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Unified Classical Thermodynamics: Primacy of Dissymmetry over Free Energy

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Abstract: In thermodynamic theory, free energy (i.e., available energy) is the concept facilitating the combined applications of the theory's two fundamental laws, the first and the second laws of thermodynamics. The critical step was taken by Kelvin, then by Helmholtz and Gibbs—that in natural processes, free energy dissipates spontaneously. With the formulation of the second law of entropy growth, this may be referred to as the dissymmetry proposition manifested in the spontaneous increase of system/environment entropy towards equilibrium. Because of Kelvin's pre-entropy law formulation of free energy, our concept of free energy is still defined, within a framework on the premise of primacy of energy, as "body's internal energy or enthalpy, subtracted by energy that is not available". This primacy of energy is called into question because the driving force to cause a system's change is the purview of the second law. This paper makes a case for an engineering thermodynamics framework, instead, to be based on the premise of the primacy of dissymmetry over free energy. With Gibbsian thermodynamics undergirded with dissymmetry proposition and engineering thermodynamics with a dissymmetry premise, the two branches of thermodynamics are unified to become classical thermodynamics.

Keywords: energy physics; free energy; energy conversion doctrine; extreme principles of equilibrium; dissymmetry premise

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1. Introduction: Free Energy vs. Nature's Dissymmetry

Fire has been used by humans for heat, light, and cooking. Then, in 1712, Newcomen invented a new use of fire, the meaning of which was provided by Thomson more than one century later with his *energy physics* explaining the invention of steam engines as the harness/transformation of high temperature heat as a form of disorganized energy (DOE) into mechanical energy, an organized energy (OE). From the very beginning, Thomson gleaned that there were two questions involved, the question raised by Carnot of *what* drives the transformation and the question raised by Joule of what *closure condition* the transformation is subject to. They will be referred to as the "two DOE questions". The answer to the latter of the two was provided by Joule himself that the closure condition is that "total energy stays the same in every transformation even though the energy of the system or subsystems may change". However, Thomson was not sufficiently clear-eyed in his synthesis of the competing claims of Carnot and Joule and the treatment of transformation by energy physics did not unequivocally separate the two questions. This remains so in today's engineering thermodynamics in terms of the theory of exergy. The theory of exergy, or the energy conversion doctrine, is one way to understand thermodynamic transformations, but the premise of free energy as the sole driver of thermodynamic transformations represents the relic of philosophical mechanism treating all phenomena reducible to locomotion (the term as used by Georgescu-Roegen in *The Entropy Law and the Economic Process*, as the "motion of atoms and molecules"). The paper argues that the new use of fire can be best encapsulated not as the discovery of energy conversion of a new form of energy in disorganized ***locomotion*** to OE but as the discovery of the phenomena of

transformation, because the latter (which involve two questions) is not reducible to the theoretical treatment of motion of atoms and molecules (for which the two questions are conflated into one with the answer provided by *equations of motion*). Not that calculations based on energy conversion give the wrong answers, the paper claims, but that treating transformations as reducible to locomotion leaves out questions about what is possible in the irreversible world of transformations. One is left with a distorted understanding of the irreversible world.

The theory of thermodynamics is based on a set of four laws of thermodynamics: the zeroth law of thermodynamics defining temperature, the first law of thermodynamics of energy conservation, the second law of thermodynamics of inexorable entropy growth, and the third law of thermodynamics defining the absolute entropy value. While the theory is incomplete with the absence of any one of the four laws, it may be said that the two principal laws of the set are the first law and the second law and that the core content of the theory is the applications of the two principal laws.

In the formative years of thermodynamics of 1850 to 1855, in ref. [1], the focus was on the combined application of the two laws for treating the interactive relationship between heat and work in terms of energy. The defining problem of thermodynamics was the motive power of heat. For this reason, Thomson (Kelvin) introduced the concept of available energy (or free energy), i.e., in the interactions between heat and work, total energy is conserved but available energy dissipates ([2]: pp. 511–514; see also [1]: Appendix II, especially [page five]). In the title of paper [2], Thomson talks about the dissipation of mechanical energy, but he clearly was referring to the dissipation of mechanical energy *and* available energy: "the universal dissipation of mechanical energy meant the universal dissipation of available energy" ([3]: p. 5). That Thomson should be credited as the sole originator of the concept was made clear by Maxwell:

> Thomson, the last but not the least of the three great founders [Clausius, Rankine, and Thomson], does not even consecrate a symbol to denote the entropy, but he was the first to clearly define the intrinsic energy of a body, and to him alone are due the ideas and definitions of the available energy and the dissipation of [available] energy. [4]

Between 1854 and 1865, Clausius developed his entropy theorem, which he referred to initially as the second fundamental theorem (the equivalence theorem of heat and work as the first fundamental theorem). The development culminated in 1865 in the formal introduction of entropy as a new thermodynamic variable, and the formulation of the entropy principle as the second law of thermodynamics.

With the introduction of entropy, we have the complete set of thermodynamic variables: pressure, volume, temperature, internal energy, and entropy. The focus of thermodynamics shifted from engineering and engineered processes of energy conversion to physics/chemistry and spontaneous natural processes driven by thermodynamic potentials. As Vemulapalli noted,

> Massieu [1869] and Gibbs [1873] steered thermodynamics in a radically different direction. Their idea was to find characteristic functions, called thermodynamic potentials, for a system and relate all thermodynamic properties of the system to these functions. Thermodynamic processes between system and surroundings are viewed as consequences of changes in thermodynamic potentials within the system, while in earlier theories the properties of a system were defined by its interaction with the surroundings. Massieu and Gibbs were perhaps the first to consider entropy as a property of the system rather than as energy unavailable for work on the surroundings. [5]

The concept employed by Gibbs for steering thermodynamics in the radically new direction was the same concept of free energy that played the key role in Thomson's investigation of engineered processes of energy conversion. However, in that shift, a fundamentally different interpretation to the nature of dissipation of free energy was considered, from the universal dissipation of free energy in energy conversion ([2]: pp. 511–514) to the spontaneous dissipation of free energy in a system's transformation toward internal equilibrium. How we should understand the shift from energy conversion as the defined problem to spontaneous transformations as the defined problem, and how to evaluate in this shift the two different interpretations to the nature of free energy dissipation will be guiding the investigation of the paper.

The paper consists of six sections (not counting Section 1 for Introduction and Section 8 for Afterword) organized into four groups: Sections 2 and 3: a summary of Gibbsian equilibrium thermodynamics, which is the outgrowth of the entropy principle formulation of the second law; Sections 4 and 5: a review of pre-entropy energy physics; Section 6: the first step of the unification of energy physics into the framework of Gibbsian ET; Section 7: the second step of the unification by generalizing the framework of Gibbsian ET into the framework of classical thermodynamics in terms of the dissymmetry premise.

Sections 2 and 3 give a summary/outline of *Gibbsian equilibrium thermodynamics*, in which thermodynamics became for the first time a complete theoretical system. In achieving this success, however, equilibrium thermodynamics leaves aside its original engineering mandate of the "harness/transformation of high temperature heat as a form of disorganized energy into mechanical energy". The defining problem became instead "the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system". In Section 3, some details are provided to describe the spontaneous tendency of systems towards equilibrium as a manifestation of the second law. This has been referred to as nature's dissymmetry in a book on *The Second Law* by Atkins. Dissymmetry and its manifestation into chaos are the themes of *The Second Law* [6]: Chapter 3 of which talks about the natural tendency of "collapsing into chaos"; the "potency of chaos" and that "the central theme of our discussion so far is that chaos can be constructive" are topics of Chapter 5; and "constructive chaos" and "patterns of chaos" are among the topics of Chapters 8 and 9. We adopt the term *dissymmetry* here as a shorthand for "inexorable growth in total entropy" or "the preferred direction of spontaneous change".

In Sections 4 and 5, the paper returns to its original engineering focus with a review of energy physics. A critical evaluation is carried out. A key point of the review is that energy physics was the result of a synthesis by Thomson to reconcile the competing claims of Carnot and Joule. One way to describe the competing claims is that there are *two* questions involved in the transformation of disorganized energy into organized energy: "the question raised by Carnot of *what* drives the transformation and the question raised by Joule of what *closure condition* the transformation is subject to". We refer to the two questions as two disorganized energy (DOE) questions. In their parallel development of engineering thermodynamics, it is shown that Thomson did not unequivocally separate the "two DOE questions", whereas in Clausius' treatment in Section 5, we find a clear separation of "positive transformation" (which drives a Carnot cycle) from "negative transformation" of heat into mechanical energy.

The success of Gibbsian equilibrium thermodynamics is attributed to the fact that it is a theoretical system of inferences (in terms of "states" or "properties" as the fundamental constructs of the theory) centered on the entropy law. The identification of negative transformation as the "extraction of heat transforming which into mechanical energy" prepares for linking Gibbsian equilibrium thermodynamics readily with applications to problems of engineering thermodynamics as shown in Section 6.

Despite the elegance of the Gibbsian ET framework, we need an "entropy-centric framework" with more flexibility for treating general transformations of disorganized energy into organized energy, meeting the separation requirement of the two DOE questions. Section 7 gives a preliminary description of such a framework, which will also be referred to as the Unified Classical Thermodynamics framework. That is, the new direction of thermodynamics taken by Clausius and Gibbs created equilibrium thermodynamics, but the shift, solely as the creation of a new branch, is not a complete project until the original engineering thermodynamics branch is unified with the new branch into a unified framework of UCT. The main point of Section 7 is that such a framework begins with the dissymmetry premise, primacy of dissymmetry over free energy. The Section also gives a critique of the theory of exergy; an examination of the meaning of reversibility in greater depth; and the allusion that, for the last three centuries, energy-centric-based entropy has led us astray with wrong inferences and how the entropy-centric framework points to a future for the co-existence of mankind and the planet.

In one sense, the paper transforms engineering thermodynamics into a theoretical system by translating the verbal "chaos can be constructive" assertion of *The Second Law* [6] into a quantitative theoretical system of classical thermodynamics unifying the two branches of equilibrium and engineering thermodynamics.

2. Application Statement Combining the First and Second Laws

Let us start with the first law,

$$dU = \delta Q - \delta W \tag{1}$$

where U is the internal energy of the system, Q the heat added to the system, and W the work produced by the system. According to the IUPAC notation, W_{IUPAC} is defined as work injected or applied to the system. Here, the sign convention adopted in (1) is the engineering sign convention for W defined as work generated by the system, whereas a work injected to the system, which must be paid for, is assigned as negative in engineering notation, i.e., $W_{IUPAC} = -W$. Or,

$$dU = \delta Q + \delta W_{IUPAC}$$

At this point, it is useful to introduce the concepts of reversibility, internal reversibility, and quasi-staticity ([7]: Section 6.5), see Figure 1, which is reproduced from [7]).

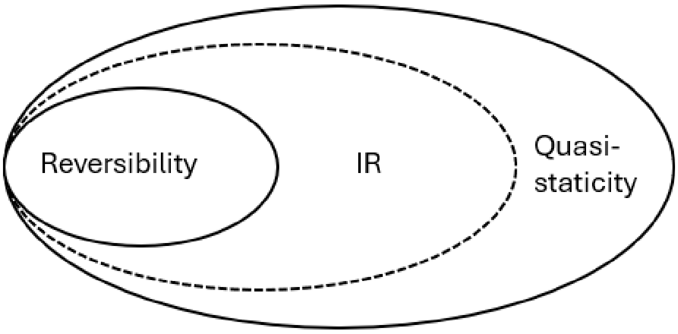


Figure 1. Venn diagram of the conditions of reversibility, internal reversibility (IR), and quasi-staticity.

Between 1854 and 1865, Clausius formulated the second law first by expressing entropy, S, to heat added to the system,

$$dS = \left({}^{\delta Q}/{}_{T}\right)_{Rev} \tag{2}$$

and the second law itself as

$$S_{final} - S_{initial} \geq 0 \tag{3}$$

Similarly, for reversible processes, the work produced by the system is $\delta W = pdV$, where p is the pressure of the system and V the volume of the system. Substitution of δW and δQ (Equation (2)) into Equation (1) yields, for reversible processes, $dU = TdS - pdV$, the combined statement of the first law and the second law.

The condition of reversibility in (2) is a severe limitation to the equation, rendering it useless: If no real process can be truly reversible, how can we apply (2) for determining the value of entropy? To answer the question, classical (Carathéodory) formalism introduced the *quasi-static process* interpretation of $dU = TdS - pdV$, and Landsberg noted, in the formalism, “the concept of reversible processes, which plays an essential role in many expositions of thermodynamics, is not required in the present approach” [8].

As noted in *A Treatise* [7], Sections 6.2 and 6.7, classical formalism is correct in pointing out that reversibility is too restrictive a condition for defining entropy. Classical formalism is mistaken, however, in replacing reversibility with quasi-staticity. An argument is made in *A Treatise* ([7]: Section 6.7) that quasi-staticity in the classical formalism,

$$(\delta Q)_{Quasi} = TdS \tag{4}$$

is *in fact* internal reversibility,

$$(\delta Q)_{IR} = TdS \tag{5}$$

The so called “quasi-static work and quasi-static heat” expressions should be “internal reversibility work and heat” expressions, $(\delta W)_{IR} = pdV$ and (5).

Referring to Figure 1, reversibility, the condition for the definition of entropy in accordance with Clausius, is the sufficient condition for the definition of entropy, while quasi-staticity is the necessary condition, and internal reversibility, IR, is the necessary and sufficient condition. Correspondingly, of the four equations,

$$dU = \delta Q - \delta W$$

$$dU = \delta Q - pdV \tag{6}$$

$$dU = TdS - \delta W \tag{7}$$

$$dU = TdS - pdV \tag{8}$$

Equation (1) always holds because it is the first law expression, while Equations (6) and (7) hold only under IR conditions when “internal reversibility work” and “internal reversibility heat” apply, respectively.

Let us turn our attention to the last equation of the set of four:

$$dU = TdS - pdV$$

Even though *A treatise* [7] refutes classical formalism’s replacement of reversibility with quasi-staticity for the definition of entropy, the innovation of classical formalism on quasi-staticity is of fundamental importance. Its introduction answers the question, “If no real process can be truly reversible, how can we determine the value of entropy without relying on Equation (2)?” It turns out that we do not need Equations (2) or (5) because of the availability of Equation (8), which holds, under the condition of quasi-staticity, for the expression being a differential form of a relation among thermodynamic state functions of U, T, S, p, and V, the values of which depend on states independent of the specific paths of the system approaching the states. We may consider a functional relation of U as a function of S and V.

Callen calls this functional relation a *fundamental relation*, [9]

$$U = U(S, V) \tag{9}$$

partial derivatives of which are identified as

$$T = T(S, V) = (\partial U/\partial S)_V \tag{10}$$

$$p = p(S, V) = -(\partial U/\partial V)_S \tag{11}$$

The validity of relations (8), (9), (10), and (11) is their quasi-staticity.

In sum, as *A Treatise* concludes, “A reversible machine remains the best or natural approach to start the consideration of the concept of entropy” ([7]: p. 152); once the introduction is made, “classical formalism is correct in pointing out that reversibility is a too restrictive condition for defining entropy”, but the proposed condition for entropy definition, quasi-staticity, "is *in fact* internal reversibility", the condition for internal reversibility work and internal reversibility heat; the importance of the proposed quasi-staticity lies not in serving as the condition for defining entropy but instead for enabling the value determination of entropy through establishing the *quasi-staticity validity* for the set of the fundamental relation, (9), its associated partial derivatives, (10) and (11), and the differential form of the fundamental relation, (8).

For an example of the value determination of entropy without involving the direct use of the entropy definition of (2) or (5), one finds, for instance, the application of Equation (16) in paper [5].

For highlighting the pivotal role *quasi-staticity validity* plays as the foundation of classical formalism, I propose to call the fundamental relation, Equation (9), the Gibbs–Carathéodory fundamental relation, and Equation (8) the Gibbs–Carathéodory equation.

3. Method of Potentials: Nature's Dissymmetry

The Gibbs–Carathéodory fundamental relation is a canonical relationship of one *canonical form*. We refer to $U = U(S, V)$ as the energy representation of the fundamental relation ([9]: pp. 28, 41). Correspondingly, $S = S(U, V)$ is referred to as the entropy representation of the fundamental relation ([9]: p. 41).

"It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy has reached a maximum, the system will be in a state of equilibrium", noted Gibbs [10]. Consider an example of an isolated composite system consisting of a subsystem$^{(1)}$ and a subsystem$^{(2)}$, details of which are found in Callen ([9]: Chapter 2). The entropic fundamental relation is

$$S = S^{(1)}\left(U^{(1)}, V^{(1)}\right) + S^{(2)}\left(U^{(2)}, V^{(2)}\right) \tag{12}$$

(12) is subject to the restriction of the closure conditions

$$U^{(1)} + U^{(2)} = constant \tag{13}$$

$$V^{(1)} + V^{(2)} = constant \tag{14}$$

Assume that such a system initially exists at $T^{(1)}{}_{ini} > T^{(2)}{}_{ini}$ and $p^{(1)}{}_{ini} > p^{(2)}{}_{ini}$. And assume that the wall separating the two subsystems that has kept the system at its initial state are replaced by a diathermal and movable wall at a given time. The system will spontaneously move towards thermodynamic equilibrium in accordance with the entropy law corresponding to a state of maximum entropy. That is,

$$dS_{equili} = 0 \tag{15}$$

Substitution of (12) into (15) yields is

$$\begin{gathered} 0 = dS_{equili} = dS^{(1)}{}_{equili} + dS^{(2)}{}_{equili} = \\ \left[\left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)}} dU^{(1)} + \left(\frac{\partial S^{(1)}}{\partial V^{(1)}}\right)_{U^{(1)}} dV^{(1)}\right] + \left[\left(\frac{\partial S^{(2)}}{\partial U^{(2)}}\right)_{V^{(2)}} dU^{(2)} + \left(\frac{\partial S^{(2)}}{\partial V^{(2)}}\right)_{U^{(2)}} dV^{(2)}\right] \end{gathered} \tag{16}$$

Note the definition of temperature, $\left(\frac{\partial S^{(1)}}{\partial U^{(1)}}\right)_{V^{(1)}} = \frac{1}{T^{(1)}}$, and of pressure, (11), therefore, $\left(\frac{\partial S^{(1)}}{\partial V^{(1)}}\right)_{U^{(1)}} = \frac{p^{(1)}}{T^{(1)}}$. It follows,

$$0 = \frac{1}{T^{(1)}} dU^{(1)} + \frac{1}{T^{(2)}} dU^{(2)} + \frac{p^{(1)}}{T^{(1)}} dV^{(1)} + \frac{p^{(2)}}{T^{(2)}} dV^{(2)}$$

In view of the closure conditions, $dU^{(2)} = -dU^{(1)}$ and $dV^{(2)} = -dV^{(1)}$, we find

$$0 = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)dU^{(1)} + \left(\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}}\right)dV^{(1)} \tag{17}$$

As this expression, $0 = dS_{equili}$, must vanish for arbitrary and independent values of $dU^{(1)}$ and $dV^{(1)}$, we must have

$$T^{(1)}{}_{equili} = T^{(2)}{}_{equili} \tag{18}$$

and

$$p^{(1)}{}_{equili} = p^{(2)}{}_{equili} \tag{19}$$

"Massieu [1869] and Gibbs [1873] steered thermodynamics in a radically different direction". In this move, as Callen noted, the formulation of thermodynamics "features states, rather than processes as fundamental constructs" ([9]: viii of first edition). Rather than the motive power of heat, the defining problem of thermodynamics became the existence of spontaneity towards equilibrium and what defines the condition of equilibrium: the existence of spontaneous direction or dissymmetric direction is the direct outcome of the entropy law, Equation (3), and the condition defining the equilibrium of maximum entropy over the constraint of constant *system* U and *system* V is an immediate inference derived from the law, Equation (15).

Variables that can be controlled and measured experimentally are p, V, and T. The first law introduces the variable U, and with the introduction, one can express U as a function of the set of any two of the variables p, V, and T, e.g., $U = U(p, V)$ or $U = U(p, T)$. These are examples of *equations of state*. The determination of equations of state is described in Chapter 7 of Callen ([9]: Chapter 7) in terms of the application of Maxwell relations. These relations arise from the equality of the mixed partial derivatives of the fundamental relation expressed in any of the various possible alternative representation. A fundamental relation, the concept that a relation is privileged if it is a relation among a canonical set, e.g., the set of U, S, and V in energy representation, is the direct outcome of the introduction from the second law of variable entropy.

Another way to describe the fundamental relation is that it is an equation of state with special status. Note that the derivatives of which give rise to the *set* of Equations (10) and (11), which individually are also equations of state but without the special status. That is, knowledge of a fundamental relation constitutes the knowledge of the complete set of the derived set of equations of state, thus the complete knowledge of the thermodynamic properties of a system, whereas a single equation of state in the set does not constitute complete knowledge of the thermodynamic properties of the system.

We can expand the significance of the fundamental relation, $U = U(S, V)$, by replacing one or both independent variable(s) with alterative(s) that can be controlled or is(are) particularly convenient in certain types of problems, for instance, replacing (S, V) with (T, V). However, the relation of $U(T, V)$ will not preserve the "complete knowledge"; $U(T, V)$ is not a fundamental equation of state as $U(S, V)$ is. One needs to find the Legendre transformation of U, which in the case of $S \to T$ replacement is the Helmholtz function, A_H ([9]: Sections 5-2 and 5-3),

$$A_H = A_H(T, V) = U - TS \tag{20}$$

$$dA_H = -SdT - pdV \tag{21}$$

$A_H(T^r, V)$ is the fundamental equation of state (fundamental relation) of an isothermal composite system in interaction with an isothermal heat reservoir at T^r. Consider next the replacement of (S, V) with (S, p). The Legendre transformation of U, in this case, is enthalpy, H ([9]: Sections 5-2 and 5-3),

$$H = H(S, p) = U + pV \tag{22}$$

$$dH = TdS + Vdp \tag{23}$$

$H(S, p^r)$ is the fundamental equation of the state of a composite system in interaction with a constant pressure reservoir. Consider further the Legendre transformation of H replacing (S, p) with (T, p). The Legendre transformation of H in this case is

$$G = G(T, p) = U + pV - TS \tag{24}$$

$$dG = -SdT + Vdp \tag{25}$$

$G(T^r, p^r)$ is the fundamental equation of state of a chemical composite system in interaction with a constant temperature, constant pressure reservoir.

Returning to the consideration of the fundamental relation, $A_H(T, V)$. Consider an isothermal composite system consisting of subsystems $V^{(1)}$ and $V^{(2)}$, which are subject to the constraint of $V^{(1)} + V^{(2)} = const$. The system is kept at constant temperature due to interaction with a heat reservoir/bath. Such a system is not an isolated system. But the totality of the composite system and the isothermal heat bath is the combined system in total is an isolated system. For the COMBINED system of the composite system and the isothermal heat bath, therefore, Equation (15) takes the form

$$d_{equi}(S + S^r) = 0 \tag{26}$$

where S^r is the entropy of the heat bath (reservoir), which is kept at a constant temperature of T^r. We may write (26) as

$$T^r d_{equi}(S + S^r) = 0 \tag{26a}$$

Since $V^{(1)} + V^{(2)} = const$ implies $\delta W = 0$, and that $\delta Q = -\delta Q^r$, with a heat bath remaining at constant T^r in which heat transmission approximates a reversible heat transmission, $\delta Q^r = T^r dS^r$, we have the following, in accordance with the first law:

$$dU = \delta Q + 0 = -\delta Q^r = -T^r dS^r$$

Through the substitution of $dS^r = -\frac{dU}{T^r}$ into (26a) yields,

$$T^r d_{equi}(S + S^r) = T^r d_{equi}S + T^r d_{equi}S^r = T^r d_{equi}S - d_{equi}U = -d_{equi}(U - T^r S) = 0 \tag{27}$$

Since the extreme of entropy is a maximum of $S + S^r$, (27) represents an equilibrium condition of minimum of $U - T^r S$, i.e., the equilibrium condition of minimum of the Helmholtz function, $A_H(T^r, V)$. The Helmholtz function of the composite system is, in view of (21), and $dT = 0$ and $V^{(1)} + V^{(2)} = const$,

$$d\left({A_H}^{(1)} + {A_H}^{(2)}\right) = -p^{(1)}dV^{(1)} - p^{(2)}dV^{(2)} = \left[-p^{(1)} + p^{(2)}\right]dV^{(1)}$$

It follows, therefore, at equilibrium,

$$d\left({A_H}^{(1)} + {A_H}^{(2)}\right) = \left[-{p^{(1)}}_{equi} + {p^{(2)}}_{equi}\right]dV^{(1)} = 0$$

that is,

$${p^{(1)}}_{equi} = {p^{(2)}}_{equi} \tag{28}$$

Consider next the case of a composite system kept at a constant pressure, p^r, consisting of subsystems $T^{(1)}$ and $T^{(2)}$. This part of discussion is further clarified by limiting the consideration to that of an isolated composite system,

$$H\left(T^{(1)}, p^r\right) + H\left(T^{(2)}, p^r\right) = H^{(1)} + H^{(2)} = const \tag{29}$$

Interaction with such an isolated system does not change the entropy of the reservoir with which it interacts. Therefore, (26) reduces to $d_{equi}S = 0$. It follows from $dS = \frac{1}{T}dH - \frac{V}{T}dp = \frac{1}{T}dH$,

$$dS = dS^{(1)} + dS^{(2)} = \frac{1}{T^{(1)}}dH^{(1)} + \frac{1}{T^{(2)}}dH^{(2)} = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)dH^{(1)}$$

which follows

$$0 = d_{equi}S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right)_{equi} dH^{(1)}, \text{therefore,}$$

$$T^{(1)}{}_{equi} = T^{(2)}{}_{equi} \tag{30}$$

We now consider the third alternate thermodynamic potential of $G = G(T, p) = U + pV - TS$. To consider this case as a composite system, we need to generalize our investigation to that of multiple component systems that are chemically active, the Gibbs function of which is

$$G(T, p, N_1, N_2, \ldots, N_r) = U + pV - TS = H - TS \tag{31}$$

which means that

$$U(S, V, N_1, N_2, \ldots, N_r), \text{ and}$$

$dU = TdS - pdV + \sum_{j=1}^{r} \mu_j dN_j$, ([9]: Chapter 2 and Section 6-4), correspondingly,

$$dG = -SdT^r + Vdp^r + \sum_{j=1}^{r} \mu_j dN_j = \sum_{j=1}^{r} \mu_j dN_j \tag{32}$$

The original form of (26a) applies in this case:

$$T^r d_{equi}(S + S^r) = 0$$

The first law leads to

$$dU = \delta Q - pdV,$$

which in view of $\delta Q = -\delta Q^r = -T^r dS^r$ becomes, $dU = -T^r dS^r - p^r dV$.
That is,

$$0 = T^r d_{equi}(S + S^r) = -d_{equi}(H - T^r S) = -d_{equi}G \tag{33}$$

We may write (32) by introducing the stoichiometric coefficients defined as

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \frac{dN_3}{\nu_3} = \cdots \equiv d\tilde{N} \tag{34}$$

Then, (32) becomes

$$dG = \sum_{j=1}^{r} \mu_j dN_j = d\tilde{N} \sum_{j=1}^{r} \nu_j \mu_j$$

The equilibrium condition (33) becomes, therefore,

$$\sum_{j=1}^{r} \nu_j \mu_j = 0 \tag{35}$$

The direct inference of the second law of thermodynamics that a system has a spontaneous tendency towards equilibrium characterized in terms of the maximization of total entropy of the system and its interacting surroundings (for isolated systems that will be the entropy of the system counted by itself) is the dissymmetry proposition of thermodynamics. One of the three cases considered in this section has the option of dealing with chemical changes and the other dealing exclusively with chemical changes. For these two cases, (27) and (33), the Helmholtz function, $U - T^r S$, and the Gibbs function, $H - T^r S$, introduced the concept of *free energy*—which supplants the old idea of affinity (the concept in accordance with the *thermal theory of affinity*) as the true measure of what drives chemical changes.

4. Kelvin and the Creation of Energy Physics: Free Energy

Whether as the Helmholtz function and the Gibbs function, or as Helmholtz free energy and Gibbs free energy, the formers are examples of the concept used as affinity that relates irreversible chemical reactions to entropy increases, whereas the latters are examples of the concept "used in connection with equilibrium states and reversible processes" for producing mechanical energy ([11]: p. 111)—this was the topic of thermodynamics in its formative years, to which we return in this section and the next section.

In the period of 1840–1851, William Thomson (Kelvin) with his years of interaction with Joule, finally became convinced of Joule's claim of interconversion between heat and work as described by Smith:

> . . . while THOMSON sees JOULE as asserting and supporting a framework of mutual convertibility he still does not himself believe that a satisfactory demonstration of the conversion of heat into work by experiment has been given. Nonetheless, THOMSON now . . . "considers it certain that the fact has only to be tried to be established experimentally, having been convinced of the mutual convertibility of the agencies by Mr. Joule's able arguments". ([2]: pp. 174–200 (1851)) So THOMSON has in effect come to accept JOULE'S conceptual framework before he has been convinced by actual experiments of the validity of the conversion of heat into work. While little of this discussion appears in the Introduction as published in 1851, THOMSON there sums up his position, having rejected heat as having a substantial nature, and holding heat to be instead "a dynamical form of mechanical effect" wherein . . . "there must be an equivalence between mechanical work and heat, as between cause and effect". ([1]: p. 268)

The 1851 paper was the culmination of Thomson's skepticism and critical evaluation of the competing ideas of Carnot's and Joule's, both ideas having elements that are convincing in themselves but also the same or other elements that are contradictory with each other. "A fuller appreciation of the conceptual problems and subtleties in Thomson's thought" can be found in Thomson's draft of the 1851 paper, which is documented and reproduced in the Appendix II of ref. [1]: *Text of William Thomson's Preliminary Draft for the "Dynamical Theory of Heat"*.

As Harman in another historical study wrote,

> In an address to the British Association in **1854**, Thomson declared that Joule's discovery of the conversion of heat into work had 'led to the greatest reform that physical science had experienced since the days of Newton', the development of energy physics. In his introductory lecture at Glasgow in **1846**, Thomson had argued that physics was to be based on the laws of dynamics, physics being the science of force. By **1851** energy had become, in his view, the primary concept on which physics was to be based. [12]

Among the 19th century scientists, Thomson was the most important holdout from embracing heat–work convertibility throughout 1840s. By 1851, however, he came to accept "equivalence between mechanical work and heat" as interpreted to be allowing conversion of heat into work. From that point onward, he became the greatest champion of the energy-central view of physics.

The fact that he "has in effect come to accept Joule's conceptual framework before he has been convinced by actual experiments of the validity of the conversion of heat into work", however, remained true. From 1851 to 1855, Thomson's research had progressed to formulate a conceptual framework of his own. It was a theoretical framework, rather than a framework based on the empirical evidence of an actual experiment. It was a framework based on the core idea that there are two fundamental laws of thermodynamics. We shall call this, because there cannot be a complete theory of thermodynamics without the concept of entropy while Thomson's second fundamental law was formulated without using the concept of entropy, not the thermo-dynamics framework but Thomson's energy physics framework.

The key step of this development was the 1852 Thomson paper ([2]: 511–514), in which he wrote, "The object of the present communication is to call attention to the remarkable consequences which follow from Carnot's proposition, that there is an absolute waste of mechanical energy available to man when heat is allowed to pass from one body to another at a lower temperature, by any means not fulfilling his criterion of a 'perfect thermo-dynamic engine,' established, on a new foundation, in the *Dynamical Theory of Heat*. As it is most certain that Creative Power alone can either call into existence or annihilate mechanical energy, the 'waste' referred to cannot be annihilation, but must be some transformation of energy". He referred to which in the draft of the 1851 paper ([1]: Appendix II, especially [page five]), as the *dissipative transformation* of *available energy*.

This was how Thomson formulated his second law of thermodynamics as well as, in a single stroke, pointed out the combined application of the two laws of thermodynamics in terms of the conservation of energy (energy cannot be annihilated) and the dissipation of available energy. Later, Helmholtz and Gibbs adopted the concept of the spontaneous dissipation of Helmholtz free energy and Gibbs free energy. Note, however, Helmholtz and Gibbs were interested in problems of physics and chemistry, not transformations between heat and work in either direction. In contrast, Kelvin was interested in the production of mechanical energy, which is the purview of engineering. Kelvin ended the barely four-page paper ([2]: 511–514) with three *general conclusions*, the second of which is:

> *General conclusion 2. Any restoration of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subjected to the will of an animated creature.*

Thomson (Kelvin) in this paper is "back to thinking directly about the Second Law, and he has cut through the technicalities, and is stating the Second Law in everyday terms", as noted by Stephen Wolfram [13]. It is significant that, in the way that he talked about "the control of man sources of power which if the opportunity of turning them to his own account had been made use of might have been rendered available" ([1]: Appendix II, especially [page six]), Thomson realized that he was dealing with an atypical law of nature, not one of the objectivity (without a model of observers) of mathematical paradigm. Wolfram may be on to something in his search for new paradigms in the case of the second law, as "a story of the interplay between underlying computational irreducibility and our nature as computationally bounded observers" [14]. Eddington in 1929 anticipated *explicitly* the view of the second law being an atypical law of nature ([15]: Chapter 4).

Even with his intuition about the unique nature of the second law, three-quarters of a century before Eddington and one and three-quarters centuries before Wolfram, Thomson in 1852 was not able to transcend the construction of the second law explicitly, beyond the pre-supposed scheme of primary laws of inexorability. He was obligated to treat the dissipation of available energy as inexorable, not only spontaneously but also universally—"any restoration of mechanical energy, without more than an equivalent of dissipation, is impossible". As the key part of the free energy principle, Thomson stated the general conclusions simply as one of the "unargued statements" ([16]: p. 94) as a law of nature of energy physics.

The principle of universal dissipation of free energy is best characterized as a "self-evident proposition" ([7]: Section 4.7). As a self-evident proposition, it has been supremely influential in the thermodynamic thought of every student of thermodynamics equal to the "supreme position among the laws of Nature" ([15]: Chapter 4) of the entropy law. Except, as Uffink told the story, this is not how Planck viewed the matter:

> If someone can be said to have codified the second law, and given it its definitive classical formulation, that someone is Max Planck. His Vorlesungen über Thermodynamik went through eleven successive editions between 1897 and 1966 and represent the authoritative exposition of thermodynamics par excellence for the first half of this century [the 20th century] . . . Planck puts the second law, the concepts of entropy and irreversibility at the very centre of thermodynamics. For him, the second law says that for all processes taking place in nature the total entropy of all systems involved increases, or, in a limiting case, remains constant . . . Increase of entropy is therefore a necessary and sufficient criterion for irreversibility. Before Planck's work there were also alternative views. We have seen that Kelvin attributed irreversibility to processes involving special forms of energy conversion. This view on irreversibility, which focuses on the 'dissipation' or 'degradation' of energy instead of an increase in entropy was still in use at the beginning of the century. . .Planck's work extinguished these views, by pointing out that mixing processes are irreversible even though there is no energy being converted or degraded. ([16]: pp. 42–43)
>
> In Planck's own words:
>
> The real meaning of the second law has frequently been looked for in a "dissipation of energy". . . [But] there are irreversible processes in which the final and initial states show exactly the same form of energy . . . They occur only for the reason that they lead to an appreciable increase of the entropy. ([17]: pp. 103–104)

Details of the example are found in [7] (Section 5.10), of how mechanical energy can be restored in a reversible process involving *no change in forms-of-energy* of an oxygen-nitrogen mixture since both elements remain at the same temperature. In a nutshell, universal dissipation of free energy as a law of nature is not tenable.

"Energy makes the world go 'round" is nonsensical [18]. "Free energy makes the world go 'round" is a much-improved statement. But the doctrine undergirding the statement, the energy-conversion doctrine, is based on the proposition of the universal dissipation of free energy, a self-evident proposition that has been falsified; free energy dissipates spontaneously, not universally. Thomson entertained the universal dissipation of free energy because pre-entropy energy physics did not make the separation of the two DOE questions unequivocal, the result of which included the shortsightedness in the understanding of entropy itself, which may be referred to as the energy-centric-based entropy principle. But in fact, as we see in Sections 2 and 3, post-1865 equilibrium thermodynamics is based on the consideration of spontaneous dissipation of free energy; it is possible to link the *energy physics problems* to the equilibrium thermodynamics framework (with unequivocal separation of the two DOE questions to be shown in Section 6) without having to entertain the universal dissipation of free energy. In Section 5, we show how Clausius' treatment of the energy physics problem can readily incorporate unequivocal separation of the two DOE questions, correspondingly leading to, in sections that follow, a more satisfactory understanding of entropy to be referred to as the entropy-centric-based entropy principle.

5. Heat and Disorganized Energy

Mechanical energy can be defined as the ability to do work. When the invention of steam engines demonstrated that heat is associated with the production of work and the discovery of the equivalence theorem by Mayer and Joule established that heat is a form of energy, disorganized energy (see [19]), this definition of mechanical energy was carried over to be the definition of energy (energies of all forms including heat energy): energy is "the capacity for doing work" [20].

It should be noted: "Before the discovery [of disorganized energy], the science of mechanics did not need an independent definition of energy. While mechanical energy of a system was indeed the capacity of the system for doing work, the mechanical-energy framework was an alternative to the force framework, an option for the science of motion. The discovery of the motive power of heat made it a necessity to introduce the concept of energy as a *generalized concept* that comprises of heat energy and mechanical energies for the science of motion and heat. The resulting energy-centric, energy physics is completely different from mechanics. Both the meaning and the role of energy are now different" ([21]: p.9). Disorganized energy, which is of a central role in the science of motion and heat, has a very different meaning from the mechanical sciences notion of energy. Unlike mechanical energy, "the newly discovered disorganized energy cannot be fully used to do work. Energy physics and orthodox thermodynamics, therefore, 'have been applying thermodynamics in the context of the pre-industrial mechanical sciences.' That means: the common 'energy' view inherited from the equivalence of heat and work is a mischaracterization of the NWCJ [Newcomen, Watt, Carnot, Joule] discovery. The real discovery is the discovery—in accordance with the concept of reversible-like compensation—of the production of work to be derived/compensated from 'transformations of natural direction' found in fuels and in renewables, not of the production of work to be derived from energy found in fuels" ([19]: p.27).

The rest of the paper below will explicate this last statement.

Before the theory was applied to spontaneous natural processes driven by thermodynamic potentials, thermodynamics was in its formative years a theory dealing with heat and work. For those applications, the theory was based on two fundamental theorems: the first fundamental theorem of the equivalence of heat and work and the second fundamental theorem of the equivalence of transformations (the transformation of heat to work, and the transformation of heat at a higher temperature to a lower temperature) ([22]: Abstract). Clausius began the development of the second fundamental theorem in 1854 with his fourth memoir ([23]: pp. 111–135). This was the real beginning of Clausius' transformation of Carnot's idea into the precise statement of the second law of thermodynamics. Xue and Guo noted,

> . . .the idea of equivalence of transformations is difficult to grasp and is not even mentioned in most thermodynamics textbooks. However, the equivalence of transformations is, we think, of momentous significance for the second law of thermodynamics, as with the equivalence of work and heat for the first law of thermodynamics ([22]: 4/9) . . .

Clausius himself regarded the "theorem of the equivalence of the transformation of heat to work, and the transformation of heat at a higher temperature to a lower temperature", rather than "heat can never pass from a colder to a warmer body without some other change", as the statement of the second law of thermodynamics ([22]: Abstract).

That "the idea of equivalence of transformations is not even mentioned in most thermodynamics textbooks" ([22]: p. 4) is most unfortunate and probably the main reason why the second law is poorly understood.

We now consider the problem of the transformation of heat into mechanical energy comparing the nuances of its meaning that separates Carnot/Clausius from Thomson (the late Thomson in his energy physics stage). First of all, we adopt the word, transformation, as a general sense while the word, conversion, as a special kind of transformation; as Clausius in his eighth memoir wrote, ". . . the difference which exists between the transfer of heat from a warmer to a colder body, and that from a colder to a warmer one ; the former may, but the latter cannot, take place of itself. This difference between the two kinds of transmission being assumed from the commencement, it can be proved that an exactly corresponding difference must exist between the conversion of work into heat, and the transformation of heat into work" ([23]: p. 290). That is, conversion is a transformation that can take place by itself; conversion of work into heat can take place by itself whereas transformation of heat into work "can only take place in such a manner as to be compensated by simultaneously occurring positive transformation" ([23]: p. 364; "compensated" and "compensation" are the terms Clausius used in his second fundamental theorem; "positive transformations" are defined as transformations that take place without compensation such as conversion).

The standard interpretation of the NWCJ discovery is the discovery of heat as a form of energy, which in the form of high temperature heat can be "converted" into mechanical energy. Let us consider an amount of heat Q_1 at a temperature T_1. Assume the availability of a heat reservoir at a temperature T_2. According to Thomson, Q_1 at a temperature T_1 can be inputted into a Carnot Cycle, the operation of which necessarily discharges a minimum amount of heat, Q_2, equal to

$$Q_2 = T_2 \cdot (Q_1/T_1) \tag{36}$$

Therefore, the maximum work derivable from Q_1 is

$$W_{Reversible} = Q_1 - Q_2 = Q_1 \cdot (1 - T_2/T_1) \tag{37}$$

In the manner of energy-centric speaking, heat, Q_1, at a temperature T_1 drives the Carnot cycle and this heat energy (or its equivalent *internal thermal energy*), a portion of which, $Q_1 \cdot (1 - T_2/T_1)$, to be referred to as free energy, is "converted" reversibly into work.

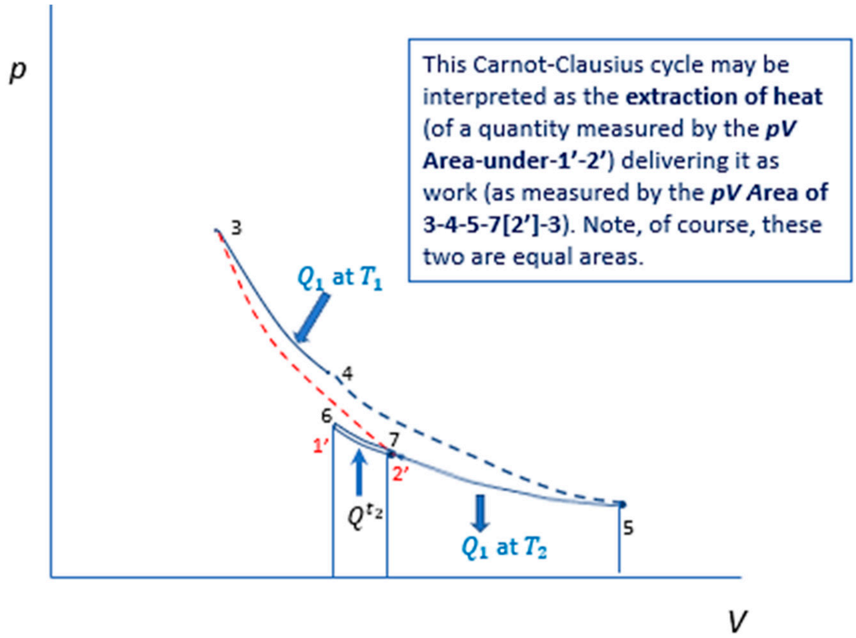
Not much is said in the literature about the role of the heat reservoir except the conclusion derived from (37) of the effect of a "*decrease in the average temperature at which heat is rejected from the system*" (see discussion below beginning with paragraph one of page 338 up to the line near the bottom of the page, "Which is the Carnot formula, (37)."). Yet the essential role of heat reservoir was pointed out by Carnot: "Heat alone is not sufficient to give birth to the impelling power: it is necessary that there should also be cold [the heat reservoir at T_2 as the heat sink]; without it, the heat would be useless". The difficulty in talking about the role of heat reservoir is that in "energy-centric speaking", there is no clear separation of the two DOE questions.

In presenting the second fundamental theorem ([23]: pp. 111–145), referring to Figure 2 below, Clausius developed his discussion by identifying the heat transmission of Q_1 from T_1 during step 3–4 to a lower temperature of the whole amount during step 5–6, i.e., an identifiable "heat transmission of Q_1 from T_1 to T_2". The second law began as the law that dictates the direction of spontaneous transformations; heat transmission is an example of which Carnot identified as a driving force. Clausius generalized the example of heat transmission into the concept of all positive, i.e., spontaneous, transformations as the *compensation* ([23]: pp. 118, 248, 290, 364) for enabling a system's transformations in negative, unnatural directions. Therefore, positive transformations are the driving force to cause a system's change, whether they are spontaneous or in an unnatural direction—i.e., what makes the world go 'round.

The follow-up of this discussion is that the first law serves as the closure condition for all transformations. The remaining issue is then, "from where does the energy of the work come?" This is answered by Clausius with his invention of a six-stage cycle, which is updated in [21], called the Carnot–Clausius cycle of the Carnot engine. It is reproduced here as Figure 2.

Figure 2 depicts the Carnot–Clausius cycle, $1'$-$2'$-3-4-5-6-$1'$, in which:

- dotted 4-5 and $2'$-3 are adiabatic steps, linking isotherm T_1 and isotherm T_2,
- isotherms 3-4 and 5-7-6 represent heat transmission of Q_1 from T_1 to T_2, noting the assumed availability of a heat reservoir/sink at T_0 which is infinitesimally colder than T_2,
- adiabatic 6-$1'$ represents adiabatic cooling over an infinitesimal temperature-difference so that $T_{1'}$ is infinitesimally colder than the temperature of the heat reservoir/sink at T_0,
- isotherm $T_{1'} - T_{2'}$ represents the extraction of heat Q^{t_2} from the T_0 heat reservoir.



This Carnot-Clausius cycle may be interpreted as the **extraction of heat** (of a quantity measured by the ***pV* Area-under-1'-2'**) delivering it as work (as measured by the ***pV Area* of 3-4-5-7[2']-3**). Note, of course, these two are equal areas.

Figure 2. The Carnot-Clausius cycle of the Carnot engine, in which a T_0 heat reservoir **doubles** as a heat sink for heat transmission which drives the process and as a heat reservoir from which the work (measured by area 3-4-5-7[2′]-3) comes. Note that $T_2(T_5 = T_6)$ is infinitesimally higher than T_0, which is infinitesimally higher than $T_{1'}(= T_{2'})$.

The notation of Q^{t_2} is explained in ([19]: Figures 3 and 7).

Q^{t_2} can be shown to equal to $Q_1 - Q_2 = W_{Reversible}$, details of which can be found in [19] and [21]. By demarcating precisely heat transmission as the driving force of the Carnot engine, the Carnot–Clausius cycle shows that the energy of the work comes from the heat extracted from the T_0 heat reservoir. It is indisputable that Carnot/ Clausius' account of how work is derived from disorganized energy is superior: identification of the heat extraction mechanism results from a clear separation of "positive transformation" (which drives a Carnot cycle) from "negative transformation" of heat into mechanical energy. It is the account that is coherent whereas the energy conversion doctrine account (in energy-centric speaking), one that is based on the proposition of universal dissipation of free energy, can become illogical and self-contradictory. Thomson's erstwhile skepticism about the validity of the conversion of heat into mechanical energy was justified! In the next section, we return to the main thesis of the paper, the primacy of dissymmetric tendency towards equilibrium (including that of heat transmission) and shall see that the Carnot/Clausius entropy/heat extraction account is also, in many cases, the only account for explaining what causes true changes in the Universe that are not reducible to locomotion.

6. Reversible Processes Approaching the Extremes of Thermodynamic Potentials

The success of Carnot/Clausius' account emphasizing the demarcated heat transmission as the entropic driving force suggests that problems of engineering thermodynamics can be treated with the same systematic approach as the problems of equilibrium thermodynamics. The identification of negative transformation as "extraction of heat transforming which into mechanical energy" prepares for linking equilibrium thermodynamics readily with applications to problems of engineering thermodynamics. Here we consider two examples corresponding to two of the three alternative thermodynamic potentials in Section 3.

The Helmholtz function may be expressed for multicomponent reactive systems as

$$A_H = A_H(T, V, N_1, N_2, \ldots) = U - TS \tag{38}$$

Application of the Helmholtz function in the general form of (38) will be commented, indirectly, in Section 7.2. In the meantime, we consider in this section its application to the pure substance of ideal gas. Use of the ideal gas example leads to crucial simplification in the demonstration and the kind of conclusion we can draw from the demonstration.

Consider a composite system made of two subsystems, subsystem$^{(1)}$ and subsystem$^{(2)}$; each is filled with N kmol of an ideal gas. Given the following assumptions:

- A heat reservoir (bath) at temperature T^r;
- Subsystem$^{(1)}$ initially at $p^{(1)}{}_{ini}$, $V^{(1)}{}_{ini}$ and $T^{(1)} = T^r$;
- Subsystem$^{(2)}$ initially at $p^{(2)}{}_{ini}$, $V^{(2)}{}_{ini}$ and $T^{(2)} = T^{(1)} = T^r$;
- $V^{(2)}{}_{ini} = 5V^{(1)}{}_{ini}$; it follows that the total system volume is

$$V = V^{(1)}{}_{ini} + V^{(2)}{}_{ini} = 6V^{(1)}{}_{ini}$$

That is, we consider the composite system to undergo an isothermal process from its initial state subject to the closure condition,

$$V^{(1)} + V^{(2)} = 6V^{(1)}{}_{ini} \tag{39}$$

The arrangement of the system, a heat bath it interacts with, and the mechanical arrangement schematically are shown in Figure 3.

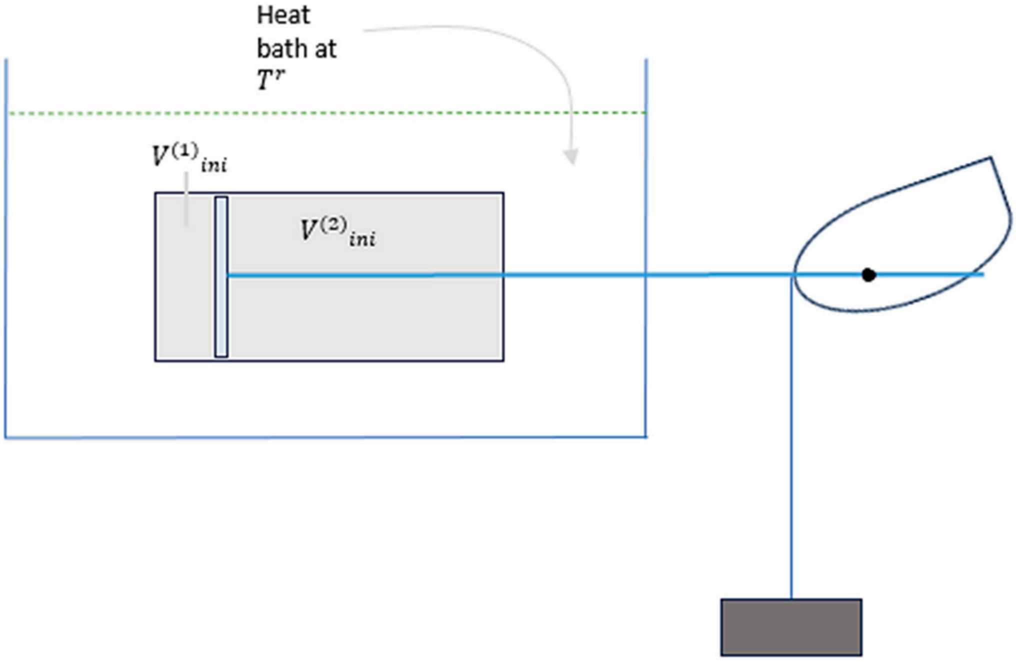


Figure 3. A composite system together with a heat bath, the composite system being at its initial state.

The initial pressures of the two subsystems are

$$p^{(1)}{}_{ini} = NRT^r/V^{(1)}{}_{ini}$$
$$p^{(2)}{}_{ini} = NRT^r/V^{(2)}{}_{ini} = NRT^r/5V^{(1)}{}_{ini} = (1/5)\cdot p^{(1)}{}_{ini}$$

The difference in $p^{(1)}{}_{ini}$ and $p^{(2)}{}_{ini}$ is balanced by the torque force exerted by the weight-cam through the piston-rod. Figures 3 and 4 (below) schematically suggest that throughout the isothermal process of the piston moving rightward, the difference in $p^{(1)}$ and $p^{(2)}$ resulting in force on the piston to the right is balanced with the weight-induced force transmitted through the piston-rod to the left. This nearly balancing suggests the process, as shown below, being sufficiently slow for heat transmission from the bath to gases in the subsystems to take place so that the two subsystems may remain isothermal at T^r. The isothermal process with subsystem$^{(1)}$ expanding from its initial volume to its final volume reversibly, therefore, results in work as shown (where the final equilibrium state is given by (28), corresponding with $V^{(1)}{}_{final} = V^{(2)}{}_{final}$ as shown in Figure 4),

$$W_{rev} = \int_{V^{(1)}{}_{ini}}^{3V^{(1)}{}_{ini}} \left(p^{(1)} - p^{(2)}\right) dV^{(1)}$$

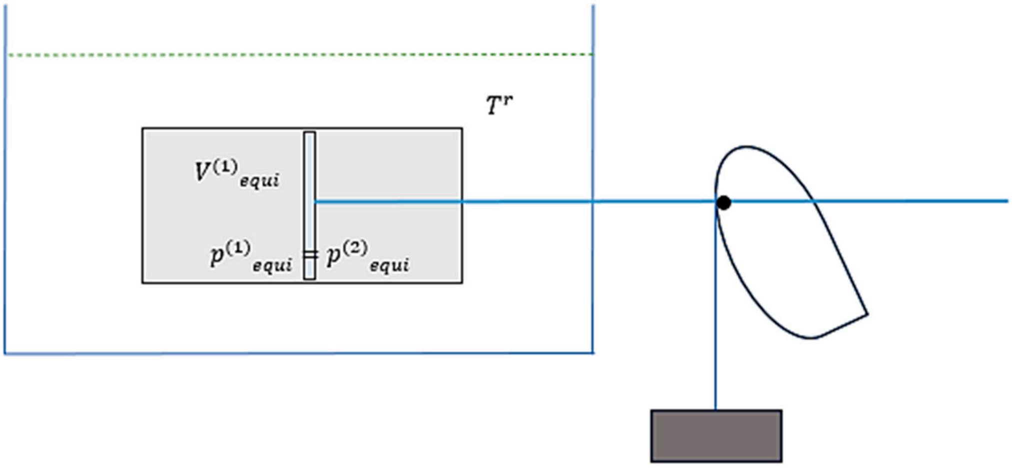


Figure 4. The composite system together with a heat bath of Figure 3 is at the final equilibrium state of the WHOLE.

In view of the closure condition (39), it becomes

$$\begin{aligned} &= N\mathcal{R}T^r \int_{V^{(1)}{}_{ini}}^{3V^{(1)}{}_{ini}} \left(\frac{1}{V^{(1)}} - \frac{1}{6V^{(1)}{}_{ini} - V^{(1)}}\right) dV^{(1)} \\ &= N\mathcal{R}T^r \left(ln\frac{3V^{(1)}{}_{ini}}{V^{(1)}{}_{ini}} + ln\frac{3V^{(1)}{}_{ini}}{5V^{(1)}{}_{ini}}\right) = 0.588N\mathcal{R}T^r \end{aligned} \tag{40}$$

Note that this reversible isothermal process results in the entropy increase of the composite system,

$$S_{final} - S_{ini} = \Delta S^{(1)} + \Delta S^{(2)} = N\mathcal{R}ln\frac{3V^{(1)}{}_{ini}}{V^{(1)}{}_{ini}} + N\mathcal{R}ln\frac{3V^{(1)}{}_{ini}}{5V^{(1)}{}_{ini}}$$

which is exactly the amount of entropy decrease of the heat bath so that the combined WHOLE "composite system and heat bath" experiences no change in entropy. This is an isothermal process approaching equilibrium reversibly in which the heat bath gives out heat of the amount of

$$W_{rev} = T^r \left(S_{final} - S_{ini}\right)_{ComSystem} \tag{41}$$

to the composite system. That is, energy of the reversible work W_{rev} comes from heat of the heat bath; heat is 100% transformed into work in the reversible manifestation of nature's dissymmetry.

A comment on the meaning of "free" is found in the "Thermodynamic free energy" page of Wikipedia, in which it writes, "This expression [of Helmholtz free energy $A_H = U - TS$] has commonly been interpreted to mean that work is extracted from the internal energy U while TS represents energy not available to perform work". While this is a serviceable interpretation of decreases in the Helmholtz function and the Gibbs function as free energy and free enthalpy, respectively, (more on this in Section 7.2) it is nonsensical for the ideal gas example here. For ideal gases in the two subsystems, $\Delta U = 0$. Instead of being "energy not available to perform work", $T^r \left(S_{final} - S_{ini}\right)_{ComSystem}$ is precisely the heat corresponding with ALL the work being produced. Rather than being waste heat (the rejected heat) in accordance with the energy conversion doctrine, heat in the heat bath *is* the source of heat for the work.

In closing this example, we note the simplification of using ideal gases to be that, as a consequence of Joule's ideal-gas law, the temperature of the ideal gas subsystems remains at constant temperature, thus, can be readily kept at the same heat bath temperature, T^r. Consideration of non-ideal-gas examples will involve both a heat extraction operation and heat-engine/heat-pump operation, the kind as shown in Figure 8.4 of A *Treatise* ([7]: p. 205), because the subsystems cannot be kept isothermal. Such a demonstration can be made in another venue that is not subject to space restriction. However, even in the absence of which, the conclusion learnt from the ideal-gas demonstration alone should not be characterized to be of limited validity as one does not characterize quantum mechanics based on the demonstration of a hydrogen atom problem solely to be of limited validity.

Consider next the example of a composite system kept at a constant pressure, p^r, consisting of subsystems $T^{(1)}$ and $T^{(2)}$. This part of the discussion is further clarified by limiting the consideration to that of an isolated composite system,

$$H\left(T^{(1)}, p^r\right) + H\left(T^{(2)}, p^r\right) = H^{(1)} + H^{(2)} = const$$

We make for such a composite system the following assumptions: an isolated composite system of two subsystems of thermal-mass blocks: block X and block Y [X is aluminum ($c_{pX} = 0.900$ kJ/kg·K, constant specific heat is assumed) with $m_X = 0.5$ kg, and Y is copper ($c_{pY} = 0.386$ kJ/kg·K, constant specific heat is assumed) with $m_Y = 1$ kg], which are, initially, at $T^{(1)} = 100$ °C and $T^{(2)} = 500$ °C, respectively (Figure 5, left). The blocks are brought together in thermal contact, triggering a spontaneous heat transfer process to a final state of 557.84 K (284.69 °C, Figure 5, right), with a corresponding entropy growth of **0.054949 kJ/K** (reproduced from [3]; see also *A Treatise* ([7]: pp. 206–210 for details).

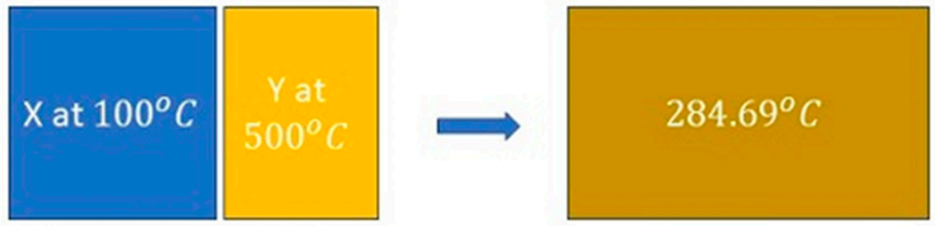


Figure 5. Spontaneous thermal event of two blocks approaching internal thermal equilibrium.

An analysis that is based on temperature dependent specific heat will be applied to the spontaneous event and the reversible event (below in Figure 6) as well. As such an analysis—as well as examples of reservoir temperatures other than that shown in Figure 6—does not materially change the conclusion drawn below, it will be reported elsewhere.

Figure 6 depicts the same system undergoing a *reversible event*. We stress that the reversible event in the present case, depicted in Figure 6, are defined in terms of the same set of initial state and final state of the spontaneous event of Figure 5. The reversible event is depicted in two phases; a heat reservoir is used in the second phase.

Phase One is an isentropic process brought about by a Carnot heat engine leading the composite thermal system to a uniform temperature of 522.4 K (249.2°C). That is, the system arrives at a uniform temperature lower than the final temperature of the spontaneous event at 557.8 K.

To bring the uniform-temperature system back to the final temperature of the spontaneous thermal event, it is necessary to use a heat reservoir in Phase Two (a Phase Two in two stages) in an arrangement shown in Figure 6 on the right, where it shows, in the first stage, a Carnot heat engine operating between a cold thermal system and heat reservoir to bring the temperature of the system to the temperature of the reservoir. In the second stage, the power produced by the Carnot heat engine is then applied to drive a Carnot heat pump to bring the system to the same final state of the spontaneous event. The reservoir temperature chosen here corresponds to the condition that the Carnot heat engine output is exactly equal to the required Carnot heat pump input.

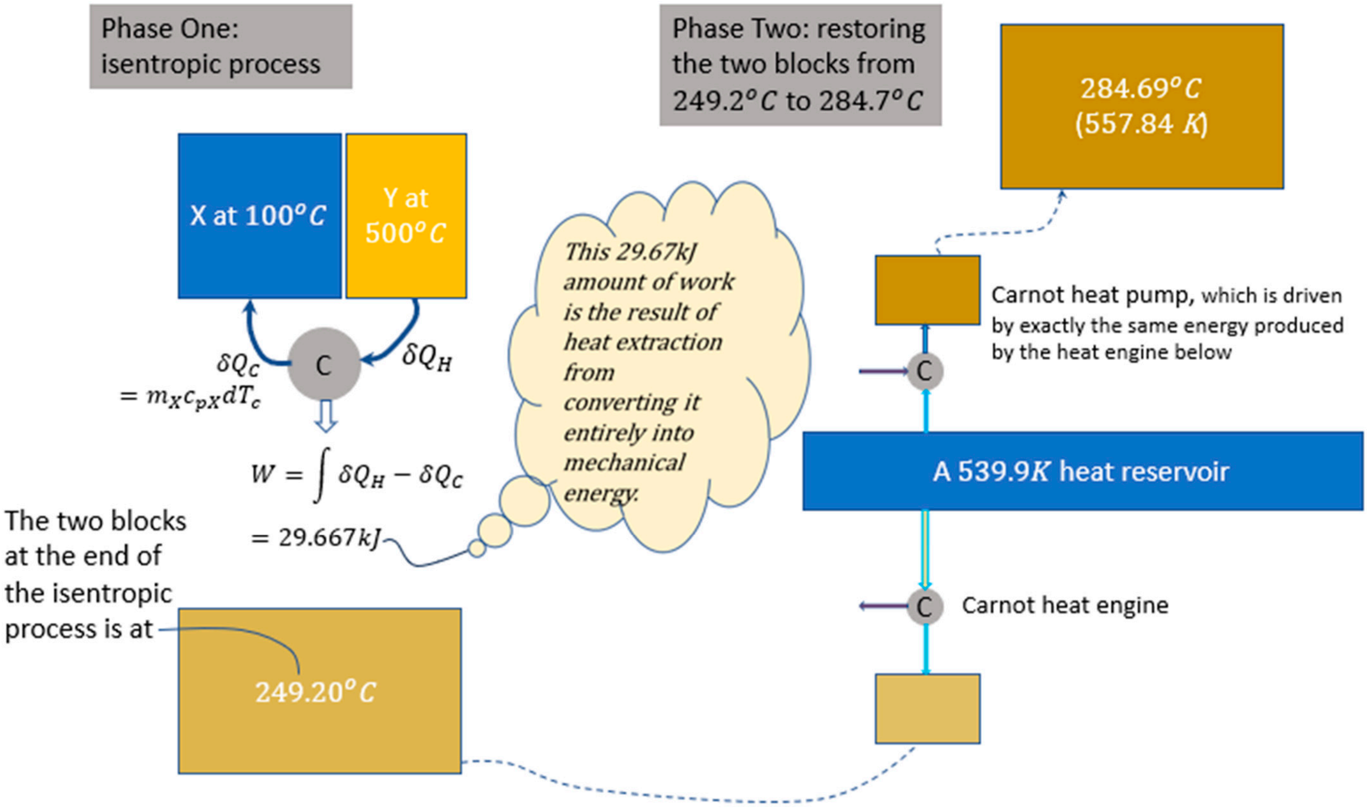


Figure 6. Reversible event in two phases: The end result is that the two phases together are equivalent to the "extraction of heat" in Phase Two for the "production of work" in Phase One of an amount, $W_{rev} = 539.9 \cdot 0.0549$.

Examples of other reservoir temperatures are given in *A Treatise* ([7]: pp. 206–210) to demonstrate the general validity that, for a given dissymmetry-driven force as exemplified in the three examples—Figure 2 as a special case of Clausius' six-stage cycles; the example of Figures 3 and 4; and the example of Figure 6—the amount of heat extracted from the heat reservoir (heat source) is propositional to the temperature of the reservoir.

Note that in Figure 5, there is neither heat exchange nor work exchange involved between the isolated system and its surroundings. In comparison with Figure 5, the overall process in Figure 6 involves a system work exchange in Phase One of 29.67 kJ and a system heat exchange with the heat reservoir in Phase Two. Energy balancing requires the two exchange values to be equal, i.e., heat extracted during Phase Two exactly equals work output during Phase One; work output is in fact derived from heat extracted from the heat reservoir, i.e.,

$$W_{rev} = T_{res} \cdot (\Delta S)_{spon} = 539.9 \times 0.054949 = 29.667 \tag{42}$$

Carnot/Clausius' account of how work is derived from disorganized energy is shown in this section to link nature's dissymmetry manifested in spontaneous processes (Section 3) with reversible harnessing for doing work (this section), providing unification of equilibrium thermodynamics and engineering thermodynamics. The energy conversion doctrine, or the theory of exergy, has never provided such unification nor a "mechanism" for reversible work; whereas the Carnot/Clausius account provides the mechanism for reversible energy transformations ([7]: Section 10.4) with a common thread: the energy of work comes from heat extracted from a heat reservoir driven by the entropy growth of nature's dissymmetry.

7. The Dissymmetry Premise and the Entropy-Centric Framework

It is shown in Section 6 that the Carnot/Clausius account can be readily incorporated into the Gibbsian ET framework. However, the mathematical framework has a limitation in the problems it can address as it is apparent from the defining problem of the framework, "the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system" ([9]: p. 26). For addressing problems of interactive systems such as those of renewable energy, we need to go beyond the problem of heat and work such as those of the Carnot engines in Section 5 and the problem examples of composite systems in Section 6. The physics of the Gibbsian entropic approach is more flexible than the mathematics of the Gibbsian ET framework. We may refer to the update of the Carnot/Clausius account with the Gibbsian entropic approach as the Carnot/Clausius/Gibbs account and, correspondingly, the framework to address problems of interactive systems as the entropy-centric Unified Classical Thermodynamics framework. The entropy-centric UCT framework is proposed for supplanting the energy-centric free energy (or energy conversion) framework. In the following, we begin with an overarching epistemological comment on this proposed change from the free energy framework to the entropy-centric UCT framework.

7.1. From Locomotion to Transformations, Primacy of Dissymmetry over Free Energy Defines an Entropy-Centric Framework of Thermodynamics

Before Carnot in 1824 pointed out that the physical world is irreversible, the systematic scientific understanding of the physical world had been that the world is reversible and that the only things that exist are atoms and molecules. All observable changes are caused by the motions of the atoms (referred to as *locomotion*). This is known as *atomism*. There are numerous meanings to talk about atomism (philosophical atomism and scientific atomic theory, etc.); as an explanatory scheme, atomism is contrasted with holism or organicism; as a realistic description of the world, the limitations of atomism and the extension of atomism to other phenomena are well known. All these are outside the scope of this discussion. The discussion here is motivated by the fact that thermodynamics emerged from the background of scientific atomism [12] so that it serves as the reference system to contextualize the scientific advancement made by Thomson and Clausius.

What Carnot discovered and Clausius theorized can be referred to as the discovery of a world of transformations, which are dissymmetric or have preferred direction, in addition to the world of locomotion, which is reversible, having no preferred direction.

In the world of locomotion, mechanical energy is the capacity for doing work; the way mechanical energy yields change to locomotion such as work is manifested by *equations of motion*. In this world, energy is conserved, and in the case of an idealized world of frictionless locomotion, mechanical energy is conserved. But it is important to note that equations of motion, the equations that describe the change to locomotion, ensure all changes meet the energy conservation closure condition, i.e., what drives changes to locomotion and what ensures all changes meeting the closure condition are conflated into one step without requiring separate steps of independent consideration.

The world of transformations is different. It is necessary to introduce energy as a generalized concept as the energy that is conserved, unifying the world of locomotion and the world of heat, while free energy is the capacity for doing work, i.e., what drives transformations. These are two DOE questions but by answering the two questions in terms of energy and free energy (or energy conversion), the two questions are not explicated as separate steps of *independent* consideration. That is, the novelty of transformations from locomotion has not been given the true breakaway that it deserves free from the context of the atomic theory of locomotion and its reductionist and deterministic nature. Even though the world of transformations cannot be encapsulated by a reductionist and deterministic theory in the strict sense, the theory of energy conversion has not been explicitly cleansed of the notion of equations of motion or change, nor explicitly renounced of the reductionist and deterministic implications associated with the equations of motion.

The energy conversion theory places thermodynamics at home with standard branches of physics that are defined epistemologically with the central role of equations of motion and the causal understanding of what Zwier referred to as the "Consensus View of Physical Causation" (CVPC) [24]. This causal understanding may be described as causality exhibited as "constant conjunction" and "invariable succession" in causal laws of equations of motion in physics. That is, physics describes systems in terms of "an autonomous model of dynamics". As Zwier wrote, "The completely autonomous evolutions of isolated systems that are familiar from physical theories in which we have complete equations of motion are somewhat foreign to thermodynamic theorizing. This is because we do not have a complete equation of motion for thermodynamic systems" ([24]: p. 149). What Zwier perceived was something unfamiliar and new in thermodynamics theorizing; however, is not shared by most thermodynamicists. The nonexistence hypothesis of equation-of-motion for energy conversion processes was made earlier by the author in an unpublished report [25], an earlier-submitted paper version which was reviewed/rejected by leading thermodynamicists (including Gyftopoulos, who signed his review of the submitted paper). One unnamed reviewer simply asserted, "the equation of the change (motion) exists for energy conversion processes". The reviewers in this instance expressed the orthodox causation view of physical sciences.

This is an example of Marshall McLuhan's "old stereotypes" habit [26] in the age of new discovery or invention. As Ulanowicz noted,

> Whenever a new tool emerged within an endeavor, practitioners tended to use it in the context of previous habits and remained blind for a while to its full potential. His [McLuhan's] example was IBM, which saw its purpose as the manufacture of business machines. It wasn't until its leaders realized they were in the business of processing information that the enterprise began to take off. [27]

Our example here is the discovery of the equivalence of heat and work, i.e., correlation of heat and work. But correlation is not necessarily causation. The discovery is encapsulated fully by the dualistic lessons of energy and dissymmetry (the two DOE questions), of which energy and CVPC are the previous habits thinking carried over from conceptualization in the reversible world of physics while dissymmetry is the discovery in the new irreversible world, the essence of which is captured by interventionist causation, a theory of causation by the philosopher James Woodward [28].

As one reviewer of the paper notes, "Dissymmetry and free energy have their own positioning and play different functions. They cannot be ranked". Ranking is not the issue. Instead, "primacy of dissymmetry" is used to express the following points that do matter. What does matter is that there are two lessons, two DOE questions; what does matter is that it is necessary to keep the two DOE questions separate because the entropy-centric framework which does that is superior to the energy-centric framework that maintains "primacy of free energy"; what does matter is that physics must transcend CVPC to comprehend the entropy-centric framework; what does matter is (see below) that only entropy-centric-based entropy can correct us from the path from which energy-centric-based entropy has led us astray.

7.2. Gibbs Free Enthalpy; Entropy Growth Potentials

The linkage of nature's dissymmetry manifested in spontaneous processes towards internal equilibrium with reversible harnessing which, for doing work in Section 6, can be generalized for spontaneous processes including dissymmetry (or spontaneity), manifested as stock entropy growth potential or ongoing entropy growth potential ([7]: Section 8.7.2). Here, we investigate the dissymmetry in Gibbs free enthalpy as manifested as heat release transformations.

In the context of multicomponent reactive systems, the Helmholtz free energy, $A_H = A_H(T, V, N_1, N_2, \ldots) = U - TS$, and the Gibbs free enthalpy, $G = G(T, p, N_1, N_2, \ldots) = H - TS$, can be interpreted similarly: the former represents a body's internal energy (e.g., as released as heat in combustion taking place in a bomb calorimeter), subtracted by energy that is not available, and the latter represents a body's enthalpy (e.g., as released as heat in combustion taking place in a isobaric combustion chamber), subtracted by enthalpy that is not available. For our purpose here, we shall use the latter example for discussion.

First of all, it is possible to consider the latter example in the same manner as the two examples in Section 6, the reversible manifestation of entropy growth as a driving force for useful work. The details can be found in a 1992 paper [29]. Here, a summary of the discussion is reproduced: Consider a mixture of 1 kmol of CO and ½ kmol of O_2. A reversible "combustion" heat engine may be constructed along the same lines as a Carnot heat engine. It also consists of four steps (see Figure 7): an isentropic compression, $RO \rightarrow 1$; an isothermal process at peak temperature, $1 \rightarrow 2 \rightarrow 3$; an isentropic expansion, $3 \rightarrow 4$; and finally, an isothermal heat transfer process at T_0, $4 \rightarrow P0$. This final isothermal process will be a heat rejection process if $(S_{R0} - S_{P0})$ is positive, or a heat absorption process if $(S_{R0} - S_{P0})$ is negative. Instead of a combustion step, the key step of the reversible engine cycle is the isothermal processes at peak temperature, $1 \rightarrow 2 \rightarrow 3$ (see also Figure 10 of [29] for examples of different peak temperatures).

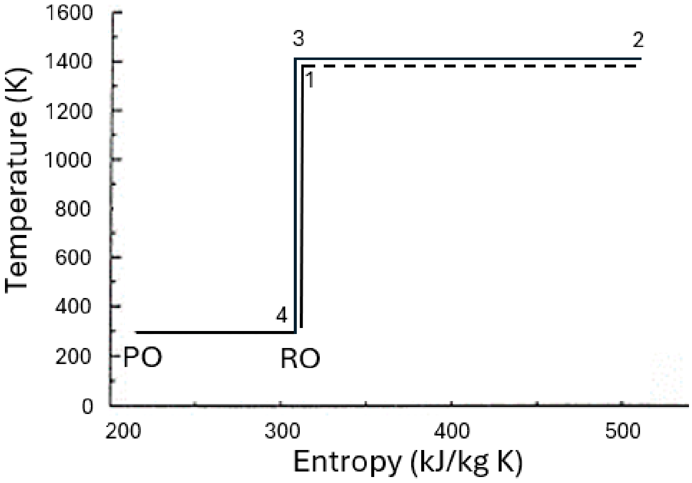


Figure 7. The reversible manifestation of Gibbs free enthalpy or free heat.

The isothermal process at peak temperature is made up of two phases (see Figure 3 of [29]). After separating each component of the mixture (CO, O_2) through corresponding semipermeable membranes into individual manifolds (mixture at 1 becoming components at 1(a), 1(b), . . .), each component undergoes an isothermal expansion, 1(a) → 2(a), 1(b) → 2(b), . . . (the first phase). This is followed by a reversible heat release reaction process (the second phase): components at 2(a), 2(b), . . . are collected through semipermeable membranes into a Van't Hoff reaction box where the reversible reaction takes place, releasing heat and producing an equilibrium mixture at "3". Note that pressure p_3 at state 3 is selected on the condition of $S_3 = S_1 (= S_{R0})$ (Note that even though point 3 and point 1 overlap each other in the figure, they represent different pressures). In that case, heat released in the reaction box exactly matches the heat required for maintaining the isothermal expansion processes of the two individual components.

This arrangement transfers the chemical affinity "released" reversibly in 2 → 3 to the enhancement of mechanical spontaneity manifested as isothermal expansions in 1 → 2. It is noted that for a reversible combustion heat engine operating with different peak operating temperatures as shown in Figure 10 of [29], our analysis shows the engine cycles reject same amount of heat as measured by the area under P0 → R0, therefore, produces the same useful work equal to Gibbs free energy.

In this sense, "Gibbs free enthalpy" corresponds to the situation that, of the "combustion heat" released in a spontaneous event, only a minimum amount of heat has to be theoretically subtracted (in fact, if the $(S_{R0} - S_{P0})$ of another mixture is negative, we would have a situation of heat addition instead of subtraction). So, we should be talking about this “work”, which equals the maximum amount of heat that can be extracted, as derived from “available heat”.

From these previous examples, whether it is the Carnot–Clausius cycle, or the two examples in Section 6, or the example of Figure 7, the logical name for the work obtained reversibly should be *available* or *free heat*, which nature’s dissymmetry makes possible. The use of free energy or free enthalpy makes some kind of sense in cases involving irreversibility, as we shall discuss the term *free flame enthalpy* below (see discussion in the paragraph beginning with “As it has been noted” after Equation (50)).

The practice of combustion technology is intrinsically irreversible; the technology led to the invention of steam engines and Carnot’s theoretical investigation. Consider the schematic diagram of Figure 8, in which a combustion chamber is depicted. The figure is in reference to Figures 2 and 7: the combustion process of a reactant mixture at T_0 and p_0 enters the chamber with enthalpy H_{R0}. The mixture is transformed into the burned product at T_{adiab} with enthalpy $H_P(T_{adiab}) = H_{R0}$. These notations are consistent with those in Figure 7. Heat transmission takes place in the chamber from the burned product to the working fluid of the Carnot heat engine, with the working fluid of state “3” entering the chamber with an operating temperature designed at $T_{peak} = T_1$. The working fluid receives heat, Q_1, corresponding to step 3 → 4. The exiting working fluid of state “4” enters the adiabatic expander of the Carnot engine at state “4”. These notations are consistent with those in Figure 2.

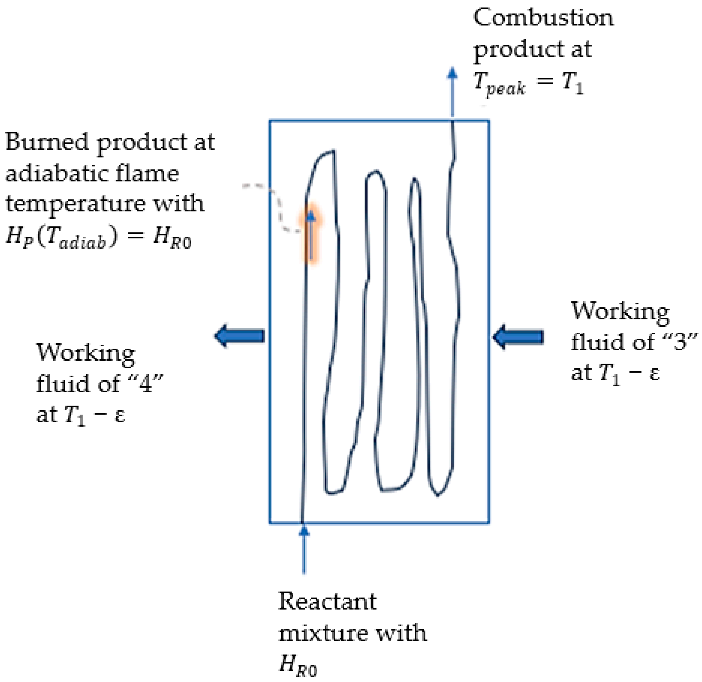


Figure 8. A combustion chamber for feeding a Carnot engine’s isothermal heat addition.

Heat added to the Carnot engine, Q_1, depends on the design selection of the working fluid peak temperature, $T_{peak} = T_1$,

$$Q_1 = H_P(T_{adiab}) - H_P(T_1) = H_{R0} - H_P(T_1) \tag{43}$$

The selection of the peak temperature is a critical design factor; a too high temperature lowers Q_1 for the Carnot heat engine while a too low peak temperature lowers the thermal efficiency of the Carnot engine. Both combustion irreversibility and a poor design selection of peak temperature impact significantly the end performance result of work production. However, these considerations are not the present focus of the paper, which addresses the teaching of the Carnot cycle and the Carnot–Clausius cycle.

We train on the role of heat reservoir for the operation of the Carnot cycle, particularly on the impact of the heat reservoir temperature on the efficiency of the Carnot cycle. The "real value of the Carnot cycle" is often described this way. "Thermal efficiency increases with an increase in the average temperature at which heat is supplied to the system or with a decrease in the average temperature at which heat is rejected from the system", wrote Cengel and Boles in the textbook *Thermodynamics, an Engineering Approach Sixth Edition* [30]. We ask what roles the heat reservoir plays in leading to the conclusion that a decrease in the average temperature at which heat is rejected from the system causes a greater fraction of Q_1 to be transformed into work.

The demarcation of heat transmission as the driving force of the Carnot engine in accordance with the Carnot–Clausius cycle can be generalized. The demarcated treatment of high-temperature heat energy Q_1 as a "driving force" of Q_1 heat transmitted from T_1 to T_2, can be generalized to the consideration of a "driving force" in association with a source-system, whether it is a composite system considered in Section 6 (two such systems considered there: Equations (41) and (42)) or the example immediately below in this subsection. We referred to, in this generalization, the "driving force" as Entropy Growth Potential, *EGP* ([7]: Sections 8.3 to 8.5). The value of *EGP* is determined by the *total* entropy growth or entropy production of the source-system and the environment the system interacts with (referred to as "source-system" + "the environment-reservoir" = *universe*),

$$(\Delta_{Growth}S)_{universe} = (\Delta S)_{sys} + (\Delta S)_{reserv} \tag{44}$$

That is, $(\Delta_G S)_{universe}$ is the total entropy growth of the Universe in a spontaneous event. Correspondingly, there is a reversible event. It has been argued in [7] that the two events define a set of infinite possibilities (the set is referred to as Poincare range) that share "*a property common to all possibilities*" ([31], also see [7]: p. 197). By letting

$$(\Delta_{Growth}S)_{universe} = (\Delta_{Potential}S)_{PoinRange} \equiv EGP \tag{45}$$

and naming it entropy growth potential, we acknowledge EGP to be the common property of all possibilities within the set of a Poincare range.

While the entropy growth of each event is different from other events, every event in the set has the same entropy growth potential, which represents the maximum (potential) useful work of each and every event in the set, corresponding to,

$$W_{max}(= W_{rev-event}) = T_{res}\cdot(\Delta_P S)_{PoinRange} = T_{res}\cdot EGP \tag{46}$$

The actual useful work produced by each specific event is less than the maximum useful work of a specific value in association with the specific entropy growth.

For the case of the Carnot–Clausius cycle, (46) takes the form of

$$W_{rev-event} = T_0\cdot EGP(T_0) \tag{47}$$

Note that in this case $EGP(T_0)$, in accordance with (45), is a function of $T_0(= T_2)$, and equals to

$$EGP(T_0) = \frac{-Q_1}{T_1} + \frac{Q_1}{T_2} = \frac{-Q_1}{T_1} + \frac{Q_1}{T_0} \tag{48}$$

It follows that the general expression, $W_{rev-event}$ (46) or (47), reduces to the special expression,

$$W_{rev-event} = T_0\cdot\frac{-Q_1}{T_1} + \frac{Q_1}{T_0} = Q_1\left(1 - \frac{T_0}{T_1}\right)$$

Which is the Carnot formula, (37).

Instead of looking at $Q_1\left(1 - \frac{T_0}{T_1}\right)$, demarcation identifies the dual roles the heat reservoir plays, as a heat sink for the EGP driving force as shown by (48), and as a heat source reservoir for the heat extraction mechanism made possible by the driving force as shown by (47). The reason for the decrease in heat rejected from the Carnot–Clausius cycle in association with a lower heat reservoir temperature is the combined result of a stronger increase in EGP, the driving force in $\frac{-Q_1}{T_1} + \frac{Q_1}{T_0}$, and a proportional decrease in extracted heat resulting from a lower heat reservoir temperature T_0 in (47), rather than of a lower heat reservoir temperature favoring the heat extraction process.

Now we consider the direct application (sans heat exchange as shown in Figure 8) of burned product, derived from the combustion of a reactant mixture at adiabatic flame temperature, with enthalpy $H_P(T_{adiab}) = H_{R0}$. Instead of discharging the burned product at a designed value of peak temperature as implied in Figure 8, for heat to be added to the Carnot cycle at approximately constant peak temperature, the burned product is designed to discharge ideally at T_0, the surroundings' temperature. This can be accomplished either as an "internal combustion heat engine" with fuel-air-reactant/burned-product as the working fluid, or as an "external combustion engine" with a fluid other than the fuel-air-reactant/burned-product, e.g., steam, as the working fluid. In the latter case, the idealization of a cycle is defined by the minimization of heat transmission irreversibility by keeping the temperature difference between the burned product and working fluid small.

Because the burned product is designed to discharge ideally at T_0, this case represents the more effective combustion application of fossil fuel. In this case, $EGP(T_0)$, in accordance with (45), becomes, in view of (44),

$$\begin{aligned} EGP(T_0) &= (\Delta S)_{sys} + (\Delta S)_{reserv} \\ &= (S_{P0} - S_P(T_{adiab}, p_0)) + \frac{(H_P(T_{adiab}, p_0) - H_{P0})}{T_0} \end{aligned} \tag{49}$$

Correspondingly,

$$W_{rev-event} = T_0 \cdot EGP(T_0) = (H_P(T_{adiab}, p_0) - H_{P0}) - T_0(S_P(T_{adiab}, p_0) - S_{P0}) \tag{50}$$

As it has been noted, the logical name for the work obtained reversibly should be *available* or *free heat*. The use of free energy or free enthalpy makes some kind of sense only when irreversible steps are involved in the practice of producing work, such as combustion, whether it is internal combustion or external combustion. Equation (50) shows, of the enthalpy released by combustion, $H_P(T_{adiab}, p_0) - H_{P0} = H_{R0} - H_{P0}$; a minimum fraction of which is not available, therefore, must be subtracted from the released enthalpy. For the reversible example of Gibbs "free enthalpy", $(H_{R0} - H_{P0}) - T_0(S_{R0} - S_{P0})$, calling $T_0(S_{R0} - S_{P0})$ unavailable can be problematic since the term may be negligible or even negative (in the latter case, enthalpy is to be added to the release enthalpy rather than to be subtracted). In the case involving irreversible steps, irreversibility ensures the amount of enthalpy to be subtracted to be significant. It is useful to call the "released enthalpy subtracted by a sizable unavailable fraction" *free flame enthalpy*, the word flame serving to remind us of the context of irreversible combustion involved in its meaning.

Thermodynamics began with a focus on the relation between heat and work and with Carnot's innovation of investigating this relation in terms of reversible processes. The analysis in this paper and particularly in this subsection suggests, however, that this historical background of thermodynamics contains, by linking heat and the discussion of reversibility so closely, a misleading notion of the true nature of reversibility. Any discussion of heat necessitates the involvement of heat release that is intrinsically irreversible. "Reversible" use of heat, such as in the Carnot cycle or the Carnot–Clausius cycle, only idealizes the part involving heat transmission, leaving the irreversible heat release hidden from consideration.

True reversibility for the whole process is represented by examples in Section 6 and the example of Figure 7. These are examples that require no heat sink or sizable heat sink. For the example of Figure 7, due to the reaction being driven by infinitesimal affinity rather than large affinity of typical combustion reactions, the required heat sink, if any, is of moderate size. For the examples in Section 6, these are examples of *pure* spontaneity, EGP of which is independent of T_0 because $(\Delta_{Growth}S)_{universe}\left(= (\Delta S)_{sys}\right)$ requires no heat discharging to the surrounding. No heat sink is required.

In these latter cases, the heat reservoir serves solely as a heat source, with the whole processes requiring no heat sink. It follows that the temperature of a heat-source reservoir can be any arbitrary one, T_X. Because EGP is not dependent of T_X, reversible work is proportional with the temperature of the heat reservoir,

$$W_{rev-event} = T_X \cdot EGP \tag{51}$$

In addition to examples in Section 6 and the example of Figure 7, the application of renewables is an example requiring no sizable heat sink. The reversible realization of all these cases represents "transformations of heat into work" in which heat extraction from the surroundings, rather than heat discharge into them, is the dominant mechanism. The real lesson of the equivalence of heat and work is the requirement of a heat reservoir to serve as a heat source, whereas a heat reservoir doubling as a sizable heat sink is the result of fossil fuel combustion practices rather than the result of physics as the consequence of the equivalence theorem. The demand of a sizable heat sink is an option, resulting from technological choice, rather than a necessity, in accordance with physics.

Calling heat discharged to a heat sink *waste heat* may be misleading [32]. In the Carnot/Clausius account, the discharged heat is "reversibly" necessary. That the equivalence theorem demands, cumulatively, the prodigious production of heat to be disposed is also an incorrect scientific interpretation of the theorem. In the scheme of true reversibility, the necessity of the discharged heat results from the irreversibility of combustion heat release. Prodigious production of heat to be disposed requiring sizable heat-sink is not demanded by the equivalence theorem, but the consequence of failing to achieve reversibility in the Carnot/Clausius account when it was adopted as the imperfect philosophical accord of the Industrial Revolution.

7.3. The Dissymmetry Premise, the Driving Force of the Irreversible World

Cropper, the chemist and historian of physics, made an observation on Thomson:

> In his discursive way, Thomson touched on every one of the major problems of thermodynamics. But except for his temperature scale and interpretation of the energy concept, his work is not found in today's textbook version of thermodynamics. Although he ranks with Clausius and Gibbs among thermodynamicists, his legacy is more limited than theirs. The comparison with Clausius is striking. These two, of about the same age, and both in possession of the Carnot legacy, had the same thermodynamic concerns. Yet it was the Clausius thermodynamic scheme, based on the two concepts of energy and entropy and their laws, that impressed Gibbs . . . left no doubt about the conceptual foundations of his theories, and gave Gibbs the requisite clues to put together the scheme we see today in thermodynamics texts. ([33]: p. 90)

It is true that in physics and chemistry the textbook version of thermodynamics follows the scheme of Clausius and Gibbs. But Thomson's legacy in engineering thermodynamics and technology is supreme as evidenced by the unchallenged acceptance of the energy conversion doctrine, or the theory of exergy, which is based on the universal dissipation of free energy or exergy. Other expressions as a part of Thomson's legacy include these widely accepted truisms: Joule's assertion of the conversion of heat to work (which Thomson initially hesitated to accept) as opposed to Carnot's assertion of the co-existence of heat transmission and work production; the assertion that heat cannot be 100% converted into mechanical energy; the naïve notion that "energy makes the world go 'round"; the sophisticated but confusing notion that the exergy portion of disorganized energy, which equals $exergy + anergy$ with the presumption of a positive-definite "anergy", makes the world go ’round. These truisms collectively are hereby referred to as the exergy/anergy doctrine, which is Thomson’s legacy.

But that legacy is directly challenged by Clausius’ second fundamental theorem, which Clausius stated in the 1865 ninth memoir as,

> The second fundamental theorem, in the form which I have given to it, asserts that all transformations occurring in nature may take place in a certain direction, which I have assumed as positive, by themselves, that is, without compensation; but that in the opposite, and consequently negative direction, they can only take place in such a manner as to be compensated by simultaneously occurring positive transformations. ([23]: p. 364)

Examples of positive transformations, which can be called conversions since they are transformations that take place by themselves, are heat transmission from high temperature to low temperature; dissipative conversion of work into heat; reaction of reactant into product. The opposite of the “dissipative conversion of work into heat” is the “transformation of heat into work”, as asserted by Joule and advocated by post-1850 Thomson. But missing from this general “understanding” of energy transformations is the precise nature of these transformations: such negative transformations of heat into work, without being “compensated by simultaneously occurring positive transformations”, are impossible in accordance with the second fundamental theorem. It is positive transformations that cause (autonomously or interventionistically) changes in nature, whether they are spontaneous changes (autonomously) or changes involving elements of the negative transformation kind (interventionistically). That is, spontaneous, positive transformations are the driving force for *all* processes in the irreversible world. The second fundamental theorem, the bedrock of the second law [22], transmutes the discovery of heat (the disorganized form of energy) by NWCJ into the discovery of the dissymmetry of spontaneous transformations. That is the dissymmetry premise, the primacy of dissymmetry over free energy, which asserts dissymmetry manifested by entropy growth to be the real driving force of the irreversible world in which real transformations happen and are made to happen.

Some notable clarifications/comments that can be drawn from the dissymmetry premise are:

1. The theory of exergy is Exhibit A of Thomson’s legacy, an awkward mixture of Thomson’s approach and the entropy principle. It is an example of what we refer to as the “energy-centric-based entropy” understanding, an understanding of entropy when we approach the subject without a clear separation of the two DOE questions. Though calculations based on exergy are not wrong, students performing the calculations have been indoctrinated to perceive entropy growth, instead of being the driver for all processes, as *only* the impediment of mechanical processes.
2. The deceptive association of high temperature heat as an “energy driving force” of a Carnot engine is due to the fact that entropy growth potentials, EGPs, in these cases require a heat sink for the disposal of heat released at high temperature; other examples, especially of the pure spontaneity kind, in the paper make it clear that that situation is a manifestation of one kind of entropy growth rather than an intrinsic feature of every EGP; the universal feature of harnessing dissymmetry manifested by entropy growth is heat extraction instead of heat disposal.
3. The second law asserts the inexorable growth of total entropy, but the law is an observational statement, which does not *directly* or *automatically* assert the outcome of an actionable possibility. It is a new concept, *entropic indeterminateness*, that will systematically organize the ideas and operational nature of harnessing entropy growth into actionable possibilities (some individual examples of which are given here in Sections 5–7).

4. The possibilities include that dissymmetry or a tendency towards equilibrium is spontaneous but not inexorable (universal), i.e., an assertion of dissymmetry is not one of unidirectionality (unidirectional means that processes opposite to that of the direction are not possible, while dissymmetry in processes towards equilibrium allows processes moving away from equilibrium only that they must be *made to happen* interventionistically).
5. A related point to Point 3 should be emphasized that *far-from-equilibrium is the precondition for extracting free energy*. There has been a lot of talk about extracting free energy, including the advocation of acceleration in extracting free energy by techno-optimists. Without safeguarding the Far·From·Equilibrium precondition, the accelerating extraction of free energy as advocated by techno-optimists will kill the goose that lays the golden eggs.

Discussion in more detail in reference to Points 3 to 5 will be given in another venue, [34], a hint of which is found in Section 8.

8. Afterword

Though Thomson did "not even consecrate a symbol to denote the entropy" in his body of scientific and engineering work, he and his fellow North British scientists and engineers were talking about entropy, or more precisely about the energy-centric-based entropy understanding: the idea that although energy of a world (a system and all other parts that it interacts with) can never be destroyed, the free energy of the world (the maximum amount of work output in a reversible operation) can be wasted or dissipated. Soon afterwards, Clausius and his fellow Berlin/Vienna/New-Haven scientists discovered dissymmetry and the molecular chaos of the world. These were two separate sciences, the North British macroscopic engineering science and the Berlin/Vienna/New-Haven microscopic molecular science. The theory of exergy carried out an unsatisfactory project to unify the two, the shortcoming of which is detailed in the paper. The paper alludes to that, in unifying equilibrium thermodynamics and engineering thermodynamics into classical thermodynamics, by referring to the entropy principle as the entropy-centric-based entropy understanding, we are referring to the macroscopic understanding of the entropy principle of molecular science. An unstated reason for the necessity in doing that is that the macroscopic concept of *entropic indeterminateness* (see Nicholas Georgescu-Roegen, *The Entropy Law and the Economic Process*: p. 12), details of which will be considered in another venue [34], is absent in molecular physics and, by stating the entropy principle in its macroscopic version, we make the concept of entropic indeterminateness relevant—thus, entropy growth drives all macroscopic processes: the dissipation of entropy growth potentials and impediment of mechanical processes spontaneously, and the production of reversible-like transformations interventionistically.

This paper argues for the primacy of the second fundamental theorem in the formulation of Unified Classical Thermodynamics (UCT). The formulation begins with the Carnot/Clausius account of *Thomson's problem*, in acknowledging the extraordinary insight of Thomson expressed in the draft of the *Dynamical Theory of Heat* paper ([2]: pp. 174–200; see [1]: Appendix II, especially "page five") and the 1852 *Universal dissipation of mechanical energy* paper ([2]: pp. 511–514). Though we argue for the superiority of the entropy-centric-based entropy understanding for achieving the eventual goal of unification, we cannot overestimate the role Thomson's problem played in setting off the processes of problem solving leading to the unification.

It is in this spirit that I suggest another question or thinking out loud by Thomson, referred to as a *new Thomson's problem*, to be a source for productive future problem solving. This is in reference to the following, from Wikiquote, ref. [35] quote by William Thomson:

> *It is conceivable that animal life might have the attribute of using the heat of surrounding matter, at its natural temperature, as a source of energy for mechanical effect . . .. The influence of animal or vegetable life on matter is infinitely beyond the range of any scientific enquiry hitherto entered on. Its power of directing the motions of moving*

> *particles, in the demonstrated daily miracle of our human free-will, and in the growth of generation after generation of plants from a single seed, are infinitely different from any possible result of the fortuitous concurrence of atoms.*

We have argued for the superiority of the *Carnot/Clausius* account for *Thomson's problem*. And throughout the paper we showed examples—the Carnot–Clausius cycle, Figure 2; the example in Figures 3 and 4; the example in Figures 5 and 6; the reversible manifestation of Gibbs "available heat" in Figure 7; and the example manifesting the "approximately" reversible "free flame enthalpy" as shown in Equation (50)—all these examples demonstrate heat extraction as the dominant mechanism for effectively harnessing the driving force of the irreversible world. Of the five examples, three of them, from the second to the fourth, represent the application of classical thermodynamics within the framework of Clausius and Gibbs, showing the *extraction of "heat of surrounding matter, at its natural temperature, as a source of energy for mechanical effect"*. We may refer to these accounts, rather than being miraculous mechanisms or some kind of probability-based statistical mechanics mechanism, as the *Carnot/Clausius/Gibbs account for the new Thomson's problem*—the UCT-based, interventionist, heat extraction mechanism account. Again, rather than miraculous or fortuitous concurrence of atoms, it is the manifestation of entropic indeterminateness [34].

"Just as the Industrial Revolution once generated change in many fields in the 19th century", wrote the architect James Wines, "so too the information revolution. . .serves as a conceptual model in the 21st century for a new approach to architecture and design. . ." [36]. I argue for the following for providing even better context for "architecture [and economic activities] to become truly green" [36]: just as the Carnot/Clausius account generated the prodigious progress for mankind during the Anthropocene, the Carnot/Clausius/Gibbs account will serve as a scientific/technological foundation for bringing about co-existence of mankind and the planetary environment at *far from equilibrium*, a Gaian state of the mankind/biosphere/Earth system.

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List of Symbols

A_H	Helmholtz function, U - TS
c_p	constant pressure specific heat
C	Celsius
EGP	entropy growth potential
DOE	disorganized energy
G	Gibbs function
h	specific enthalpy
H	enthalpy
H_P	enthalpy of reactant
H_R	enthalpy of product
K	kelvin
kJ	kilo joule
m	mass
N	mole number
$\tilde{N}$	$d\tilde{N} = dN_j/\nu_j$
OE	organized energy
p	pressure
p^r	pressure of the reservoir
$P0$	product at the standard temperature, T_0

Q	heat exchange
Q_1	heat supplied to the Carnot engine
Q_{IR}	heat exchange of an IR event
Q_{Quasi}	heat exchange of a quasi-static event
R	universal gas constant
$R0$	reactant at the standard temperature, T_0
S	entropy
S_{equili}	entropy at the internal equilibrium of system, where it is maximized
t	specific temperature of certain scale
T	absolute temperature
T_0	standard temperature
T_{adiab}	adiabatic flame temperature
T_{peak}	peak operating temperature
T_{res}	temperature of a reservoir from which heat is extracted
T_X	the arbitrary temperature of a reservoir available for heat extraction
T^r	temperature of the reservoir which a system interacts with
U	internal energy
V	volume
W	work
μ	molar Gibbs potential
ν	stoichiometric coefficient

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