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Research Article

General Thermodynamically Unification of the First and Second Laws of Thermodynamics

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Abstract

The unification of the first and second laws of thermodynamics into a single equation has long been a key goal in thermodynamic research. However, significant mathematical and physical challenges have hindered its achievement. In this paper, we go a step further and seek a general as well as completely thermodynamically unification of these laws. The generality, energy fundamental-based and statistical perspective of the Boltzmann entropy equation can provide a valuable solution to unify the first and second laws of classical thermodynamics. Here, "entropy generation function" is considered as a function that takes a measure of lost available work of any thermodynamic energy conversion system, and also "integrator function" is considered as a function that is applied for the mathematical unification. Also, the quasi-statistical approach of entropy is considered as an approach that studies macroscopic energy components instead of studying the energy of individual particles. So, in this paper, by applying the entropy generation function g, as a novel integrator function, we consider the second law as an equality. In the following, using a new quasi-statistical approach to the entropy with the same base as Boltzmann entropy equation, function g is derived. Finally, we extract two innovative general thermodynamically equations resulting from unification of the first and second laws of classical thermodynamics as well as a novel general thermodynamically unified second law equation is established. Contrary to what is common in classical thermodynamics, the established unified equations are sufficient for the thermodynamically analysis of physical processes, and there is no need to add any additional condition relation or non-thermodynamic quantity. In fact, we are looking for a general thermodynamically unification of the first and second laws, which is one of the highlights of this paper. Finally, a general mathematical-physical validation is presented and in the general case, it is shown that there are no contradictions in the established unified equations.

Keywords: *Unified thermodynamically equation; general unified thermodynamics; entropy; statistical approach; integrator function.*

1. Introduction

First, it is necessary to state that what we mean by general thermodynamically unification of the first and second laws of thermodynamics is that the relevant integration is studied without any additional assumptions rather than well-known expressions of these laws, or the existence of non-thermodynamic quantities or even thermodynamic quantities that are not directly present on the well-known expressions of the first and second laws. This is one of the main highlights that we are going to address in this paper.

The unification of scientific laws has special importance among scientists [1-8]. The unification of the first and second laws of thermodynamics can directly apply the second law into the thermodynamically analysis. However, due to the mathematical and physical challenges involved, the subject is known as an important challenge for scientists yet. Usually, the first law of thermodynamics is known as internal energy definition and the second law is known as definition of entropy [9-13]. Although by establishment of more advanced scientific theories, such as quantum mechanics theory and statistical mechanics theory, the first law is still used in its classical form to a significant extent, but due to the expansion of different definitions and criteria for entropy, the second law is available in different formulations. So, we may be at the peak of confusion related to the second law, or in other words, classical thermodynamics [14-18]. In the perspective of classical thermodynamics, the second law is provided by an inequality, and is not directly used in the analysis of problems, and it is proposed as a condition relation for the results of the first law. It is important to note that the Gibbs function, as a function that has energy and entropy in its definition, can be considered as one of the first attempts to integrate energy and entropy in a single quantity. While it does not provide specific information on the integration of these laws into a single law, and does not address this issue. In fact, Gibb's function has the necessary condition needed by an integrator function in the subject.

Although the unification of the first and second laws of thermodynamics can provide further achievements of the basic aspects of these two fundamental laws, success in this case depends on establishing the relationship between entropy and internal energy. While the classical perspective does not provide such as this connection, it is necessary to use other scientific theories and perspectives. It is thought

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that the perspective of statistical mechanics as well as Boltzmann entropy equation gives the most general and accepted approach of entropy at present [19-20]. Considering that the basis of Boltzmann entropy equation is related to the energy of substructures by Einstein, Maxwell or Fermi-Dirac equations, applying Boltzmann point of view can provide the fundamental conditions for this unification. However, considering that the direct relationship between classical thermodynamics and Boltzmann entropy equation cannot be analyzed, it is necessary to use other approaches with a common basis as the Boltzmann entropy equation [21-29].

The quasi-statistical approach to entropy has a common basis with Boltzmann entropy equation, and is also written based on the activated components of energy in the physical processes [29, 34]. So, in terms of the physical concepts and mathematical tools required, the quasi-statistical approach to entropy meets the requirements set forth. More details about the conditions, concepts, and mathematical tools needed to integrate scientific laws across different perspectives can be found in the references [30-31].

In this paper, we are working towards a general thermodynamically unification of the first and second laws of thermodynamics. The goal of general thermodynamically unification is to study the unification of these laws without any additional assumptions or the addition of quantities that are not directly present in the first and second laws of thermodynamics. For this purpose, by considering the entropy generation function as a novel integrator function, the second law of thermodynamics is written as an equality. In the following, using the quasi-statistical perspective of entropy, the novel integrator function is calculated, and the desired general thermodynamically unified equations are extracted. Also, using novel established unified equations, the general thermodynamically unified second law is also established. The general thermodynamically unified equations will be sufficient independently for the thermodynamically analysis of physical processes, and there is no need to check any other additional conditions. In fact, as expected, the general established unified equations have the effects of the first and second laws simultaneously.

2. Theoretical Background

Combining the laws of thermodynamics and presenting them with a single equation is not an attempt that has "not been done so far". The question of whether there is a unifying framework for related theories in the same discipline is a common question for the authors of the references [1-31] have been cited in the introduction. However, there are several sections where individual theorem sets are exceptional cases of a single unifying result or where a single perspective on how to proceed as a field of mathematics develops can be applied fruitfully on the many branches of the subject.

The macroscopic scale values of energy are independent of the macroscopic scale values of entropy [32]. However, the Gibbs function G is a beautiful relation combining energy and entropy in a single term as follows:

$$G = H - TS \tag{1}$$

Where H is enthalpy, T is temperature and S is entropy. In fact, the Gibbs equation (the Gibbs function) provides an early cornerstone (as an integrator function) for combining the first and second laws of thermodynamics. However, for this case, it uses a new function that does not exist directly in the first or second law of thermodynamics. So, a new function will to be added. Also, the basis of the definition of the Gibbs function are not related to the unification of the laws of thermodynamics and do not make any attempt in this subject. In fact, the Gibbs function only gives a combined function of energy and entropy. So, it can be considered as an integrator function to the draft subject.

As an example, in the context of trying to unify the first and second laws of thermodynamics, reference [33] develops a combined of the first and second laws of thermodynamics using the principles of classical statistical mechanics. Figure 1 takes the physical concepts as well as mathematical tools used to derivation of the combined equation of the first and second laws of thermodynamics in reference [33]:

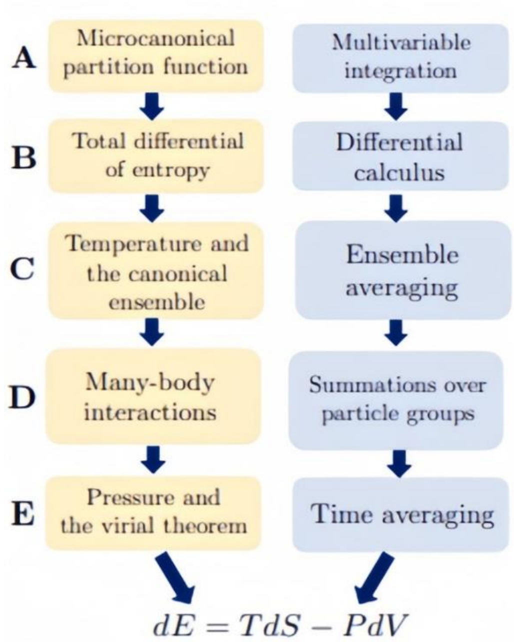

Figure 1. The physical concepts (left) and mathematical tools (right) used to derivation of the combined equation of the first and second laws of thermodynamics [33].

So, classical thermodynamics as well as statistical mechanics are used in reference [33] to derivation a combined equation of the first and second laws of thermodynamics. More details can be reached in the old or new versions of reference [33]. It can be deduced that using the principles and concepts of statistical mechanics alongside thermodynamics provides the needed conditions for unification the first and second laws of thermodynamics. In fact, thermodynamics alone cannot be unified and it is necessary to use appropriate physical concepts and mathematical tools.

3. Methodology

Given what we know on the nature of entropy produced in physical processes, in this paper we intend to use the entropy generation as an integrator function. So, considering entropy generation function g, as a novel integrator function, Eqs. (2)-(3) gives the first and second laws of thermodynamics:

$$\dot{U} = \dot{Q} - \dot{W} \tag{2}$$

$$\dot{S} = \frac{\dot{Q}}{T} + g \tag{3}$$

Where U is internal energy, $\dot{Q}$ is rate of the heat exchange, $\dot{W}$ is rate of the work done, S is entropy, and T is temperature. So, two equations can be derived as follows:

$$\dot{U} = T\dot{S} - \dot{W} + h \tag{4}$$

$$T\dot{S} = \dot{Q} - h \tag{5}$$

That $h \equiv -Tg$. So, it is necessary to derive the novel integrator function h first. In fact, considering the innovative completely thermodynamically approach, the main challenge on unification the first and second laws is the deriving of this novel integrator function. Here it is necessary to use the existing perspectives on entropy. Clearly, classical thermodynamics cannot provide such conditions to derive the function h, neither from the fundamentals nor from the mathematical point of view. In fact, the general views on entropy, either mathematically or physically, do not provide the necessary conditions for the general unification of the first and second laws of classical thermodynamics. From the perspective of the physical foundations, the Boltzmann entropy equation provides the necessary physical conditions for the desired unification. Although from a mathematical point of view, it is not applicable to derive the function h. Therefore, it is necessary to use other approaches related to entropy with a common basis as Boltzmann entropy equation [16, 21, 23-29]. This approach will be discussed in the following.

3.1 Quasi-Statistical Approach to the Entropy

Figure 2 takes the energy component's approach has been established by Energy Structure Theory [29, 34]:

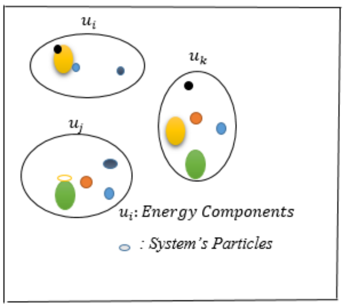

Figure 2. Energy Component's Approach [29].

Where u_i are known as energy components of the system. Each particle may participate in the several of energy components. Using energy component's approach and energy structure equation as well as a novel energy conservation principle, Energy Structure Theory establishes a quasi-statistical equation to entropy as follows:

$$\delta S = K_{MS}\, \delta[\ln(W_U)] \tag{6}$$

That K_{MS} is known as a universal constant. As discussed in reference [29, 34], the quasi-statistical perspective to entropy has common foundations to the Boltzmann entropy equation. And also:

$$\mathrm{W_U} = \prod_{\mathrm{j=1}}^{\mathrm{m}} \mathrm{w_{u_j}} \tag{7}$$

That:

$$w_{u_j} = \dot{U}_j \tag{8}$$

Considering path $1 \to 2$ as a quasi-static path, as well as path $1 \to 2'$ as a general path, Figure 3 takes the variation of $\dot{U}_j$ as difference between two different paths as follows [29, 34]:

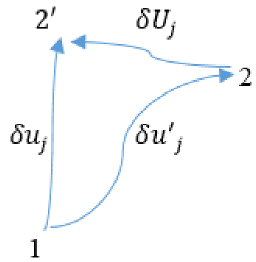

Figure 3. Difference between two different paths [34].

In fact, figure 3 illustrates the difference in entropy, Sgen, between a quasi-static path (Pquasi-$1 \to 2$) and a general path (Pgen-$1 \to 2'$). This comparison is based on the energy structure equation and the entropy generation function, which are grounded in the Boltzmann entropy framework. Finally, given the necessary physical and mathematical conditions discussed, the quasi-statistical approach to entropy provides a suitable solution for the general thermodynamically unification of the first and second laws. In fact, the quasi-statistical approach to entropy provides the necessary physical and mathematical conditions for deriving the considered integrator function (the generated entropy function). In the following, we will discuss the general thermodynamically calculation of this function.

3.2 Mathematical Development: Two Innovative General Thermodynamically Unified Equations

So, using quasi-statistical approach to the entropy with the same base as Boltzmann entropy equation has been established by Energy Structure Theory:

$$\delta S = K_{MS}\delta[lnW_U] \tag{9}$$

$$\dot{S} = K_{MS}\frac{\dot{W}_U}{W_U} = K_{MS}\frac{\ddot{U}}{\dot{U}} \tag{10}$$

So:

$$\dot{S} = K_{MS}\left(\frac{\dot{T}\dot{S}+T\ddot{S}-\ddot{W}-\dot{h}}{T\dot{S}-\dot{W}+h}\right) \tag{11}$$

Therefore, Eq. (11) can be rewritten as follows:

$$\dot{h} - \frac{\dot{S}}{K_{MS}}h = -\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}} \tag{12}$$

Eq. (12), in its current expression, is a general thermodynamically equation. Finally, function h is extracted as follows:

$$h = \frac{1}{e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}} \int \left[\left(e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}\right).\left(-\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}}\right)\right]dt + C_2 \tag{13}$$

It is necessary to state here that the function h satisfies the necessary and sufficient energy structure conditions discussed in references [29, 34]. So, entropy generation function (considered novel integrator function) is extracted as follows:

$$g = -\frac{h}{T} = \frac{-1}{Te^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}} \int \left[\left(e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}\right).\left(-\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}}\right)\right] dt + C_2 \quad (14)$$

Eq. (14) takes the entropy generation function (the considered integrator function). In fact, it gives the thermodynamically structure of the function g. Therefore, as can be deduced from Eq. (14), the entropy generation function, both physically and mathematically, is a suitable function for use as an integrator function in general thermodynamically unifying the first and second laws of thermodynamics.

So, two novel general thermodynamically unified equations are established as follows:

$$\dot{U} = T\dot{S} - \dot{W} + \frac{1}{e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}} \int \left[\left(e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}\right).\left(-\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}}\right)\right] dt + C_2 \quad (15)$$

And also:

$$T\dot{S} = \dot{Q} - \frac{1}{e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}} \int \left[\left(e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}\right).\left(-\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}}\right)\right] dt + C_2 \quad (16)$$

Eq. (15) includes the internal energy, while in Eq. (16), internal energy is not directly observed. This issue does not make a difference in the foundations of these equations. In fact, the foundations of the general thermodynamically novel established unified Eqs. (15)-(16) are based on the statistical approach to entropy and the entropy generation function g. Mathematically, the unified Eq. (16) can be described as including fewer thermodynamically quantities, which may can achieve more unification.

4. Novel General Thermodynamically Unified Second Law

The general thermodynamically unified second law is a rewrite of Clausius formulation in the equality formulation considering the first law of thermodynamics as well as Boltzmann approach to the entropy to apply irreversibility effects on the Clausius formulation of the second law. So, Eq. (5) takes an initial unified second law equation considering entropy generation function as the needed integrator function. Therefore, by replacing entropy generation function g, the novel general thermodynamically unified second law equation is established as follows:

$$\dot{S} = \frac{\dot{Q}}{T} - \frac{1}{T}\left[\frac{1}{e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}} \int \left[\left(e^{\int\left(-\frac{\dot{S}}{K_{MS}}\right)dt+C_1}\right).\left(-\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}}\right)\right] dt + C_2\right] \quad (17)$$

Eq. (14) gives a new very important perspective on the second law. In the established general thermodynamically unified equation of the second law, in addition to the second derivative of entropy, terms related to the way of doing work are also seen, which are related to the effects of irreversibility. In the following, the validity of Eqs. (10)-(14) is discussed from the perspective of structure and required conditions.

5. Results and Discussion

The unified Eqs. (15)-(17) are both mathematically and physically equivalent. In this part, a physical-mathematical discussion is presented on the general verification of the established unified equations (step by step). The unified Eqs. (15)-(17) were extracted from the unification of first and second laws of thermodynamics. The entropy generation function g was considered as the integrator function, and was then calculated mathematically. In the following, using entropy generation function g as well as well-known formulations of the first and second laws of thermodynamics, the unified equations were established.

At first, it is necessary to be noted that the unification carried out in this paper, is in the general thermodynamic case and no additional assumptions are made. In fact, the calculations are based directly on the sufficiently well-known expressions of the first and second laws of thermodynamics as well as using sufficiently validated and accepted mathematical tools. So, from a mathematical point of view, the discussion of the calculations of extracting the integrator function g, Eq. (13) is the main topic to validation discussion. Differential Eq. (12) is written in such a way that it falls into the category of first-order linear differential equations [35]. Therefore, if it satisfies the conditions of uniqueness of the response over its entire required domain as an integrator function for unification the first and second laws of thermodynamics, the mathematical validation is complete. In order to study Eq. (12), it is initially considered that:

$$p \equiv -\frac{\dot{S}}{K_{MS}} \quad (18)$$

$$q \equiv -\dot{T}\dot{S} - T\ddot{S} + \ddot{W} + \frac{T}{K_{MS}}\dot{S}^2 - \frac{\dot{S}\dot{W}}{K_{MS}} \quad (19)$$

As can be seen, the functions p and q are fully defined in the domain of thermodynamic values and also have no singular points. Therefore, function h calculated in Eq. (13) is fully defined in the domain of thermodynamic values of the first and second laws of thermodynamics, is valid, and is also acceptable as an integrator function. So, all the calculation steps performed to extract the unified equations can also be concluded and performed reversibly. This means that Eqs. (15)-(17) completely encompass the first and second laws of thermodynamics. Also, just as these equations can be derived from the combination of the first and second laws of thermodynamics, the reverse calculations can also be completed and the first and second laws can be derived. Therefore, all necessary and sufficient conditions are satisfied in the established equations.

Although the discussion presented is complete, it can be stated that from another perspective, it is clearly deduced that Eqs. (15)-(17) satisfy the necessary and sufficient energy structure and the compatibility conditions established by energy structure theory. The energy structure equation as well as the corresponding compatibility conditions are fully developed in references [26, 29, 34].

6. Conclusions

The attempt to unify scientific theories as a matter of great importance has a long history among scientists. The physical meaning of unification in scientific theories (or physical laws as well as principles) is to add the effects of different laws to each other, and extract the desired unified equation. Considering that in the unifications it is necessary to use an additional model, perspective or equation, therefore, it is seriously necessary to emphasize that the unifications in different ways do not necessarily lead to a similar equation. In fact, applying the effects of scientific laws on each other using different approaches can lead to different unified equations. In fact, part of the features, mathematics and applications of the unified equation goes back to the additional perspective used in the unification. Physical and mathematical challenges are the main challenges from the perspective of the possibility of unification scientific laws. From the physical point of view, it is necessary to establish the foundations required by the additional perspective used in unification, and from the mathematical point of view, it must be also possible to apply the additional perspective by mathematical operators.

The pursuit of unification in thermodynamics occupies a great special place. In other words, the first law of thermodynamics uses the quantity of internal energy to express the conservation of energy based on work done and heat exchanged in thermodynamic processes. Meanwhile, the second law of thermodynamics by defining the entropy quantity provides a necessary condition for the processes to be carried out. By the expansion of different definitions on the entropy, the expressions of the second law have also been expanded. It is in this situation that the unification of the first and second laws of thermodynamics becomes more important. The perspective of classical thermodynamics cannot get a specific idea in line with this unification. Also, the extended definitions on the entropy are generally not applicable either mathematically or physically for the purpose of unification. In the meantime, the statistical physics approach to entropy, which provides the Boltzmann entropy equation, provides the necessary physical foundations to unify the first and second laws of thermodynamics. From the mathematical point of view, Boltzmann entropy equation cannot be applied in the unification of classical thermodynamics. For this reason, it is necessary to use other views of entropy that have a common basis with Boltzmann entropy equation. The quasi-statistical approach, which has a common basis as the Boltzmann entropy equation, also provides the necessary conditions from a mathematical point of view. In this case, the unification of the first and second laws of thermodynamics using Boltzmann statistical perspective leads to the formation of a deep link between the classical expressions of the first and second laws with the approach of statistical physics. Also, the unified expression of the second law rewrites it as an equality, which brings a direct place in the analysis of problems for this law.

Since we were looking for a general thermodynamically unification of the first and second laws of classical thermodynamics, we considered the energy generation function as the integrator function, and also extracted the considered integrator function in a general and completely thermodynamically expression using the quasi-statistical perspective of entropy. Finally, two innovative general thermodynamically unified equations were extracted from the unification of first and second laws of classical thermodynamics. In the following, the very important issue of the general thermodynamically expression of the second law was pursued, and in fact, the second law in its general thermodynamically unified expression was established as an equality. Finally, it is important to be noted that the unified Eqs. (15)-(17) are both mathematically and physically equivalent, and depending on our needs for analyzing a particular problem, either of them can be used.

Established novel Eqs. (15)-(17) have the general structure of unified thermodynamics. According to energy structure theory, these equations are required to satisfy the necessary and sufficient conditions of energy structure equation as well as the compatibility conditions. Eqs. (15)-(17) clearly satisfy the desired conditions in references [29, 34].

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Nomenclature

U: Internal energy [J]
Q: Heat transfer [J]
W: Work [J]
k_{MS}: Universal constant of quasi-statistical entropy
T: Temperature [K]
s : Entropy of the system [J/K]

Greek Letters

g: Entropy generation function [J/K]
h: Irreversibility [J/K]

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