

**On a New Theoretical Analysis
of the Foundations of Classical Thermodynamics**

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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 the 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, heat energy, entropy, temperature) contain logical errors. The existence of logical errors is irrefutable proof of the incorrectness of thermodynamics. The correct foundations are proposed. They are as follows.

(1) Correct formulation of the first law of thermodynamics.

If U , Q , W are internal energy, heat energy, and non-heat energy of the system, respectively, and U 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

$$\frac{dU(Q, W)}{dt} = \left(\frac{\partial U}{\partial Q} \right)_W \frac{dQ}{dt} + \left(\frac{\partial U}{\partial W} \right)_Q \frac{dW}{dt} \text{ where } t \text{ and } \eta \equiv - \left(\frac{\partial U}{\partial W} \right)_Q / \left(\frac{\partial U}{\partial Q} \right)_W \text{ are time and}$$

the measure of mutual transformation of forms of energy, respectively.

(2) Correct formulation of the second law of thermodynamics.

If: (a) a molecule of isolated ideal gas is an individual quantum particle. The energy of the molecule represents a discrete random quantity. The f_n is the probability that the molecule is in the energetic quantum state n and has the energy, E_n , $n = 0, 1, 2, \dots$ where $E_0 = 0$ is the origin of the counting of the random quantity; (b) the expression $f_n = f_0 \exp(-E_n/T_{(\text{statistical})})$, $0 < T_{(\text{statistical})} < E_\infty$ is Gibbs quantum canonical distribution where $T_{(\text{statistical})}$ is the statistical temperature; (c) the correct relationship between the statistical-average (microscopic) energy E of the molecule, the statistical-average (microscopic) entropy s of molecule, and the statistical temperature $T_{(\text{statistical})}$ of the molecule) has the form: $E = sT_{(\text{statistical})}$, $0 < s < 1$, $\lim_{T_{(\text{statistical})} \rightarrow 0} s = 0$

where $E \equiv \sum_{n=0}^{\infty} E_n f_n$, $s \equiv \sum_{n=0}^{\infty} s_n f_n$, $s_n \equiv E_n/T_{(\text{statistical})} = -\ln(f_n/f_0)$, – then the correct formulation of the second law of thermodynamics has the form: $Q_{(\text{macroscopic})} = S_{(\text{macroscopic})} T_{(\text{statistical})}$, $Q_{(\text{macroscopic})} = N_{(\text{macroscopic})} E$, $S_{(\text{macroscopic})} = N_{(\text{macroscopic})} s$, where $N_{(\text{macroscopic})}$ is total (macroscopic) number of molecules in the system.

(3) Correct formulation of the equation of state.

If the movement of molecules (quantum particles) is the cause of gas pressure, then the expression $Q_{(\text{macroscopic})} = pV$ is the unique correct formulation of the “equation of statistical state” where p ,

$V \equiv N_{(\text{macroscopic})} / \bar{\mu}_{(\text{macroscopic})}$, $N_{(\text{macroscopic})} \equiv \bar{\mu}_{(\text{macroscopic})} V$, and $\bar{\mu}_{(\text{macroscopic})}$ are pressure, volume of molecular gas, total number of molecules in the gas, and average number of molecules in a unit volume, respectively.

Thus, the new theoretical analysis leads to the correct formulation of the foundations of thermodynamics and, consequently, promotes progress in science.