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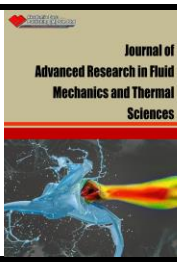

A General Solution to the Different Formulations of the Second Law of Thermodynamics

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ABSTRACT

The second law of thermodynamics is one of the most important physical laws that has been extracted by different formulations. In this paper, a new approach to study different formulations of the second law is extracted based on the energy components of the system as well as introducing the independent and dependent energy components concepts. Also, two main formulations of classical thermodynamics, and also entropy from the perspective of general physics are discussed based on the energy components of the system for constant applied energy to the system in different conditions. Kelvin-Plank and Clausius formulations, as two main classical formulations, are all assertions about impossible processes. Considering the energy structure equation of the system, as an equation to formulate the performed process using activated energy components, it is shown that different formulations of the second law of thermodynamics represent the same concept in the perspective of the energy structure. Finally, a new general formulation to the second law, based on the energy structure of the system is extracted, and the equivalence as the other formulations is shown. The presented formulation is extracted based on the dependent and independent activated energy components, and in fact, shows all possible paths in the considered energy applying to the system.

1. Introduction

The Second law of thermodynamics is the most important physical law that has been established in all branches of science [1,2]. Carnot can be known as the funder of the second law because he was the first one that introduced irreversibility by presented Carnot's cycles [3]. In classical thermodynamics, there are two main formulations to the second law: Kelvin-Plank and Clausius formulations [4-6]. These formulations are all assertions about impossible processes. Also, some formulations are presented to the second law that relies on assertions about the possible processes [6]. For example, Caratheodory formulation is another formulation in the classical thermodynamics to the second law that is extracted for possible processes [7-10]. Clausius formulates the second law by introducing entropy quantity [11]. Based on this formulation, entropy must be increased always.

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Therefore, the sign of the generated entropy can be known as a physical direction for physical processes [12,13]. The physical significant of the entropy is the loss of the useful energy and exchange it to the heat in the perspective of the classical thermodynamics [6,14-16]. The formulation of the entropy in classical thermodynamics is used to equilibrium states, and no attempt is made to define it otherwise [6]. Also, from the perspective of statistical physics, entropy is raised as a quantity that depends on the available probability of the system at a special energy level and is calculated by investigating the microstates and macrostate of the system [17,18]. Therefore, the second law will be equivalent to the fact that the probability of the system will be increased always [17].

The second law is also one of the most important laws in other branches of science. For example, the second law of thermodynamics is the most important law in psychology [18,19]. Also, mechanothermodynamics, as a new branch of physics, uses the second law as the base of analysis of MTD systems [20-22]. Also, some references use the second law to investigate the nano-scale systems [23-25].

Also, there are generalized formulations to the second law [26-29]. For example, statistical physics studies the second law from the possible perspective of the micro and macrostates. And also, Lagrangian variational formulation is extracted in the case of non-equilibrium thermodynamics [30]. In this case, entropy production is used as the most important concept to study irreversibility. Also, there are some formulations to the second law based on the possible way to energy exchange in the considered process [31]. The second law can be re-formulated to the discrete open systems [32]. Some of the other main general approaches to the second law can be seen in references [33-35]. However, there are some challenges to the second law [36-39].

In this paper, at first, an energy structure is extracted for physical processes by introducing independent and dependent energy components of the system. In the following, different formulations of the second law are discussed from the perspective of the energy structure of the system. In fact, the variation of the energy structure equation is studied for constant applied energy to the system in different conditions. Also, bases on the energy structure equation of the system, a general formulation to the second law is presented that the classical and statistical formulations of the second law can be resultant from. The presented formulation shows all feasible processes when some energy is applied to the system in different conditions.

2. Kelvin-Plank Formulations of The Second Law from Energy Structure Perspective

Figure 1 shows a scheme of heat engine that works between two hot and cold sources [5]

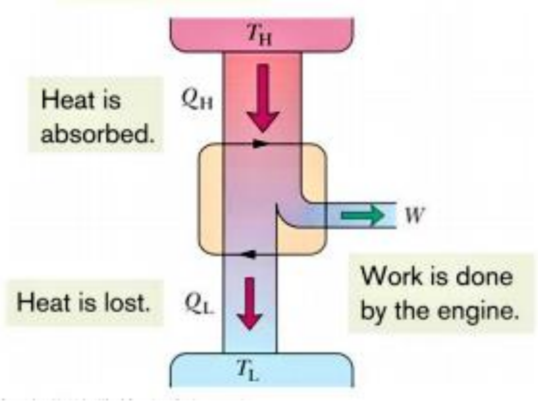

Fig. 1. Scheme of heat engine [5]

Based on the Kelvin-Plank formulation to the heat engine shown in Figure 1, no process is possible the sole result of which is that a body cooled and work is done [6]. Therefore, there must exist a body to heat. Based on the energy conservation principle to the heat engine shown in Figure 1, $Q_L + W = Q_H$. And also, based on the Carnot's rule to the reversible cycles, the most work can be done is $W_{Carnot} = (1 - \frac{T_C}{T_H})Q_H$, and $Q_{L_{Carnot}} = Q_H - W_{Carnot}$. When Irreversibility exists in the cycle, the work done is less than W_{Carnot}. Therefore, $W_{Carnot} - W \geq 0$, and also $Q_{C_{Carnot}} - Q_C \leq 0$.

To investigate the heat engine shown in Figure 1, for constant applied heat of hot source to the system in different conditions, at the first step, based on the energy conservation principle and the Carnot's rule, Eq. (1) can be written in the variation form

$$\delta Q_{L_{Carnot}} + \delta Q_{L_{Irreversible}} = \delta Q_H - \delta W \tag{1}$$

That $\delta Q_{L_{Irreversible}}$ will be activated in irreversible cycles. In fact, in the case that applied heat from hot source to the system has non-zero rate [5]. Also, since δW depends on the rate of δQ_H, $\delta Q_{L_{Irreversible}}$ also can be considered as a function of the rate of the work done. In other words, the energy component $\delta Q_{L_{Irreversible}}$ will be activated whenever the component W has non-zero rate. If the rate of δW increases, the irreversibility will also increase. Therefore, due to this fact, Eq. (2) can be deduced

$$\frac{\partial(\delta \dot{Q}_{L_{Irreversible}})}{\partial(\delta \dot{W})} > 0 \tag{2}$$

Eq. (2) can be rewritten as follows

$$\frac{\partial(\dot{Q}_{L_{Irreversible}})}{\partial(\dot{W})} > 0 \tag{3}$$

Therefore, for all possible processes that can be done by the heat engine shown in Figure 1, Eq. (4) will be deduced

$$[\frac{\partial(\dot{Q}_{L_{Irreversible}})}{\partial(\dot{W})}](\delta W_{Carnot} - \delta W) \geq 0 \tag{4}$$

In other point of view, to investigate the heat engine shown in Figure 1, based on its energy structure and for constant applied heat from hot source, Eq. (5) is considered

$$U_{E-C} = W + Q_{L_{Irreversible}} \tag{5}$$

Where U_{E-C} shows the energy changed in the performed processes when the same Q_H is applied to the system in different conditions. This equation can be rewritten as follows

$$U_{E-C} = W + h_W(\dot{W}) \tag{6}$$

That $h_W(\dot{W})$ is a function of $\dot{W}$. Therefore, Eq. (4) can be rewritten as follows

$$[\frac{\partial h_W}{\partial(\dot{W})}](\delta W_{Carnot} - \delta W) \geq 0 \tag{7}$$

Eq. (7) is equivalent to the Kelvin-Plank statement of the second law and is extracted based on the energy components of the system.

3. Clausius Formulation of the Second Law from Energy Structure Perspective

Figure 2 shows scheme of a refrigeration that work between two heat and cold sources [5]

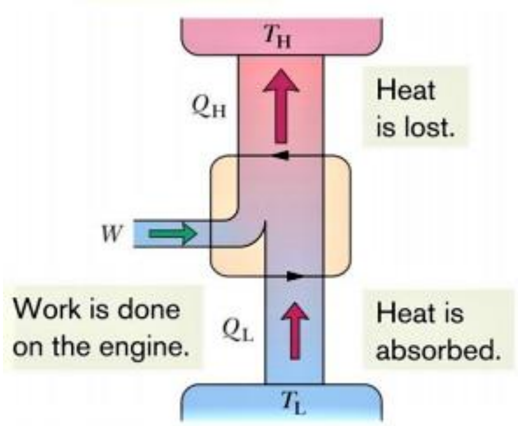

Fig. 2. Scheme of a refrigeration [5]

Based on the Clausius statement to the refrigeration shown in Figure 2, no process is possible that the sole result of which is that heat is transferred from a cooler body to a hotter one [6]. Therefore, to work done, it is needed that some heat transfers from the cold body to the hot body.

For the Carnot's pump, for constant work done on the system, the most heat that can be transferred from the cold body to the hot body is $Q_{L_{Carnot}} = \left(\frac{T_L}{T_H - T_L}\right) W$. Also, in general, the energy conservation principle can be rewritten as follows in the variation form

$$\delta Q_{L_{Carnot}} - \delta Q_{L_{Irreversible}} = \delta Q_H - \delta W \tag{8}$$

That $\delta Q_{L_{Irreversible}}$ related to the irreversibility in the refrigeration, and depends on the rate of the work done [5]. This quantity can also be considered as a function of the rate of Q_H. In fact, the energy component $\delta Q_{L_{Irreversible}}$ will be activated whenever the component Q_H has non-zero rate. If the rate of the charging heat from the hot body increases, also the irreversibility effects increase. Therefore

$$\frac{\partial(\delta Q_{L_{Irreversible}})}{\partial(\delta \dot{Q}_H)} > 0 \tag{9}$$

or

$$\frac{\partial(\delta Q_{L_{Irreversible}})}{\partial(\delta \dot{Q}_H)} > 0 \tag{10}$$

Therefore, Eq. (11) can be deduced for the refrigeration shown in Figure 2

$$\left[\frac{\partial(\delta Q_{L_{Irreversible}})}{\partial(\delta \dot{Q}_H)}\right](\delta Q_{L_{Irreversible}} - \delta Q_{L_{Carnot}}) \geq 0 \tag{11}$$

In other point of view, to investigate the refrigeration shown in Figure 2, based on its energy structure, Eq. (12) can be considered

$$U_{E-C} = Q_H + Q_{L_{Irreversible}} \tag{12}$$

Where U_{E-C} the energy changed in the performed processes when the same work is done on the system in different conditions. This equation can be rewritten as follows

$$U_{E-C} = Q_{L_{Irreversible}} + h_L(\dot{Q}_{L_{Irreversible}}) \tag{13}$$

That $h_L(\dot{Q}_{L_{Irreversible}})$ is a function of $\dot{Q}_{L_{Irreversible}}$. Therefore, Eq. (11) can be rewritten as follows

$$[\frac{\partial h_L}{\partial(\dot{Q}_{L_{Irreversible}})}](\delta Q_{L_{Irreversible}} - \delta Q_{L_{Carnot}}) \geq 0 \tag{14}$$

Eq. (14) is equivalent to the Clausius statement of the second law, and is extracted based on the energy components of the system.

4. Entropy from the Perspective of the General Physics

In this part, entropy from the perspective of the general physics is presented.

4.1 Statistical Physics

Statistical physics investigates entropy from a microstructure point of view. Boltzmann focuses on the evolution of a particular macroscopic system. Given Boltzmann's perspective, it is necessary to consider the entropy of a system as a function of the probability that the system will reach the considered particular state at the desired energy level [40]

$$S = f(W) \tag{15}$$

Where S is entropy and W is the probability in the desired state. If the different states are combined, then it is necessary to add their entropy, although the probability will be the product of the probabilities. Therefore

$$S = S_1 + S_2 \tag{16}$$

$$f((W_1.W_2) = f(W_1) + f(W_2) \tag{17}$$

Using of the Boltzmann’s perspective and also using Eq. (16) and Eq. (17), Eq. (18) can take the absolute value of entropy as a function of the probability

$$S = kln(W) + constant \tag{18}$$

That k is a universal constant.

4.2 Quantum Perspective of The Statistical Physics

In the quantum perspective of the statistical physics, some equations for W are presented for particle systems as a function of the number of particles, and a weighting factor of energy levels [41]. For example, the Fermi-Dirac equation is as follows

$$W = \prod_j \frac{g_j!}{(g_j-1)!N_j!} \tag{19}$$

That N_j is the number of particles with the weighting factor of energy level g_j.

Eq. (18) can be used to calculate the absolute value of entropy. This equation also determines the general dependence between entropy and probability. Eq. (18) also relates the macroscopic state of the system to its microscopic states. In fact, the probability of a physical system depends on the available states at a particular level of energy [42]. In this case, increasing entropy will increase the probability of availability [40]. Methods such as the non-equilibrium statistical operator can be used to investigate irreversibility from the point of view of statistical mechanics [44,45]. Eq. (18) is agreed with the generalized Clausius entropy, when the system has local equilibrium [46].

5. Second Law from the Perspective of the Energy Structure

In a system, the instantaneous reversal of the motion of every moving particle causes the system to move backward, each particle along its old path at the same speed as before when in the same position. In physical dynamics this simple and perfect reversibility fails, on account of forces depending on friction of solids; imperfect fluidity of fluids; imperfect elasticity of solids; inequalities of temperature and consequent conduction of heat produced by stresses in solids and fluids; imperfect magnetic retentiveness; residual electric polarization of dielectrics; generation of heat by electric currents induced by motion; diffusion of fluids, solution of solids in fluids and other chemical changes and absorption of radiant heat and light. The dissipation of the energy investigation can be done by studying the dynamics of the particles [43,47-52].

When a physical system experiences a physical process, some energy may be applied to the system, and in a resultant, some of the energy components of the system will be activated. Some of the activated components are related to the irreversible processes, and the remaining are related to the reversible processes. From another perspective, for special applied energy to the system, some components change independently, and the remaining will change depending on the independent component. Dependent components can depend on the amount and rate of the independent components. Therefore, Eq. (20) can be considered as the energy structure of the system in a particular process

$$U_{E-C} = (u_1 + u_2 + \cdots + u_m) + [g_1 + \cdots + g_k] + [h_1 + \cdots + h_n] \tag{20}$$

where

$$g_j = g_j(u_1, u_2, \dots, u_m) \tag{21}$$

$$h_p = h_p(\dot{u}_1, \dots, \dot{u}_m) \tag{22}$$

That u_i are independent components, g_j and h_p are dependent components of energy. Components h_p do not active in quasi-static condition.

If some energy is applied to the system, once in a quasi-static path and once in a general path, Eq. (23)-(28) must be established

$$\delta u_j + \sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\delta u_j\right) + \sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\delta \dot{u}_j\right) = \delta u'_j + \sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\delta u'_j\right) \tag{23}$$

Where δu_j is the variation of the u_j when $\dot{u}_j \neq 0$, as the value of energy δU_T is given to the system. Also, $\delta u'_j$ is the variation of the u_j when $\dot{u}_j \cong 0$, as the value of energy δU_T is given to the system. Therefore

$$\left(1 + \sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\right)\right)\left(\delta u_j - \delta u'_j\right) = -\left(\sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)\delta \dot{u}_j \tag{24}$$

$$-\left[\frac{\left(\sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1+\sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\right)\right)}\right] = \frac{\left(\delta u_j - \delta u'_j\right)}{\delta \dot{u}_j} \tag{25}$$

$$-\left[\frac{\left(\sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1+\sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\right)\right)}\right]\left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) = \frac{\left(\delta u_j - \delta u'_j\right)}{\delta \dot{u}_j}\left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) \tag{26}$$

$$\left[\frac{\left(\sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1+\sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\right)\right)}\right]\left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) = -\frac{\left(\delta u_j - \delta u'_j\right)^2}{\dot{u}_j \delta \dot{u}_j} \tag{27}$$

Since the quasi-static path is used as a reference path, therefore

$$\left[\frac{\left(\sum_{p=1}^{n}\left(\frac{\partial h_p}{\partial \dot{u}_j}\right)\right)}{\left(1+\sum_{i=1}^{k}\left(\frac{\partial g_i}{\partial u_j}\right)\right)}\right]\left(\frac{\delta u_j - \delta u'_j}{\dot{u}_j}\right) \leq 0 \tag{28}$$

Relation (28) shows the physical direction of physical processes based on the energy structure of the system. Also, relation (28) must be established in all performed processes. In section 6, it will be shown that this relation can extract Kelvin-Plank and Clausius formulations of the second law as well as entropy from the perspective of the statistical physics.

6. Extracting Different Formulations of the Second Law

In this part, different classical and statistical formulations of the second law are extracted from relation (28).

6.1 Kelvin-Plank Formulation

By assumption W as independent component and $Q_{L_{Irreversible}}$ as dependent component, due to this fact that functions g_i are zero in this case, relation (28) can be rewritten as follows

$$[\frac{\partial Q_{L_{Irreversible}}}{\partial(\dot{W})}](\delta W_{Carnot} - \delta W) \geq 0 \tag{29}$$

That is equivalence as the relation (7).

6.2 Clausius Formulation

By assumption $Q_{L_{Irreversible}}$ as independent component and Q_H as dependent component, due to this fact that functions g_i are zero in this case, relation (28) can be rewritten as follows

$$[\frac{\partial Q_H}{\partial(\dot{Q}_{L_{Irreversible}})}](\delta Q_{L_{Irreversible}} - \delta Q_{L_{Carnot}}) \geq 0 \tag{30}$$

That is equivalence as the relation (14).

6.3 Entropy from The Perspective of The Statistical Physics

By assumption the variable change $\delta U_j = \delta u_j - \delta u'_j$, and using Eq. (24), relation (31) will be deduced from relation (28) as follows

$$\left(-\frac{\delta \dot{U}_j}{\dot{U}_j}\right) \leq 0 \tag{31}$$

or

$$\delta[\ln(\dot{U}_j)] \geq 0 \tag{32}$$

Given that all of the independent components are applied to relation (32), therefore

$$\delta\,[\ln(\dot{U}_1)] + \delta[\ln(\dot{U}_2)] + \cdots + \delta\,[\ln(\dot{U}_m)] \geq 0 \tag{33}$$

$$\delta[\ln(\textstyle\prod_{j=1}^{m} \dot{U}_j)] \geq 0 \tag{34}$$

Relation (34) has the same base as the Eq. (18).

7. Conclusions

From the perspective of classical thermodynamics, there are two main formulations to the second law: Kelvin-Plank and Clausius formulations. These two main classical formulations are all assertions about impossible processes. Considering the entropy as a physical quantity to present a statement to the second law of thermodynamics, based on these formulations, it can result that entropy increases always. Entropy is the most important physical quantity that is raised by the second law of thermodynamics.

Statistical physics studies entropy using a statistical approach. In fact, from the perspective of statistical physics, Boltzmann's equation is used to calculate the absolute value of the entropy based on the microstates of the system. In fact, entropy in a considered state is supposed as a function of the possibility of that state. Therefore, all microstates of the system must be investigated.

Considering the energy component of the system to formulate the second law of thermodynamics, relations (7) and (14) are equivalent to the Kelvin-Plank and Clausius formulations of the second law that are extracted based on Eq. (5) and Eq. (13) as the energy structure of the considered systems in the considered process.

In part 5, an energy structure equation is presented (Eq. (23)), and is investigated for constant applied energy to the system in different conditions. A quasi-static path is used as the reference path, and the variation of the energy structure is studied in general paths. Using this approach, relation (28) is extracted as the physical direction of the physical processes based on the activated energy components of the system.

Finally, equivalences of relation (28) as different formulations of the second law are shown. In fact, this relation presents a new general formulation to the second law based on the energy structure of the system in the performed processes.

The presented formulation is extracted directly based on the energy components of the system. In fact, this formulation shows the possible paths of the variation of the energy structure equation in the considered energy applying.

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