

$$\mathbf{v}_{iC} = \boldsymbol{\Omega} \times \mathbf{r}_i + \mathbf{u}_i. \quad (4)$$

Substituting, further, equality (4) into the second term of equation (3), we obtain the identity:

$$\frac{1}{2} \sum_{i=1}^N m_i \mathbf{v}_{iC}^2 = \frac{1}{2} I \boldsymbol{\Omega}^2 + \frac{1}{2} \sum_{i=1}^N m_i \mathbf{u}_i^2, \quad (5)$$

where

$$I = \sum_{i=1}^N m_i \rho_i^2, \quad (6)$$

$$\rho_i = |\mathbf{r}_i| \cdot \sin(\widehat{\boldsymbol{\Omega}, \mathbf{r}_i}). \quad (7)$$

Note that the term  $\sum_{i=1}^N m_i \mathbf{u}_i \cdot (\boldsymbol{\Omega} \times \mathbf{r}_i) = \boldsymbol{\Omega} \cdot \sum_{i=1}^N (\mathbf{r}_i \times m_i \mathbf{u}_i) = 0$  due to the randomness of the movement of the particles forming the macroscopic system.

Summarizing all of the above, we see that the kinetic energy of the particles of the system in the system of its center of mass can be written as follows:

$$K_C = \frac{1}{2} \sum_{i=1}^N I_i \boldsymbol{\omega}_i^2 + \frac{1}{2} \sum_{i=1}^N m_i \mathbf{u}_i^2 + \frac{1}{2} I \boldsymbol{\Omega}^2. \quad (8)$$

The total kinetic energy of the system can be written as the sum of two terms that are essentially different in physical nature:

$$K = K_1 + K_2, \quad (9)$$

where

$$K_1 = \frac{1}{2} \sum_{i=1}^N I_i \boldsymbol{\omega}_i^2 + \frac{1}{2} \sum_{i=1}^N m_i \mathbf{u}_i^2 - \quad (10)$$

contribution to the total kinetic energy of the system due to the motion of particles relative to the center of mass of the macroscopic system,

$$K_2 = \frac{1}{2} I \boldsymbol{\Omega}^2 + \frac{1}{2} M \mathbf{v}^2, \quad (11)$$

where  $M = \sum_{i=1}^N m_i$ , is the contribution due to the motion of the macroscopic system as a whole.

Now we can write the final expression for the total energy of the macroscopic system:

$$E = E^{(\text{out})} + E^{(\text{int})}, \quad (12)$$

where

$$E^{(\text{out})} = \frac{1}{2}M\mathbf{v}^2 + \frac{1}{2}I\Omega^2 + \Pi^{(\text{out})} - \quad (13)$$

energy, which, based on their considerations of expediency, it is reasonable to call external. The value

$$E^{(\text{int})} = U = \frac{1}{2} \sum_{i=1}^N m_i \mathbf{u}_i^2 + \frac{1}{2} \sum_{i=1}^N I_i \omega_i^2 + \Pi^{(\text{int})} - \quad (14)$$

it is expedient to call the internal energy of a macroscopic system.

So, we have proved that the total mechanical energy of any macroscopic system can be represented as the sum of two terms (13) and (14) that are essentially different in physical nature, which it is reasonable to call the external and internal energy of the macroscopic system, respectively.

## 2.2. Formulation minus the second law of thermodynamics

Let us now formulate the minus second law of thermodynamics, otherwise called the postulate of additivity: the internal energy of a macroscopic thermodynamic system is equal to the sum of the internal energies of any two of its macroscopic thermodynamic subsystems that do not have common macroscopic thermodynamic subsystems and together form a given (macroscopic) thermodynamic system. Thus, for a (macroscopic) thermodynamic system, it is possible to neglect the term  $U_{12}$  in the expression for the total internal energy of the system:

$$U = U_1 + U_2 + U_{12}, \quad (15)$$

where  $U_1$  and  $U_2$  are the internal energies of the macroscopic thermodynamic subsystems referred to in the formulation minus the second law of thermodynamics (having no common macroscopic subsystems and together forming this one), and  $U_{12}$  — energy of interaction of these subsystems. It is important to emphasize that in the aforementioned formulation of the law, we are talking about macroscopic thermodynamic subsystems (a macroscopic thermodynamic system). This law completely loses its force on the microscales of atoms and molecules that make up a thermodynamic system. For example, when calculating the internal energy density of a crystal, one should take into account not only the energy of the electron-electron and ion-ion interactions, but also the energy of the electron-ion interaction. In the next paragraph, we will give an example of a system that does not satisfy the minus second law of thermodynamics (i.e., one where the term  $U_{12}$  in formula (15) cannot be neglected even when passing to macroscales) and, thus, is not a thermodynamic.

## 2.3. Newtonian gravitating globe as an example of a macroscopic system with non-additive energy

Consider a homogeneous globe of mass  $M$  and radius  $R$  that creates a Newtonian gravitational field. The potential energy of the gravitational interaction of all small masses forming the globe

is expressed by the following sixfold integral

$$\Pi = -\frac{1}{2} \iiint \iiint \frac{G dm_1 dm_2}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}, \quad (16)$$

where  $G$  is the gravitational constant,

$$dm_i = \frac{M}{\frac{4}{3}\pi R^3} dx_i dy_i dz_i, \quad i \in \{1, 2\}. \quad (17)$$

Integral (16) is well known in potential theory. Its value is easiest to calculate by successive calculation of two triple integrals. In this case, the first of them is calculated by the transition to a cylindrical coordinate system, and the second — to a spherical one (see e.g. tutorial [10]). The result is the well-known answer:

$$\Pi = -\frac{3}{5} \frac{GM^2}{R}. \quad (18)$$

For our purposes, it is more expedient to write the right side of formula (18) in variables  $\rho$  (density) and  $V$  (volume) (instead of  $M$  and  $R$ ). Substituting elementary equalities  $M = \rho V$  and  $R = \left(\frac{3V}{4\pi}\right)^{\frac{1}{3}}$  into formula (18), we find an expression for  $\Pi$  in the form we need:

$$\Pi = -\frac{\sqrt[3]{36\pi}}{5} G \rho^2 V^{\frac{5}{3}}. \quad (19)$$

Considering, further, that, firstly, the kinetic energy of the particles forming the globe is proportional to their number  $N$ , and, secondly, that the volume  $V$  of the gravitating globe is also proportional to this number, we find that the internal energy of the gravitating globe can be written as follows:

$$U = aN - bN^{\frac{5}{3}}, \quad (20)$$

where  $a$  and  $b$  are positive constants. The necessary and sufficient condition for a macroscopic system to satisfy the postulate of additivity is, obviously, that the internal energy of this macroscopic system be proportional to the number of particles in the system. That is why the condition under which the gravitating globe satisfies the minus second law of thermodynamics is, obviously, that the first term on the right side of (20) be substantially greater than the second:

$$aN \gg bN^{\frac{5}{3}}, \quad (21)$$

or, in other words,

$$N \ll \left(\frac{a}{b}\right)^{\frac{3}{2}}, \quad (22)$$

i.e., the number of particles must be significantly less than the value  $\left(\frac{a}{b}\right)^{\frac{3}{2}}$ . For macroscopic systems of small sizes, for example, a ball from a bearing, this condition, of course, is satisfied, i.e., a ball from a bearing satisfies minus the second law of thermodynamics. For, for example, planet Earth, this condition, on the contrary, is not fulfilled. That is, the planet Earth does not satisfy minus the second law of thermodynamics.

For the convenience of the reader, we present here specific estimates of the quantities  $a$ ,  $b$ ,  $\left(\frac{a}{b}\right)^{\frac{3}{2}}$  for the steel from which the bearing balls are made. Substituting known physical

constants and reference data  $k_B = 1.38067 \cdot 10^{-16} \frac{\text{erg}}{\text{K}}$ ,  $T = 273.15\text{K}$ ,  $G = 6.6743 \cdot 10^{-8} \frac{\text{cm}^3}{\text{g} \cdot \text{c}^2}$ ,  
 $\rho = 6.68 \frac{\text{g}}{\text{cm}^3}$ ,  $M = 180 \frac{\text{g}}{\text{mol}}$ ,  $N_A = 6 \cdot 10^{23} \frac{1}{\text{mol}}$  into easily derivable formulas for  $a$  and  $b$ , we get

$$a = \frac{3}{2} k_B T = 56.57 \cdot 10^{-15} \text{erg}, \quad (23)$$

$$b = \frac{\sqrt[3]{36\pi}}{5} G \rho^{\frac{1}{3}} \left( \frac{M}{N_A} \right)^{\frac{5}{3}} = 16.34 \cdot 10^{-44} \text{erg}, \quad (24)$$

$$\left( \frac{a}{b} \right)^{\frac{3}{2}} = 2.04 \cdot 10^{44}. \quad (25)$$

It is interesting to compare the result (25) with the fact that, as shown by elementary calculations, the number of molecules in a ball from a bearing with a radius of 0.5 cm is approximately  $N_{\text{bear}} = 1.17 \cdot 10^{22}$ , while as if the "ball" had the radius of the Earth, this amount would be  $N_{PE} = 2.42 \cdot 10^{49}$ . As we can see, numerical estimates fully confirm criterion (22), under which the additivity postulate is valid.

### 3. Minus the first law of thermodynamics

#### 3.1. Motivational considerations

The most important quantity to deal with in thermodynamics is work. This concept is first encountered in mechanics and subsequently occurs many times in all other branches of physics. Let us recall the expressions encountered in various sections of physics for the work done by one or another type of matter. In mechanics, the work done by the force  $\mathbf{F} = F_x \mathbf{e}_x + F_y \mathbf{e}_y + F_z \mathbf{e}_z$  on a material point when it moves to  $d\mathbf{r} = dx \mathbf{e}_x + dy \mathbf{e}_y + dz \mathbf{e}_z$ , is equal to

$$\delta A = \mathbf{F} d\mathbf{r} = F_x dx + F_y dy + F_z dz. \quad (26)$$

The work done by the forces arising from the deformation of a solid body, per unit volume of this body, is equal to

$$\delta A = - \sum_{i=1}^3 \sum_{j=1}^3 \sigma_{ij} d\varepsilon_{ij}, \quad (27)$$

where  $\sigma_{ij}$ ,  $i \in \{1, 2, 3\}$ , — stress tensor components,  $\varepsilon_{ij}$ ,  $i \in \{1, 2, 3\}$ , — strain tensor components. When a rigid body rotates through an angle  $d\boldsymbol{\varphi} = d\varphi_x \mathbf{e}_x + d\varphi_y \mathbf{e}_y + d\varphi_z \mathbf{e}_z$  under the action of a moment of forces  $\mathbf{M} = M_x \mathbf{e}_x + M_y \mathbf{e}_y + M_z \mathbf{e}_z$ , the force that creates this moment does work

$$\delta A = \mathbf{M} d\boldsymbol{\varphi} = M_x d\varphi_x + M_y d\varphi_y + M_z d\varphi_z. \quad (28)$$

Let us give further examples from molecular physics. The pressure forces of a gas that creates pressure  $p$ , when its volume changes by  $dV$ , do work

$$\delta A = p dV. \quad (29)$$

The work done by tension forces in a thin film with surface tension  $\sigma$  when its surface area changes by  $dS$  is equal to

$$\delta A = -\sigma dS. \quad (30)$$

But in the case of a gas enclosed in a soap bubble, the thermodynamic work of the "gas + bubble" system is already equal to

$$\delta A = pdV - \sigma dS, \quad (31)$$

at that, in the general case, there is no connection between the quantities  $dS$  and  $dV$ . The connection appears only in the case of a homothetic change of its volume by the bubble.

Let us give further examples from electromagnetism. Recall that the work of external forces of an electric battery with EMF  $E$  when a charge  $dq$  passes through it is equal to

$$\delta A = Edq. \quad (32)$$

Finally, the work done by the electric field in a unit volume of a dielectric with an elementary change in the electric field in it is equal to

$$\delta A = -\frac{1}{4\pi} \mathbf{E} d\mathbf{D} = -\frac{1}{4\pi} (E_x dD_x + E_y dD_y + E_z dD_z), \quad (33)$$

where  $E_i$ ,  $i \in \{x, y, z\}$ , —  $i$ -th component of the electric field strength in the dielectric,  $D_i$ ,  $i \in \{x, y, z\}$ , —  $i$ -th component of electric field induction in a dielectric. An analogue of the expression (30) in the case of magnetics is written as follows:

$$\delta A = -\frac{1}{4\pi} \mathbf{H} d\mathbf{B} = -\frac{1}{4\pi} (H_x dB_x + H_y dB_y + H_z dB_z), \quad (34)$$

where  $H_i$ ,  $i \in \{x, y, z\}$ , —  $i$ -th component of the magnetic field strength in the magnetic,  $B_i$ ,  $i \in \{x, y, z\}$ , —  $i$ -th component of magnetic field induction in a magnetic.

One look at expressions (23)–(31) is enough to notice that in all cases the work is a differential 1-form (otherwise called the Pfaffian form). It is this observation in a strict formulation reflects the minus first law of thermodynamics. In addition, this law introduces the most important concepts of thermodynamic forces and thermodynamic coordinates into thermodynamics.

### 3.2. The concept of equilibrium and non-equilibrium thermodynamic processes

There can be, generally speaking, a lot of states of thermodynamic equilibrium, in which, according to the minus third law of thermodynamics, any thermodynamic system comes. Trying to strictly axiomatize thermodynamics, we currently do not have even the most elementary of its apparatus, and for this reason we are not in a position to indicate any real way to distinguish between two different states of thermodynamic equilibrium. From a purely logical point of view, this does not prevent us, however, from formulating the most important concept of a thermodynamically equilibrium process. We will say that a macroscopic (not necessarily thermodynamic) system participates in a process if its state changes over time (in other words, the macroscopic parameters characterizing the system change over time). A process in which it is the thermodynamic system that participates will be called equilibrium if at any time of this process the system is in a state of thermodynamic equilibrium. If at any time the state of the thermodynamic system is not in equilibrium, then such a process is called nonequilibrium. However, it may also happen that in some time intervals the state of the thermodynamic system at any of their moments is in equilibrium, and in other time intervals at any of their moments, on the contrary, it is nonequilibrium. In this case, we are simply dealing with a situation where equilibrium processes are replaced by nonequilibrium ones.

In addition to the concepts of equilibrium and nonequilibrium processes, an important role in thermodynamics is played by the concept of the so-called quasi-static process — a process in which the parameters characterizing a macroscopic system change physically infinitely slowly. Mathematically, the condition of the quasi-static process can be expressed as follows:

$$\frac{da}{dt} = \dot{a} \ll \frac{\Delta a}{\tau}, \quad (35)$$

where  $\dot{a} = \frac{da}{dt}$  is the derivative of the parameter  $a$  characterizing the system with respect to time,  $\Delta a$  is the deviation of the parameter  $a$  from the thermodynamically equilibrium value,  $\tau$  is the relaxation time of the parameter  $a$  (i.e., the time during which it changes by  $\Delta a$ , eventually taking on the value that it has in a state of thermodynamic equilibrium).

Obviously, any equilibrium process is quasi-static. On the contrary, not every quasi-static process is equilibrium. As a classic example of such a non-equilibrium quasi-static process, the process of heat exchange between bodies with different temperatures, arbitrarily slowed down by the introduction of thermal resistance between them, is usually given.

### 3.3. Formulation minus the first law of thermodynamics

We now turn to the formulation of the minus first law of thermodynamics. In its most general formulation, it states the following. For each thermodynamic system in the state of its thermodynamic equilibrium, there are such quantities  $x_1, x_2, \dots, x_n$ , each of which corresponds to the quantity  $X_i$ ,  $i \in \{1, 2, \dots, n\}$ , such that the work of this thermodynamic system in a thermodynamically equilibrium process in which the thermodynamic system passes from a state with parameters  $x_1^{(0)}, x_2^{(0)}, \dots, x_n^{(0)}$  to a state with parameters  $x_1^{(1)}, x_2^{(1)}, \dots, x_n^{(1)}$ , can be calculated as an integral from  $(x_1^{(0)}, x_2^{(0)}, \dots, x_n^{(0)})$  to  $(x_1^{(1)}, x_2^{(1)}, \dots, x_n^{(1)})$  of the following differential 1-form:

$$\delta A = \sum_{i=1}^n X_i dx_i. \quad (36)$$

Quantities  $x_1, x_2, \dots, x_n$ , referred to in the formulation minus the first law of thermodynamics are called the thermodynamic coordinates of the thermodynamic system, the quantity  $X_i$ ,  $i \in \{1, 2, \dots, n\}$  is the thermodynamic force corresponding to the thermodynamic coordinate  $x_i$ , the number  $n$  is the number of degrees of freedom of the thermodynamic system. In the case of  $n = 1$ , the thermodynamic system is called simple. In conclusion, we note that in order to directly calculate the work performed by a thermodynamic system in a thermodynamically equilibrium process using formula (33), it is, of course, required to know the functional dependences

$$X_i = X_i(x_1, x_2, \dots, x_n), \quad i \in \{1, 2, \dots, n\}. \quad (37)$$

## Conclusion

In this article, we successively introduced minus the third, minus the second, and minus the first law of thermodynamics. Of course, these principles are not enough for a logically rigorous construction of thermodynamic science. We have not discussed the zeroth law of thermodynamics and some essential remarks on the first, second, and third laws of thermodynamics in this paper, solely due to lack of space. The author plans to discuss these issues in the next article, which in essence will be a direct continuation of this article.



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## К вопросу о строгой аксиоматизации термодинамики

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**Аннотация.** В статье предпринята попытка строгой аксиоматизации термодинамики, т. е. построения такого ее изложения, при котором все ее изложение вытекает из нескольких аксиом. При этом оказывается, что классическая точка зрения, состоящая в том, что все здание термодинамики может быть построено на пяти началах (так называемые минус первый, нулевой, первый, второй и третий законы термодинамики), не выдерживает критики - количество аксиом существенно больше. Попытка выявить логическую необходимость введения этих аксиом в основания термодинамики и выявление самой их физической сущности (формулировка) и предприняты в данной статье.

**Ключевые слова:** основания термодинамики, минус третий закон термодинамики, состояние термодинамического равновесия, минус второй закон термодинамики, внутренняя энергия термодинамической системы, минус первый закон термодинамики, термодинамическая работа.