

IS CLASSICAL THERMODYNAMICS THE UNIQUE PHYSICAL THEORY WHICH WILL NEVER BE REFUTED?

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Abstract: A new theoretical analysis of the generally accepted foundations of classical thermodynamics is proposed. The principle of the unity of formal logic and rational dialectics is a methodological basis of the analysis. The result is as follows: the foundations of classical thermodynamics (i.e., the first and second laws, equation of state, concepts of internal energy, of heat energy, of entropy, of temperature) contain logical errors. The existence of logical errors is irrefutable proof of incorrectness of thermodynamics. The correct statistical foundations are proposed.

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INTRODUCTION

As is known, thermodynamics is a branch of physics which deals with the heat energy and work of a system. It is a fundamental part of the physical science. The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, cell biology, biomedical engineering, and materials science. The starting point for most thermodynamic considerations are four laws of classical thermodynamics: about internal energy, heat energy, entropy, and temperature. These laws do not depend on the details of the interactions or the systems being studied and postulate that: (a) energy can be exchanged between physical systems as heat and work; (b) there exist a quantity named entropy. The main concepts “internal energy”, “heat energy”, “entropy”, and “temperature” are not defined within the framework of thermodynamics. Therefore, classical thermodynamics – a phenomenological theory – should be scientifically grounded and explained by molecular-kinetic theory and statistical physics. Statistical interpretation of the second and third laws of thermodynamics is an object of statistical thermodynamics: the statistical interpretation is to derive all macroscopic properties from the statistical properties of moving constituent particles and the interactions between them. The result of great efforts putted into substantiation of the foundations of thermodynamics in 20th century can be expressed by A. Einstein’s words: “Classical thermodynamics is the unique classical physical theory which will be never refuted”. However, this statement was recently refuted: it was shown [1-9] for the first time that the foundations of classical thermodynamics and statistical physics contain logical errors. Consequently, there is the problem of truth in thermodynamics and statistical physics.

From the formal-logical point of view, thermodynamics and statistical physics cannot be compared with each other if there is no logical relations (identity, subordination, collateral subordination, partial coincidence, discrepancy) between thermodynamic and statistical concepts. Therefore, substantiation and explanation of thermodynamics means establishment of

logical relations between thermodynamic and quantum-statistical concepts: “General relationship between energy and temperature can be understood only with the help of probabilistic consideration. The problem of temperature connects very closely with quantum hypothesis” (M. Planck). The correct base for comparison of the concepts is Gibbs quantum canonical distribution, and the principle of the unity of formal logic and of rational dialectics represents the methodological basis of the analysis. In connection with [1-9], the critical analysis of the generally accepted foundations of classical thermodynamics (i.e., the first and second laws, equation of state, concepts of internal energy, heat energy, entropy, temperature) are proposed in this work. The purpose of the analysis is to prove that the standard foundations contain logical (mathematical) errors and to offer the correct formulations.

1. METHODOLOGICAL BASIS FOR THE THEORETICAL ANALYSIS

Modern theoretical physics consists of the set of theories but does not contain criterion of the truth of physical theories. In my opinion, lack of the criterion of the truth of theories in theoretical physics is explained by the fact that the system of physical (i.e. special scientific) concepts and laws is incomplete: it does not include many universal (i.e. the general scientific) concepts and laws. The complete system – the system of physical concepts and the laws supplemented with the system of universal concepts and laws – would represent not only basis of physics but also methodological basis for the deductive analysis of physics. From this point of view, the unified criterion of the truth of physical theory should be formulated as follows: a physical (i.e. special scientific) theory must not contradict the system of the universal (i.e. general scientific) concepts and laws. The system of the universal concepts and laws represents a unity of formal logic and of rational dialectics. And this unity is a science of most general laws of development of the Nature, human society, and correct thinking. Consequently, this system is a methodological basis for a critical analysis of physical theories. The main dialectics principle is the principle of objectivity of human knowledge. It is formulated as follows: objective laws and truth must be invariant under choice of means and methods of cognition, i.e. under change of properties of system of reference (in particular, objective laws and truth must not contain references to devices, procedure and accuracy of measurement or of calculation).

Thus, the principle of the unity of formal logic and of rational dialectics is the correct methodological basis for the proposed theoretical analysis of thermodynamics.

2. CORRECT FORMULATION OF THE FIRST LAW OF THERMODYNAMICS

As is known, the generally accepted first law of thermodynamics reads as follows: the change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system. The first law is given by the differential expression

$$dU = dQ + dW$$

where U, Q, W are internal energy, heat energy, and non-heat energy of the system, respectively. But this expression does not take into consideration the empirical fact that there is mutual transformation of heat energy and the work in practice. One should take into consideration this empirical fact in the following way. From mathematical point of view, quantities U, Q, W are in the following relation: U is a function of two independent variables, Q, W . Therefore, the correct formulation of the first law must be based on the concepts of function and differential of function. Really, if internal energy U of system is a function of two independent variables, $Q = Q(t)$ (describing of the heat form of energy) and $W = W(t)$

(describing non-heat form of energy), then the correct formulation of the first law of thermodynamics is

$$\frac{dU(Q, W)}{dt} = \left(\frac{\partial U}{\partial Q} \right)_W \frac{dQ}{dt} + \left(\frac{\partial U}{\partial W} \right)_Q \frac{dW}{dt}$$

where t and $\eta \equiv -\left(\frac{\partial U}{\partial W} \right)_Q / \left(\frac{\partial U}{\partial Q} \right)_W$ are time and measure of mutual transformation of forms of energy, respectively. (For example, the energy of the molecules which absorbs laser radiation is a non-heat form of energy). Consequently, the generally accepted formulation of the first law of thermodynamics represents a logical (mathematical) error because its content (i.e. special assertion) is not a law (i.e. general assertion).

3. CORRECT FORMULATION OF THE SECOND LAW OF THERMODYNAMICS

As is known, the generally accepted second law of thermodynamics reads as follows: the total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value. The second law is given by the differential expression

$$dS_{(\text{thermodynamic})} = dQ_{(\text{thermodynamic})} / T_{(\text{thermodynamic})}, \quad 0 < T_{(\text{thermodynamic})} < \infty$$

where $Q_{(\text{thermodynamic})}$, $S_{(\text{thermodynamic})}$, $T_{(\text{thermodynamic})}$ are the thermodynamic heat energy, the thermodynamic entropy, and the thermodynamic temperature of the system. In order to research this expression, one should establish logical relations between concepts “thermodynamic heat energy”, “thermodynamic entropy”, “thermodynamic temperature” and concepts “statistical heat energy”, “statistical entropy”, “statistical temperature”. Correct solution of this problem is based on Gibbs quantum canonical distribution which represents the correct and complete quantum-statistical description of isolated macroscopic system – ideal gas of molecules (quantum particles) – in thermodynamic equilibrium.

Gibbs quantum canonical distribution is consequence of the following set of principles [10-12] and premises:

(1) The principle of motion of quantum particle: the motion is the form of existence of quantum particle; the motion represents unity of internal and external (i.e. translatory) motions.

(2) The principle of energy of quantum particle: the energy E_n , $n = 0, 1, 2, \dots$ (where n is the energetic quantum number) is inalienable property of a quantum particle. Energy levels n of the quantum particle arise and disappear only as a result of absorption and emission of other quantum particles, respectively. (Consequently, the problem of quantization of energy is not the Schrödinger problem of eigenvalues).

(3) The principle of equivalence of energy E_n and frequency $h\nu_n$ of quantum particle: energy E_n is related to frequency $h\nu_n$ by the formula $E_n \equiv h\nu_n$ where h and ν_n are the Planck constant (i.e. quantum of action) and the frequency of the periodic process of mutual transformation of the internal and external motions, respectively. The concepts of energy E_n and of frequency $h\nu_n$ are identical ones. Multiplication of the quantities h and ν_n is permitted by logic law of identity if h is an oscillating quantity.

(4) The principle of speed of translatory motion of quantum particle: the speed v_n is defined by the formula $v_n \equiv \lambda_n \nu_n$ where λ_n is the size (the diameter) of the particle. The λ_n equals the distance traveled the particle for the oscillation period $\tau_n \equiv 1/\nu_n$. This translatory motion is a result of contraction and extension of the size (diameter) of the particle. Therefore, the translatory motion of the quantum particle relative to a reference system is an absolute one. The absolute motion is invariant under choice of a reference system. This statement means that the velocity addition theorem for quantum particle is not valid.

(5) The principle of mass and momentum of quantum particle: the mass m_n and the momentum p_n are defined by the formula $E_n \equiv (E_n/\nu_n^2)\nu_n^2 \equiv m_n v_n^2 \equiv p_n v_n$. The concept of mass m_n and the concept of energy E_n are not identical ones. Therefore, the formula $E_n \equiv m_n v_n^2$ does not express the principle of equivalency of mass and energy.

(6) A molecule of isolated ideal gas is individual quantum particle. The energy of the molecule represents discrete random quantity since molecules collide with each other in a random way.

(7) The random quantity takes on the values E_n , $n=0, 1, 2, \dots$ where $E_0=0$ is origin of counting of the random quantity;

(8) f_n is probability that molecule is in energetic quantum state n and has energy E_n . The probabilities f_n give complete quantum-statistical description of the ideal gas of molecules.

(9) Rule of addition of probabilities has the following form:

$$\sum_{n=0}^{\infty} f_n = 1$$

where

$$0 < f_n < 1, \quad \lim_{n \rightarrow \infty} (f_{n+1}/f_n) < 1.$$

(10) Rule of combination (multiplication) of probabilities for independent random events has the following form:

$$f_{n,m} = f_n f_m$$

where $f_{n,m}$ is combined probability that two molecules have energy $E_n + E_m$. In this case, f_n is the exponential function (A. Cauchy, 1821):

$$f_n = f_0 \exp(-\beta E_n)$$

where $1/\beta$ is a statistical parameter of molecule. The parameter $1/\beta$ is introduced for mathematical reasons: quantity βE_n must be dimensionless one. This parameter is consequence of existence of energy spectrum of quantum particle (atom, molecule) and does not depend on structure of energy spectrum. If the parameter was dependent on n it would represent value of some (indefinable) random quantity.

(11) The parameter

$$1/\beta = -E_n / \ln(f_n/f_0)$$

or (in other form)

$$1/\beta = -(E_{n+1} - E_n) / \ln(f_{n+1}/f_n)$$

represents physical-statistical property of molecules of gas and has both mathematical and physical meaning. From mathematical point of view, $1/\beta$ is a continuous and limited variable. From physical point of view, $1/\beta$ is the physical quantity which has energy dimension. Zero is origin of counting of this physical-statistical quantity and is the same for molecule of any kind. Range of existence of this parameter is defined by the relationship

$$0 < 1/\beta < E_\infty .$$

Quantum-statistical description of ideal gas of molecules loses statistical meaning outside this range: (a) if $1/\beta = 0$, then the energy of the molecule is not a random quantity; (b) if $1/\beta = E_\infty$, then the set $\sum_{n=0}^{\infty} f_n$ is diverged.

(12) The parameter $1/\beta$ has the same value for any (every) molecule of the system. Consequently, $1/\beta$ is the universal statistical parameter (i.e. statistical potential) of the system. This parameter has essential property of temperature. As is empirically known, this property is that temperature has the same value for every part (subsystem) of system if the system is in a state of heat equilibrium. Therefore, the identity

$$1/\beta \equiv T_{(\text{statistical})}$$

is the conjecture, the postulate. Owing to this postulate, the function f_n is called Gibbs canonical distribution, and the temperature $T_{(\text{statistical})}$ is called absolute temperature. The absolute temperature is temperature in the sense of the concept ‘‘Gibbs quantum canonical distribution’’. The absolute temperature does not depend on the existence of a thermometer (device).

It follows from above that

$$f_n = f_0 \exp(-E_n/T_{(\text{statistical})})$$

is Gibbs quantum canonical distribution. It has objective meaning because E_n and $T_{(\text{statistical})}$ are independent of existence of a thermometer. Gibbs quantum canonical distribution defines the correct relationship between the statistical-average (microscopic) energy E of molecule, the statistical-average (microscopic) entropy s of molecule, and the statistical temperature $T_{(\text{statistical})}$ of molecule. This relationship has the form:

$$E = sT_{(\text{statistical})}, \quad 0 < s < 1, \quad \lim_{T_{(\text{statistical})} \rightarrow 0} s = 0$$

where

$$E \equiv \sum_{n=0}^{\infty} E_n f_n, \quad s \equiv \sum_{n=0}^{\infty} s_n f_n, \quad s_n \equiv E_n / T_{(\text{statistical})} = -\ln(f_n / f_0).$$

Obviously, the heat energy E is a nonlinear function of the $T_{(\text{statistical})}$ because entropy s depends on the $T_{(\text{statistical})}$. In the case of binary gaseous mixture, it follows from the condition $T_{(\text{statistical})} = T'_{(\text{statistical})}$ of thermal equilibrium that, generally speaking, $E \neq E'$ where E and E' are the statistical-average energies of molecules of components.

The correct relationship between microscopic and macroscopic quantities has the form:

$$Q_{(\text{macroscopic})} = S_{(\text{macroscopic})} T_{(\text{statistical})}, \quad Q_{(\text{macroscopic})} = N_{(\text{macroscopic})} E, \quad S_{(\text{macroscopic})} = N_{(\text{macroscopic})} s,$$

where $N_{(\text{macroscopic})}$ is total (macroscopic) number of molecules in the system. The following statement follows from this relationship. If: (a) the relationship

$$Q_{(\text{macroscopic})} = S_{(\text{macroscopic})} T_{(\text{statistical})}$$

is correct; (b) the identities

$$Q_{(\text{thermodynamic})} \equiv Q_{(\text{macroscopic})}, \quad S_{(\text{thermodynamic})} \equiv S_{(\text{macroscopic})}, \quad T_{(\text{thermodynamic})} \equiv T_{(\text{statistical})}$$

is valid (i.e. thermodynamics concepts “thermodynamic heat energy”, “thermodynamic entropy”, and “thermodynamic temperature” are identical with the concepts “macroscopic heat energy”, “macroscopic entropy”, and “statistical temperature”, respectively), – then the generally accepted formulation of the second law of thermodynamics is incorrect. Since the ranges

$$0 < T_{(\text{thermodynamic})} < \infty, \quad 0 < T_{(\text{statistical})} < E_{\infty}$$

of existence of $T_{(\text{thermodynamic})}$ and $T_{(\text{statistical})}$ differ in degree, there exist partial coincidence between concepts “thermodynamic temperature” and “statistical temperature”.

Thus, the generally accepted second law of thermodynamics represents a logical (mathematical) error.

4. CORRECT FORMULATION OF THE EQUATION OF STATE

As is known, if movement of molecules (quantum particles) is cause of gas pressure, then average pressure $\bar{p}_{(\text{macroscopic})}$ of molecules of gas is defined by the unique relationship

$$\bar{p}_{(\text{macroscopic})} = \bar{\mu}_{(\text{macroscopic})} \bar{E}$$

where $\bar{\mu}_{(\text{macroscopic})}$ and \bar{E} are average number of molecules in unit volume and average energy of one molecule, respectively. This relationship represents the correct “equation of state” of gas.

In the case of heat movement of molecules, average energy \bar{E} of one molecule is E . Putting

$$E = \bar{p}_{(\text{macroscopic})} / \bar{\mu}_{(\text{macroscopic})}$$

into the left part of the relationship

$$Q_{(\text{macroscopic})} = S_{(\text{macroscopic})} T_{(\text{statistical})},$$

one can express “equation of state” in the “heat” form:

$$Q_{(\text{macroscopic})} = \bar{p}_{(\text{macroscopic})} V_{(\text{macroscopic})}, \quad \text{i.e.} \quad S_{(\text{macroscopic})} T_{(\text{statistical})} = \bar{p}_{(\text{macroscopic})} V,$$

where

$$V \equiv N_{(\text{macroscopic})} / \bar{\mu}_{(\text{macroscopic})}, \quad N_{(\text{macroscopic})} \equiv \bar{\mu}_{(\text{macroscopic})} V$$

are volume of molecular gas and total number of molecules in gas, respectively. If $E_n = E_1 n$ and $E_1 / T_{(\text{statistical})} \ll 1$, then value of entropy at the high-temperature limit is approximately equal to one, $s \approx 1$, and heat “equation of state” takes the following linear form:

$$\bar{p}_{(\text{macroscopic})} V \approx N_{(\text{macroscopic})} T_{(\text{statistical})}.$$

Distinction between this form and standard thermodynamic “equation of state”,

$$\bar{p}_{(\text{macroscopic})} V = N_{(\text{macroscopic})} T_{(\text{thermodynamic})},$$

is not only distinction in degree, but also distinction in kind. In order to explain qualitative and quantitative determinacy of the $T_{(\text{thermodynamic})}$, one should consider the gas system in development.

As is known, the rational dialectics principle reads as follows: one should consider the system in development. In accordance with this principle, one should consider the following development of the gas system absorbing energy without limitation:

$$(gas\ of\ molecules) \rightarrow (gas\ of\ atoms) \rightarrow (gas\ of\ elementary\ particles).$$

The system “gas of elementary particles” does not obey Gibbs quantum canonical distribution. Consequently, the elementary particles (photons, electrons etc.) have no statistical temperature, and the system is not in heat equilibrium. Moreover, the system have no thermodynamic temperature because there is no the heat form of energy in this system. There exist the concept of average energy of elementary particle only: $\bar{E}_{(\text{photon})}$, $\bar{E}_{(\text{electron})}$ etc. . If one measures the average energy with the help thermometer, the thermometer will read the temperature: $T_{(\text{photons})}$, $T_{(\text{electrons})}$ etc. . Temperature (i.e., physical property of the thermometer, the device, contacting the gas) exists only as measure of the thermometer, i.e. as the unity of qualitative and quantitative determinacy of the thermometer, as the ordered set of the thermometer states (thermometer

readings). The concept of temperatures $T_{(\text{photons})}$, $T_{(\text{electrons})}$ is the conventional concept connecting with the existence of the concept of thermometer (device). From formal-logical point of view, it means that the concept of thermodynamic temperature connects inseparably with the concept of thermometer: the concept “thermodynamic temperature” exists as consequence of the concept “thermometer”. Consequently, concepts “thermodynamic temperature” and “statistical temperature” are not identical ones, and the concept “thermodynamic temperature” has no objective meaning.

Thus, the expression $Q_{(\text{macroscopic})} = \bar{p}_{(\text{macroscopic})} V$ is the unique correct formulation of the “equation of statistical state”. The generally accepted formulation of “equation of thermodynamic state” represents a logical (mathematical) error because, firstly, $T_{(\text{thermodynamic})}$ has no qualitative determinacy at $T_{(\text{thermodynamic})} \rightarrow \infty$ and, secondly, the concept of thermodynamic temperature is logically erroneous and non-objective one.

5. DISCUSSION

As is known, formal logic is a science of the laws of correct thinking. One of its main principles is that definition of scientific concept must be exact and complete. However, classical thermodynamics does not satisfy this principle: within the framework of classical thermodynamics – a phenomenological theory, – one cannot give exact and complete definition of the thermodynamic concepts (i.e. concepts of internal energy, of heat energy, of entropy, of temperature). In order to define thermodynamic concepts one should include the concepts of thermodynamic instruments (thermometer, calorimeter etc.) and of measurement in the theory. Theory including concepts of instrument (device) and of measurement is non-objective, and a phenomenological theory excluding these concepts has no scientific meaning. This is the qualitative determinacy of any phenomenological theory. Therefore, the phenomenological, non-objective theory (classical thermodynamics) must be scientifically grounded and interpreted by the objective theory (statistical physics) which has the same object of scientific research. However, a part of results of the phenomenological theory loses scientific meaning at the grounding and interpreting.

CONCLUSION

Thus, the correct theoretical analysis shows that classical thermodynamics – a phenomenological theory – is not an objective theory. Its foundations (i.e., the first and second laws, equation of state, concepts of internal energy, of heat energy, of entropy, of temperature) contain logical (mathematical) errors. The existence of logical errors is irrefutable proof of incorrectness of classical thermodynamics. These errors are explained by the global cause: the errors are a collateral and inevitable result of inductive method of knowledge of the Nature, i.e. result of movement from formation of separate concepts to formation of system of concepts. The inductive way of development in physics is characterized, for example, by A. Einstein’s words: (a) *there has been formed a view that the foundations of physics were finally established and the work of a theoretical physicist should be to bring a theory in correspondence with all the time increasing abundance of the investigated phenomena. Nobody thought that a need for radical rebuilding of the basis of all physics could arise;* (b) *but the progress of science will cause revolution in its foundations. Our notions of physical reality never can be final ones. We should be always ready to change axiomatic basis of physics to substantiate facts of perception in logically most perfect form.* It follows from these words that “the progress in (inductive) science is the underlining of difficulties” (N. Bohr). And non-objective, incorrect theories should be replaced by objective, correct theories.

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