THE CRITICAL ANALYSIS
OF THE FOUNDATIONS OF CLASSICAL THERMODYNAMICS

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Abstract. The critical 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 main 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.

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 is 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 subject 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 [26, 27, 37, 38] 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.

In the formal-logical point of view, thermodynamics and statistical physics cannot be compared with each other if there are 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 accordance with works [26, 27, 37, 38], 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) is proposed in the present work. The purpose of the analysis is to prove that the standard foundations contain logical (mathematical) errors and to offer the correct formulations.

1. The 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 $\eta \equiv -\left(\frac{\partial U}{\partial W}\right)_Q \bigg/ \left(\frac{\partial U}{\partial Q}\right)_W$ 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).

2. The 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 to a maximum value. The second law is given by the differential expression

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

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 has the form:

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

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 relation 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 relation has the form:

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

where

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

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 relation between microscopic and macroscopic quantities has the form:

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

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

(a) the relation

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

is correct;

(b) the identities

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

are 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.

3. The 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 relation

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

where $\bar{\mu}_{(\text{macroscopic})}$ and $\bar{E}$ are average number of molecules in unit volume and average energy of one molecule, respectively. This relation 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 relation

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

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

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

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:

(gas of molecules) → *(gas of atoms)* → *(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 $T_{(\text{thermodynamic})} \to \infty$ and, secondly, the concept of thermodynamic temperature is logically erroneous and non-objective one.

4. 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.

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