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Commentary

Energeia Physics: An Amendment to the Joule-Thomson-Maxwell Energy Narrative

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In the eighteenth century, mankind, British inventors among the first, discovered in steam engines a new use of coal fire—a discovery that led to the advent in the nineteenth century of a *science of heat*, a new branch of physics. The core of this science is referred to as the Joule-Thomson-Maxwell energy conversion narrative. The principle of the degradation of energy was central to the energy conversion narrative. The principle and the later entropy principle are so closely connected that "entropy and the dissipation of energy are as inseparable as Siamese twins." But Maxwell had a different take: "the doctrine of the dissipation of energy is closely connected with that of the growth of entropy but is by no means identical with it." One logical choice for the energy conversion narrative with universal degradation of energy is that the narrative needs a first step to initiate it. But insisting that *every* step of the narrative be an energy conversion step, including the starting step of the reversible transformation of a chemical mixture into a chemical product and work, is a mistake. The paper examines the narrative critically, arriving at a conclusion that pinpoints why energy dissipation is "by no means identical with" entropy growth.

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> "Energy makes the world go round." Based on the scientific contributions of Joule, William Thomson, Rankine, Clausius and others in the nineteenth century, we have thermodynamics, the physics of heat and energy, offering us a universally accepted, coherent and autonomous theoretical system on how energy keeps the world going round. The core of this science is referred to as the Joule-Thomson-Maxwell energy conversion narrative. The coherence of the theory narrative, though, is marred by one missing piece in

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its storyline. The paper proposes an easy repairing-step based on a later development of the theory, Gibbsian thermodynamics, for making the JTM energy narrative thread "unbroken."

The definition of energy plays an integral part in the energy narrative. Energy, etymologically, means activity or actuality. The word has been in the general lexicon since Aristotle, who adopted the term *energeia* to mean potentiality and actuality. The first significant use of the word as a scientific term is attributed to Thomas Young: "The use of the term energy, in a scientific sense, to express the quantity of work a body can do, was introduced by Dr. Young" (Maxwell [1]: p. 91). This definition of *energy*, as "the capacity of doing work" (Maxwell [2]: 54) or "the capacity for performing work" (Kent [3]), represents one key element in how a North British group of scientists and engineers, including Joule, Thomson, and Maxwell, in the nineteenth century transformed physics, the science of motion, first in terms of a theory of work, then into a theory of energy, which may be referred to as *energy physics*. The existence of a rigorous definition goes a long way for theory formulation, but the lack of a rigorous definition is not a major obstacle for doing research. In that case, a definition, even if it is not a rigorous one, can be useful if it captures some fundamental characteristic of all phenomena under study. For energy phenomena, "there is only one fundamental and universal characteristic of energy which we can be sure holds true for all its various forms and that is its conservation ... The principal source of confusion in the case of energy arises from using *one* characteristic attribute, and that not of a universal one, as a 'definition' of energy" ([4]: 568; see also *the trouble with defining energy*, [5]). It is worth noting that the narratives of energeia, i.e., energy in layman's terms escaping an elemental definition, are often more compelling than the narrative of energy. In addition to the opening sentence of the paper, we may cite the *keynote remarks at CERAWeek 2025* by the US Energy Secretary C Wright: "Energy is the enabler of everything that we do. Everything. Energy is not a sector of the economy; it is the sector that enables every other sector. Energy is life" ([6]). This remark is perfect if we paraphrase it as: "Energeia is the enabler of everything that we do. Everything. The energy industry is not a sector of the economy; it is the sector that enables every other sector. Energeia is life."

Besides the definition of energy, another common understanding in association with the JTM energy narrative is the following. This understanding may be referred to as a truism: it is a truism universally accepted that "entropy and the dissipation of energy are as inseparable as Siamese twins in the thought of every student of thermodynamics" [7]. "Entropy grows inexorably" was a law of nature established by Clausius, while the "principle of the degradation of energy" was an earlier "doctrine" formulated by W.

Thomson. Maxwell had a somewhat different take on the two ideas: "the doctrine of the dissipation of energy is closely connected with that of the growth of entropy but is by no means identical with it," [[1]: p.192].

We may connect our three focuses—the JTM energy narrative, the energy narrative with a "rigorous definition of energy" vs. the stories of energeia (without an elemental definition), and Maxwell's comment on energy dissipation vs. entropy growth—as three specific aspects in the nineteenth-century answer to address an overarching question that urgently requires critical assessment for the twenty-first century. The invention of steam engines was a historic event in which man discovered a new *general-purpose technology* (GPT) that elevates its existence and survival to another level. [Electricity, steam, and information and communications technologies (ICT, or AI as the direction ICT is taking today) are generally regarded as being among the most important GPTs.] The question is, "*what is the real nature of the steam/fossil-fuels GPT discovery?*" Sadi Carnot took the first step toward articulating an answer: it was the discovery of the "motive power of heat." Though he did not emphasize the discovery of heat as a substance, it was rather that the discovery was that of a heat transfer phenomenon. It fell to William Thomson to formulate the authoritative and most influential answer: it was the discovery of new forms of energy that are interconvertible with heat, but the "meaning of 'energy' involved in every conversion from one form to another is "practically inseparable from the concept of a conservation principle" [[8]: p.13]. Because of this inseparability, Feynman argued instead that "we have no knowledge of what [the new form of] energy *is*." Other than that energy is the *abstract idea* of "a numerical quantity which does not change when something happens" [9]. We have two conceptions of energy from high authority. And they conflict with each other. Maxwell is another participant, ([1][2][4][7]), in this debate. This paper is about the resolution of the conflict.

For that, the paper makes the following points. The Joule-Thomson-Maxwell energy narrative represents the core of a theory erected on the two laws of thermodynamics with an additional foundational element, energy as "the capacity for doing work," or energy metaphysics. The paper's thesis is:

> A major part of the narrative, i.e., the part occupied by the ***principle of the degradation of energy*** steps, works; the narrative breaks down at the single, initiating step, the step in which the narrative substitutes "reversible chemical change" with an additional element, the metaphysical notion of "energy as the capacity for doing work." Clausius' and Gibbs' contributions—Clausius' concept of "compensated by simultaneously occurring positive

> transformations," and Gibbs' treatment of chemical changes, which serve as the required positive transformations—make the additional element, energy metaphysics, unnecessary, thus enabling the repair of the JTM narrative.

Thomson and Feynman are both right: With the repaired narrative, Thomson is right that the *steam-internal•combustion/fossil-fuels* GPT is evidenced, by examples, as a "new kind of resource" of sublime consequences. Feynman is right that, as energy, we can have no knowledge of it (other than the metaphysical kind) but we can have knowledge of irreversible transformations in terms of "reversible extractable-heat" or "reversible-like extractable-heat," explaining the resources' sublime consequences.

1. Dissymmetry and energy-conservation in events of transformation, the two laws of thermodynamics

We begin with a statement of the two laws of thermodynamics:

First law of thermodynamics (Britannica version):

> *The change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings. In other words, energy cannot be created or destroyed but merely converted from one form to another.*

Second law of thermodynamics (Britannica version):

> *Heat does not flow spontaneously from a colder region to a hotter region, or, equivalently, heat at a given temperature cannot be converted, solely, into work. Consequently, the entropy of an isolated system, or heat energy per unit temperature, increases over time toward some maximum value. Thus, all isolated systems tend toward equilibrium states in which entropy is at a maximum and no energy is available to do useful work.* ([10]: the word "entirely" in the original is replaced with ", solely,"; the word "closed" is replaced by "isolated")

Both the first and second laws are inexorable laws of nature. The first law is a law of conservation, the inexorable conservation of total energy in every event. The second law is a law of transformation, the inexorable growth of entropy in the universe in every transformation event. Thermodynamics, the study of transformation events, emerged in the eighteenth and nineteenth centuries from mechanical sciences, sciences that succeeded in describing nature in terms of a set of laws of "locomotion" of mechanical entities, e.g., “positions and momentums” of atoms and molecules. The set of Newton’s laws of motion is one example. The mathematical versions of such laws of locomotion are referred to with the general name of *equations of motion* (EOMs). Inferences from EOMs have proven to be so successful that EOMs themselves, “though non-physical,” are considered “timeless, absolute, and unchangeable essences of all things,” a metaphysical idea that goes all the way back to the Platonic-Cartesian ideal.

Events of locomotion, as governed by EOMs, are reversible and deterministic, i.e., events involving no change or happening. Equations of motion also ensure such events to be energy conservation events. It is worth noting that, with the central role of EOMs, no *independent* assertion of energy conservation is necessary for such events. Moving from events of locomotion to events of transformation, which are no longer governed by EOMs, heat phenomena of transformation were new phenomena discovered in nineteenth-century physics for which it is necessary to have an independent assertion of energy conservation. “Energy” was the first new fundamental concept introduced in the new branch of physics ([8][11]).

Following the introduction of energy, Clausius, in 1865, introduced the second new fundamental concept for the new phenomena of transformation, “entropy” [[12]:327-374]. On his road to entropy and the second law, Clausius began, in 1854 [[12]:111-135], with updating Carnot’s realization of the existence of dissymmetry in phenomena of transformation. Dissymmetry is shorthand for the tendency of transformation that *“uncompensated” transformations can take place only in a preferred direction*. We refer to transformations, or processes, exhibiting such a tendency as spontaneous, or irreversible, processes. Examples of spontaneous processes include: heat flows uncompensated from a hot body to a cold body; conversion occurs uncompensated from work to heat. Processes opposite to spontaneous processes are possible, but they occur only when they are compensated by other spontaneous processes.

The two laws of thermodynamics, the first law of thermodynamics (1842-1852) and the second law of thermodynamics (1852; 1854-1865), are *independent* laws. It is worth noting that, though the idea of entropy and the definite second law of thermodynamics as the entropy law are attributed to Carnot (1824), Clausius (1854-1865), and Gibbs (1875-1878), an earlier 1852 version of the second law of thermodynamics was established by William Thomson in a four-page paper ([13]: 511-14), as the principle of the degradation of energy—without using the concept of entropy. Because Thomson talks about the two ideas both in terms of energy, total energy and its conservation and available energy and its degradation, a state of confusion has existed ever since with regard to the *independence* of the two laws.

2. The Joule-Thomson-Maxwell energy conversion narrative

We backtrack our investigation of the Joule-Thomson-Maxwell (JTM) energy conversion narrative with a review of how the early investigators came to these understandings.

Garver noted, “All of the early investigators in the theory of energy received a peculiar bias from the fact that the theory of energy was developed from the theory of work—the production of ‘useful work’ being one of the most important problems in the life of nations as of men” [[4]: 571].

In systems of classical mechanics, mechanical energy *is* the capacity for doing work. The mechanism of how kinetic energy and potential energy are converted to work is provided by EOMs. In the case of generalized energy, the work-energy relation as energy as “capacity for doing work” still applies to a special group of problems, the storage of mechanical energy in a work reservoir and the retrieval of mechanical energy from the reservoir, with both steps of storing and retrieving having an efficiency of nearly 100%. Here we are talking about the electric form of mechanical energy (in the general sense).

That kind of storage is one characteristic necessary for a GPT, enabling the wide distribution and deployment of the GPT. It is a necessary element of the energy conversion narrative. We now go back to the mainline thread of the narrative, that of energy conversion.

We could have started with Carnot for a story of thermodynamics. But as our mainline thread is energy conversion, we start with Joule. Joule and Mayer, independently, established in the 1840s the *mechanical equivalent of heat*: in an excellent history-of-science article, Kipnis noted, “the term ‘mechanical equivalent of heat’ appeared in many articles, usually meaning a number without an explicit association with any theory. Yet, many physicists agreed that the theory behind MEH was the principle of convertibility” [[14]: 2018]. Both Mayer and Joule supported the principle of convertibility. However, logically, “while Mayer might have convinced himself that the numerical equality of the two forces necessarily followed from an application of the metaphysical notion ‘cause equals effect’, its demonstrability to others was questionable” [[14]: 2017]. That is, logically the MEH heat and work equivalence can be associated with either convertibility between heat and work, or coexistence or proportionality between heat and work. While the majority of scientists and engineers, contemporaries of Mayer and Joule, were in the convertibility camp, as Kipnis noted, “neither Carnot and Clapeyron nor Holtzmann and Thomson [(before 1847, the year he met Joule), as well as Hirn and Jacobi] thought that heat could be converted into work. Apparently, before 1850 they assumed a certain association between heat and work, such that the two existed independently of one another but could influence each other.

For instance, Carnot's supposition that work was created by a mere transfer of heat by expanding gas, in fact, implied such a coexistence" [[14]: 2032].

Nevertheless, the minority camp faded away while Mayer and Joule's interpretation of MEH triumphed to become the entrenched doctrine that heat could be converted into work that continues today. The following in this section will describe the JTM energy narrative that followed this doctrine.

Rankine, Clausius, and Thomson, once sufficiently convinced of the constancy of MEH, began reforming thermodynamics on the basis of the principle of convertibility [[14]:2036]. While Joule emphasized that energy cannot be created or destroyed, Thomson (later, Lord Kelvin) was more interested in the intricacy of the nature of conversion, in which the *direction* of conversion, whether it is the conversion of heat into work or the conversion of work into heat, matters.

The dissipation of mechanical energy via friction in association with mechanical work has been well established. It has been accepted that the *spontaneous* conversion of mechanical energy into heat energy is without limit. However, in accordance with conventional wisdom, the *opposite* conversion from heat to work is subject to strict limitation. The second law addresses these directional issues. The prelude to the second law is the Clausius statement and the Kelvin–Planck statement, which state, respectively, "*Heat does not flow spontaneously from a colder region to a hotter region*" and "*Heat at a given temperature cannot be converted solely into work*" (from the above second law of thermodynamics).

Note the latter statement: the word "solely" in the Kelvin-Planck statement has often been mistakenly stated as "*Heat at a given temperature cannot be converted entirely into work*" as it is in the quoted source Britannica article. Therefore, the idea of "the conversion from heat to work is subject to strict limitation."

Thomson (Kelvin) himself considered the issue with more nuance. By pondering a rhetorical question, Thomson began his investigation. The question, referred to as the Thomson conundrum, [[15]:281], is: noting that the work produced in a Carnot cycle is lost in a workless heat transfer, how to account, though no destruction of energy ever occurs, for this loss? Thomson came to see the difference between "destruction" and "dissipation" (or "degradation"): though no energy of a body is destroyed, the "available energy" of a body is dissipated continuously and spontaneously.

The setup of a Carnot cycle can be used for calculating available energy and demonstrating the phenomenon of its degradation. Consider a high-temperature heat reservoir of constant volume, a hot body of large thermal mass, at T_1 in interaction with another surrounding heat reservoir at T_0.

Consider first the amount of $\mathbf{Q_1}$ that leaves the high-temperature reservoir, directly transferring to become heat in the T_0-reservoir. In this spontaneous transformation, Q_1 of the amount, $T_1 \Delta S_{res-T_1} = |\Delta U_{res-T_1}|$, is transformed into an energy of the same amount at T_0, in which it is completely unavailable for work.

Consider now an indirect way (via a Carnot cycle) of heat flowing from T_1 to T_0. $Res - T_1$ supplies Q_1 at T_1 to the cycle. What is the amount of energy as a fraction of Q_1 that the reversible cycle yields as work? Since no energy becomes unavailable during a reversible process, the work yielded by the reversible cycle is the maximum amount of work. This is also the available energy of Q_1 that is lost during the direct transfer of Q_1 in the workless heat transfer.

The value is determined by first calculating the minimum heat rejection to the heat reservoir: the application of the second law,

$$\Delta S_{res-T_1} + \Delta S_{res-T_0} = 0 \tag{1}$$

yields $MinimumHeatRejection = Q_1 \left(\frac{T_0}{T_1}\right)$. Correspondingly, the maximum useful work, i.e., the available energy, is,

$$available \bullet energy = Q_1 - T_0 \bullet \frac{|Q_1|}{T_1} = |\Delta U_{res-T_1}| - T_0 \bullet |\Delta S_{res-T_1}| \tag{2}$$

Thomson (Kelvin) first formulated the second law in terms of the Kelvin-Planck statement. His second formulation of the second law, in terms of available energy and the degradation of available energy, has been referred to as the energy principle. [16] It is worth noting

> The energy principle is not the principle of conservation of energy. The principle of conservation of energy in its original narrow sense merely acknowledges the possibility of energy transformation subject to energy constancy during all energy transformations, without any indication of the preferred direction of transformations. Now, the energy principle gives a preferred direction, in addition to energy constancy, of energy transformations ... Before the 1852 paper, heat and mechanical work and their equivalence were the focus of thermodynamics in the investigation of Carnot, Mayer, Joule, and Clausius ... The preferred direction of spontaneous changes was represented by the Clausius statement and the Kelvin–Planck statement in terms of heat, heat transfer, and work. With the energy principle, thermodynamics began shifting from heat–work equivalence to the

> new focus, energy and the transformation of energy. The process of this change in focus from heat to energy was a long one with detours along the way, the eventual completion of which was the formulation of the theory of exergy. [[16]:84–85]

The treatment of the preferred direction for chemical transformations was successfully completed in the important milestone, the introduction of Helmholtz free energy and Gibbs free energy. In a most interesting study of interactions among Thomson, Tait, Clausius, Maxwell, and Gibbs, the science historian Daub made the comment, "... Gibbs brought together the two traditions of entropy and dissipation. The unification was, however, only implicit, since Gibbs talked only of entropy, not of availability. The first explicit formulation was Maxwell's, in his revised discussion of available energy in 1876" ([7]: 353–354). The following is a reproduction of Maxwell's discussion of available energy, which can be linked to the official Helmholtz free energy.

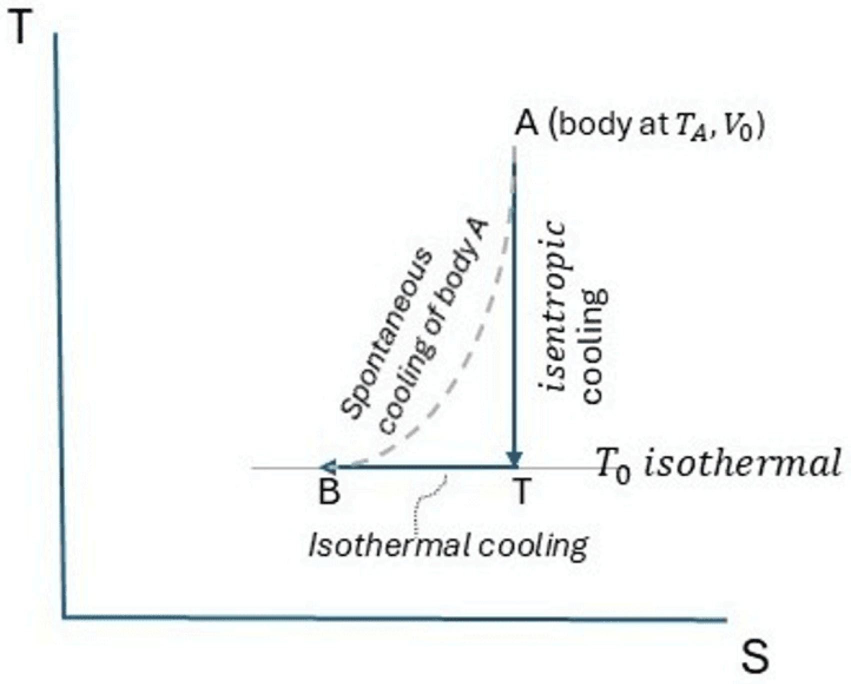

Figure 1. A part of the internal energy of a hot body that becomes unavailable to do work due to the body's high entropy, i.e., $S_A - S_B$

Consider changes in the internal energy and entropy of a finite thermal mass body at T_A and V_0 initially, referred to as state A, see Fig. 1, undergoing a spontaneous, irreversible step ending at T_0 and V_0, referred to as state $B(T_0, V_0)$. The body is in interaction with a surrounding heat reservoir at T_0, the same kind of heat reservoir as in the above case. In this case, the consumption of internal energy, instead of resulting from a very large thermal mass giving out heat with no drop in its temperature, is associated with the finite thermal mass experiencing a drop in temperature toward and ending at T_0.

Similarly to the Carnot cycle setup, consider a spontaneous (workless), or direct, cooling from A to B. Alternately, consider a virtual, or indirect, change from A to B consisting of, referring to Fig. 1, an isentropic change, AT, and an isothermal cooling, TB.

The first law demands all possible changes from A to B meet,

$$U_A - U_B = -Q + W \tag{3}$$

For the workless heat cooling, we have,

$$U_A - U_B = -Q_{AB} \tag{4}$$

For the isentropic cooling and the isothermal cooling, we apply the following expressions, respectively,

$$U_A - U_T = W_{rev} \tag{5}$$

$$U_T - U_B = -Q_{rev} = |Q_{rev}| \tag{6}$$

Note that $-Q + W = W_{rev} + |Q_{rev}|$. Since the reversible isothermal cooling to the heat reservoir, $|Q_{rev}|$, is the minimum necessary cooling, which the second law determines to be $T_0\,(S_T - S_B) = T_0\,(S_A - S_B)$, the reversible isentropic work, $U_A - U_T$, is the maximum work. In other words, the available energy of $U_A - U_B$ is

$$W_{useful} = U_A - U_T = U_A - U_B - (U_T - U_B) = (U_A - U_B) - T_0\,(S_A - S_B) \tag{7}$$

In *Theory of Heat*, Maxwell noted, "This is the part of the energy which is available for mechanical purposes under the circumstances in which the body is placed, namely, when surrounded by a medium at temperature *T* [T_0]..." ([1], p. 189). Both Eq. (2) and Eq. (7) assume the form,

$$available \bullet IE = IE - unavailable\ energy \tag{8}$$

It is important to note that an unanswered question for both the Carnot cycle and the virtual process described by Maxwell is the source that maintains the high-temperature reservoir or the finite thermal mass. Typically, the source is combustion heat release, which is an irreversible process. A *complete* consideration of these examples necessitates the inclusion of combustion heat release. The celebrated reversible Carnot cycle, therefore, is not a truly reversible cycle, an observation that has been made in a recent paper [[17]:339]. Nor is the "reversible" process ATB a truly reversible set of steps.

Maxwell's demonstration of ATB has to be amended by considering that the body begins an adiabatic prequel-step undergoing a change from (T_0, V_0), when the body is made up of a reactant mixture at state *R*0, to (T_A, V_0), when the body is filled with a high-temperature product mixture at T_A as a

result of reaction heat release ending at state *A*. See Fig. 2. If one assumes that the reactant mixture's entropy value at $(T_0,\ V_0)$ is approximately equal to the product's entropy value at $(T_0,\ V_0)$, i.e., $S_{R0} \approx S_{P0}\,(= S_B)$, the sequence of processes, *R*0(B) ATB, is a "closed" cycle in the T-S diagram. Note that step *R*0A is an isochoric process with adiabatic idealization; hence,

$$U_{R0}\,(T_0) = (U_P)_A\,(T_A)\,. \tag{9}$$

This, the assumption $S_{R0} \approx S_{P0}\,(= S_B)$, is referred to as the "air-standard assumption." However, such a sequence of processes is intrinsically an open sequence of processes, and the entropy value of the reactant mixture, S_{R0}, is generally different from the entropy value of the product mixture, S_{P0}. These possibilities are suggested in Fig. 2.

As shown in Fig. 2, Path 1 refers to path $R0_1 \bullet A_1 \bullet T_1 \bullet B$, for which the entropy of the reactant mixture, S_{R0}, is smaller than the entropy of the product mixture, S_{P0}. Path 2 refers to path $R0_2 \bullet A_2 \bullet T_2 \bullet B$, for which the entropy of the reactant mixture, S_{R0}, is greater than the entropy of the product mixture, S_{P0}. We shall discuss how Helmholtz introduced Helmholtz free energy and identified the original cause of the unavailable energy in Fig. 1 as well as the implications of the above observations.

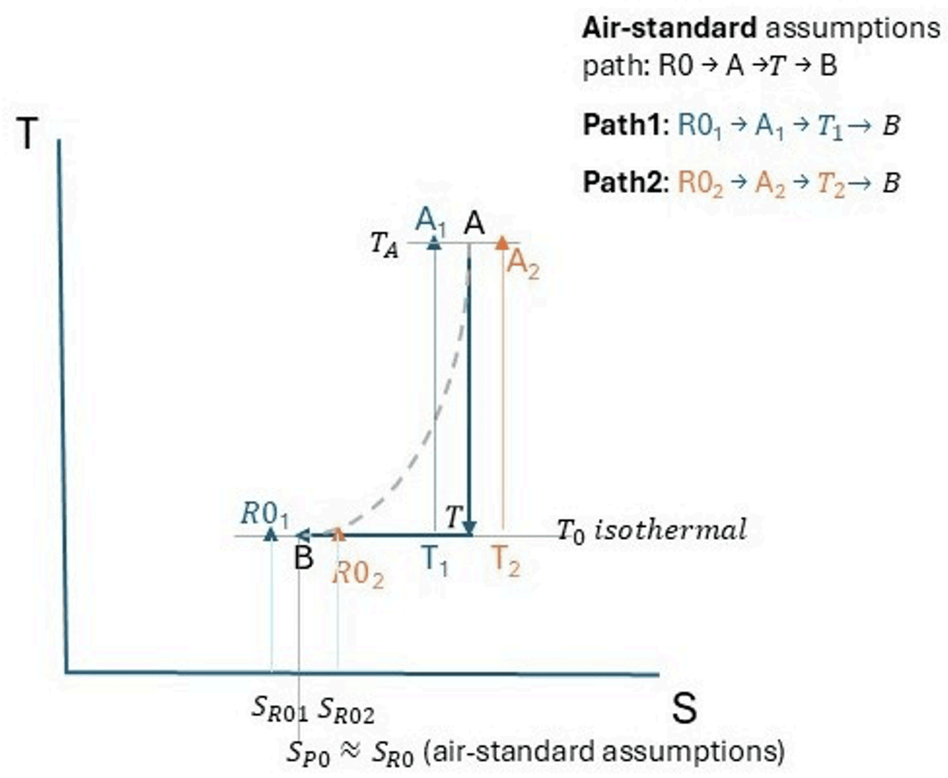

Figure 2. Connecting the entropy gain that causes part of the internal energy to become unavailable to a combustion heat release step. This will be referred to as a first irreversible process: j = 1 in Eq. (36).

3. Gibbsian thermodynamics: Helmholtz free energy and Gibbs free enthalpy

Between his 1854 Fourth Memoir and 1865 Ninth Memoir, Clausius introduced the Second Fundamental Theorem and the concept of entropy. This development, together with the Clausius statement and the Kelvin-Planck statement, may be summarized into the Second Law of Thermodynamics (the JTM energy narrative version):

> *Heat does not flow spontaneously from a colder region to a hotter region, or, equivalently, heat at a given temperature cannot be converted, solely, into work. Consequently, the entropy of an isolated system, or heat energy per unit temperature, increases over time toward some maximum*

> *value defining its equilibrium state. While energy cannot be created or destroyed, energy during irreversible processes is continuously becoming unavailable for work.*

The second law, the entropy law, is a powerful universal principle with the broadest applicability. But this paper focuses on a twofold principal application of the law: in Section 2, the law, together with the first law, is applied to determine the "quantity of work a body can do"; in this section, the sweeping single assertion of the law is shown to be translated successfully to determine the "preferred direction in the change for a body" in three situations (and by implication for all situations [17]). The second application is an example of Gibbsian thermodynamics translating a powerful but nonspecific assertion into a precise prescription—a shining example of the best of physics.

The former case of engineering thermodynamics, referred to as energy physics, is an incomplete project. But, as will be argued in the section that follows, Section 4, the precision and elegance of Gibbsian thermodynamics offers a way for the repair of energy physics, the JTM energy conversion narrative, by unifying the two principal applications. The idea of unifying energy physics and Gibbsian thermodynamics has been preliminarily outlined in an earlier paper [17]. This paper will arrive at a quantitative conclusion that places the principle of the degradation of energy and an updated understanding of reversible processes in a coherent relation, thus making a stronger case for unification.

Continuing the above Fig. 2 example, we consider the specifics of using the second law to determine the "preferred direction in the change for a body" at *R*0. To arrive at a prescription for a finite change of state of a system with its preferred direction, we must know such external conditions as allow $dS \geq 0$ to be integrated (see below for details). Since the external conditions can be chosen at will, there are several of them, of which three are considered.

First, we may keep the temperature T (= T^r) and the volume V (= V^r) constant (isothermal-isochoric process). For these external conditions, the fundamental relation, $U = U(S, V, N_1, N_2, \cdots, N_n)$, takes the form (see [17]),

$$A_H \equiv U - TS = A_H(T, V, N_1, \cdots) \tag{10}$$

Correspondingly,

$$dA_H = -SdT - pdV + \sum_{j=1}^{n} \mu_j dN_j \tag{11}$$

where A_H is the Helmholtz function. Here we study a chemical system and investigate how, between two states of the system, the initial state and the final state, i.e., the state of the reactant mixture and the state of the product mixture, of the system are determined.

The system is kept at a constant temperature in 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 an isolated system. The COMBINED system of the system and the isothermal heat bath, therefore, meets, in accordance with the second law,

$$T^r d(S + S^r) \geq 0 \tag{12}$$

Inequality (12) reduces to, at equilibrium,

$$T^r d_{equili}\left(S + S^r\right) = 0 \tag{13}$$

With $\delta W = 0$ and $\delta Q = -\delta Q^r$, the first law yields, $dU = -\delta Q^r = -T^r dS^r$. Eqs. (12) and (13) become, in view of (11) and the first law,

$$T^r d\left(S + S^r\right) = -d\left(U - T^r S\right) = -dA_H \geq 0 \tag{14}$$

$$T^r d_{eq}\left(S + S^r\right) = -d_{eq}\left(U - T^r S\right) = -d_{eq} A_H = 0 \tag{15}$$

The equilibrium condition corresponding with the maximization of total entropy, Eq. (13), assumes Condition (15), or minimization of the Helmholtz function, which is widely known as minimization of Helmholtz free energy.

That is, with the introduction of the stoichiometric coefficients,

$$\frac{dN_1}{\nu_1} = \frac{dN_1}{\nu_1} = \cdots = d\widetilde{N} \tag{16}$$

Eq. (11) becomes

$$dA_H = -SdT - pdV + \sum_{j=1}^{n} \mu_j dN_j = \sum_{j=1}^{n} \mu_j dN_j = d\widetilde{N} \sum_{j=1}^{n} \nu_j \mu_j \tag{17}$$

That is, (15) becomes the condition of

$$\sum_{j=1}^{n} \nu_j \mu_j = 0 \tag{18}$$

This concludes that the chemical change is along a virtual, quasi-static path of isothermal-isochoric conditions in the direction of decreasing Helmholtz free energy, ending under the equilibrium condition (18).

Secondly, consider a case similar to the above example by keeping the temperature T (= T^r), but instead a different composite system, made of $V^{(1)}$ and $V^{(2)}$, of constant total volume: $V^{(1)} + V^{(2)} = V^{(1)+(2)}$. For these external conditions, the fundamental relation, $U = U^{(1)}\left(S^{(1)}, V^{(1)}\right) + U^{(2)}\left(S^{(2)}, V^{(2)}\right)$, takes the form

$$\begin{aligned} A_H &= {A_H}^{(1)}\left(T^r, V^{(1)}\right) + {A_H}^{(2)}\left(T^r, V^{(2)}\right) \\ &= U^{(1)} + U^{(2)} - T^r(S^{(1)} + S^{(2)}) \end{aligned} \tag{19}$$

Correspondingly,

$$dA_H = -p^{(1)}dV^{(1)} - p^{(2)}dV^{(2)} \tag{20}$$

Application of the second law, (12), leads to the following set of equations:

$$T^r d\left(S + S^r\right) = T^r dS - dU = -d\left(A_H\right) \geq 0 \tag{21}$$

$$T^r d_{equi}\left(S + S^r\right) = T^r d_{equi}S - d_{equi}U = -d_{equi}\left(A_H\right) = 0 \tag{22}$$

$$d_{equili}\left({A_H}^{(1)} + {A_H}^{(2)}\right) = \left[-{p^{(1)}}_{equi} + {p^{(2)}}_{equi}\right] d_{equili}V^{(1)} = 0 \tag{23}$$

It follows that,

$${p^{(1)}}_{equi} = {p^{(2)}}_{equi} \tag{24}$$

This concludes that the composite system changes spontaneously along a virtual, quasi-static path of isothermal conditions in the direction of decreasing Helmholtz free energy, ending under the equilibrium condition, (24), of equal pressures of both parts of the composite system.

We now consider the **third case**, the second example of chemical change under constant T^r and p^r. The fundamental relation takes the form,

$$G = G(T, p) = U + p^r V - T^r S = H - T^r S \tag{25}$$

And its differential as,

$$dG = -SdT^r + Vdp^r + \sum_{j=1}^{r} \mu_j dN_j = \sum_{j=1}^{r} \mu_j dN_j \tag{26}$$

Application of the second law, (12), and by using the relation, $dU = -T^r dS^r - p^r dV$, leads to the following set of equations:

$$T^r d\left(S + S^r\right) = -d(H - T^r S) = -dG \geq 0 \tag{27}$$

It reduces to, at equilibrium,

$$d_{equili}G = \sum_{j=1}^{r} \mu_j d_{equili}N_j = d_{equili}\widetilde{N} \sum_{j=1}^{r} \nu_j \mu_j \tag{28}$$

That is,

$$\sum_{j=1}^{r} \nu_j \mu_j = 0 \tag{29}$$

This concludes that the composite system changes spontaneously along a virtual, quasi-static path of isothermal/isobaric conditions in the direction of decreasing Gibbs free energy, ending under the equilibrium condition (29), which determines the composition of the product mixture.

It is worth noting that the integration of the Helmholtz function and the Gibbs function yields, respectively,

$$\begin{gathered} \int_{Reac}^{Prod} -dA_H = (A_H)_{R0} - (A_H)_{P0} \\ = (U_{R0} - U_{P0}) - T^r (S_{R0} - S_{P0}) \end{gathered} \tag{30}$$

$$\begin{gathered} \int_{Reac}^{Prod} -dG = G_{R0} - G_{P0} \\ = (H_{R0} - H_{P0}) - T^r (S_{R0} - S_{P0}) \end{gathered} \tag{31}$$

They have been referred to as Helmholtz free energy and Gibbs free energy, or Gibbs free enthalpy. The term “free energy” has been entrenched in the scientific literature, both as an explanation of the preferred direction of chemical changes and as a representation of available “energy.” The latter use of the two terms will be critically examined in Section 4.

4. Energeia physics, the repair of the JTM energy narrative

The central question of energy physics, i.e., the JTM energy narrative treated in Section 2, is the “quantity of work a body can do.” While the central question of Gibbsian thermodynamics, treated in Section 3, is the “preferred direction in the change for a body.” We see in Section 3 that Gibbsian thermodynamics succeeded in addressing the latter question on the bedrock of the second law, whereas the JTM energy narrative’s handling of the former question remained incomplete, necessitating the repair of the narrative by incorporating the best result of Gibbsian thermodynamics for its completion. We may refer to this development as a unification of *both* branches, instead (see [17]), since the development as shown in the following also removes an important misunderstanding of Helmholtz free energy and Gibbs free enthalpy within Gibbsian thermodynamics in its interpretation of both terms, an interpretation that is carried over from the JTM energy narrative.

Here we argue that the *complete* JTM energy narrative is based on two laws of thermodynamics and one additional foundational element, energy metaphysics. To highlight that the fundamental contradiction in the narrative results from contamination by energy metaphysics of the first law, depriving the second law of its full power, we deliberately show here a first law statement that incorporates the energy metaphysics: Combined statement of the energy metaphysics assertion and the first law (The JTM energy narrative version):

> *The exergetic content of energy is the capacity for doing work. The change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings. In other words, energy cannot be created or destroyed but merely converted from one form to another.*

Referring back to Fig. 2, *R*0→A of an open cycle *R*0·A·T·B is interpreted as the irreversible combustion of $(A_H)_{R0} - (A_H)_P(T_A, V_0) = [U_{R0} - U_{PA}(T_A, V_0)] - T^r[S_{R0} - S_{PA}(T_A, V_0)]$. Since irreversible combustion is an adiabatic workless process, the expression reduces to,

$$(A_H)_{R0} - (A_H)_{PA}(T_A, V_0) = T^r[S_{PA}(T_A, V_0) - S_{R0}] \tag{32}$$

This is a special case of the *principle of the degradation of energy*, as Zemansky's interpretation of Thomson's formulation of the second law, [[18]:199-202, Eq. (8-13)],

$$unavailable\ energy = T^r(S_{final} - S_{initial}) \tag{33}$$

A statement of which, *energy is continuously becoming unavailable for work*, is incorporated in the second version of the second law in Section 3. Eq. (7) assumes the form, applying adiabatic workless combustion heat release involving no change in internal energy,

$$\begin{aligned} W_{useful} = (U_{R0} - U_{P0}) - T^r(S_A - S_{P0}) = [(A_H)_{R0} - (A_H)_{P0}] \\ -T^r(S_A - S_{R0}) \end{aligned} \tag{34}$$

That is,

$$W_{useful} = [(A_H)_{R0} - (A_H)_{P0}] - unavailable\ energy_{R0\to A} \tag{35}$$

Generally, we may write for multiple irreversible processes,

$$W_{useful} = [(A_H)_{R0} - (A_H)_{P0}] - \sum_{j=1}^{m} unavailable\ energy_{(Initial\to final)^j} \tag{36}$$

We now focus on (36), in which the part that is foundational beyond question is the term, $\sum_{j=1}^{m} unavailable\ energy_{(Initial\to final)^j}$, the principle of the degradation of energy. This is referenced in the JTM energy narrative version of the second law above. It is important to note that the principle applies to each irreversible process term as a separate individual term. Significantly, one major inference of thinking in terms of the energy conversion narrative in accordance with the principle is that the energy narrative needs a first step, a different kind of step from “unavailable energy steps,” initiating the narrative. Clearly, logic does not demand that the initiating step must also be an energy conversion step.

Confusion between the expectation of a “different kind of step” and the “habitual thinking that the initiating step is also an energy conversion step” is a stumbling block to understanding thermodynamics.

Planck presciently identified the stumbling block to understanding thermodynamics in the understanding of the second law: “The problem of formulating the second law correctly has occupied physicists for decades. A long time passed before it was recognized that the content of the second law is not *exhausted* if ... every process in nature is resolved into a series of energy transformations and the direction of each individual transformation is enquired into” ([[19]: 51], italics added).

Planck is correct. But the trouble lies also in how we understand the first law. What happened is that the JTM energy narrative version of the first law (above in this section) rears its head: the whole set of processes, including the initiating one, is treated exhaustively as energy transformations, or energy conversions. In the initiating process, the energy in a reactive mixture, or the disorganized energy of any thermal/chemically-reactive body, is treated in terms of the energy’s exergetic content, [[16]:184–186].

Logically, though each irreversible process can be treated as a separate individual item in (36), it does not follow that $U_{R0} - U_{P0}$ can be subdivided into separate items, $(A_H)_{R0\to P0}$ and $-T^r(S_{R0} - S_{P0})$. As it has been presented that

Given

$(A_H)_{R0\to P0} = (U_{R0} - U_{P0}) - T^r(S_{R0} - S_{P0})$,

and let $G \equiv (U_{R0} - U_{P0}) - (A_H)_{R0\to P0} = T^r(S_{R0} - S_{P0})$,

“following Helmholtz, we call $(A_H)_{R0\to P0}$ the ‘free’ energy, G the ‘bound’ energy” [[19]:81].

There is nothing wrong with calling $(A_H)_{R0\to P0}$ the ‘free’ energy, but calling G the ‘bound’ energy implies that U can be subdivided into A_H and G and that A_H is a part of U; therefore, $A_H \leq U$. This interpretation of free energy is the result of applying the JTM narrative treatment, in (36), of unavailable energy to treat bound energy—a misapplication of the principle of the degradation of energy.

Any counterexample can be used to reject such a metaphysical interpretation:

CounExam1. Referring to Fig. 2, the case of $S_{R0} < S_{P0}$ leads to $(A_H)_{R0\to P0} > U_{R0} - U_{P0}$.

CounExam2. Referring to the case of $V^{(1)} + V^{(2)} = V^{(1)+(2)}$, it has been shown in reference [[17]:331] that reversible work

$$W_{rev} = T^r(S_{final} - S_{ini})_{ComSystem}$$

equals $-G$, i.e., the negative of the bound energy. Instead of being one that is to be subtracted from the internal energy as unavailable energy, it itself equals reversible work, whereas the internal energy, of which free energy is associated as a part, experiences no change.

CounExam3. In the theory of exergy, the so-called exergy/anergy doctrine, [[17]: 341], asserts that $energy = exergy + anergy$ with the implication that $energy \geq exergy$. That is, anergy is positive definite. However, it has been known that these conditions are subject to violation.

Planck's observation has proven to be correct.

Maxwell wrote in Matter and Motion, "Energy cannot exist except in connexion with matter. Hence since, in the space between the sun and the earth, the luminous and thermal radiations, which have left the sun and which have not reached the earth, possess energy, the amount of which per cubic mile can be measured, this energy must belong to matter existing in the interplanetary spaces, and since it is only by the light which reaches us that we become aware of the existence of the most remote stars, we conclude that the matter which transmits light is disseminated through the whole of the visible universe [[2]: 89-90]. Photons are not matter, but they certainly cannot experience thermodynamic transformation events without matter.

Emphasizing Maxwell's point, we call "energy phenomena" that are involved as the mutual action between matter facilitating thermodynamic transformations "energeia phenomena." Thermodynamic transformations involve both the energy principle and the entropy principle. Whereas "energy" is identified with the energy principle, the first law of conservation, "energeia" is necessarily identified with the energy principle and the entropy principle, the second law of transformations.

A new theoretical system of energeia physics is in order. Here, we take a first trial step, taking the liberty of summarizing a third version of the two laws:

The first law of thermodynamics (The energeia physics version):

> *Energy is a measure of energeia such that the total energy of the energeias of every event is constant or remains a conserved quantity. Energeia exists in various forms; all forms of energeia are connected, as manifested by the conservation of energy associated with every event/change. The change in a system's internal energy is equal to the difference between heat added to the system from its surroundings and work done by the system on its surroundings.*

The second law of thermodynamics (The energeia physics version):

> *Entropy is a measure of energeia that entropy of energeias of the universe always grows. Consequently, the entropy of an isolated system increases over time toward some maximum value defining its equilibrium state. The total entropy of non-isolated, interactive systems increases because of the empirical fact of the general disequilibrium states of macroscopic interactive systems. These tendencies can be theoretically harnessed into virtual reversible processes producing mechanical energy followed by irreversible processes continuously degrading mechanical energy making it unavailable for work.*

With the third version of the second law, we have a new interpretation of (36) that its first RHS term as "harnessing entropy growth into virtual reversible processes." This last version of the two laws and Eq. (36), now defined in its new interpretation, together with its companion Eq. (37) summarize the main conclusions of the paper,

$$W_{useful} = (G_{R0} - G_{P0}) - \sum_{j=1}^{m} unavailable\ energy_{(Initial \to final)^j} \qquad (37)$$

Maxwell noted, "the doctrine of the dissipation of energy is closely connected with that of the growth of entropy but is by no means identical with it." There has been a tendency to associate entropy growth entirely with the principle of the degradation of energy; thus, entropy growth is synonymous with energy degradation. With the first terms on the RHS of (36) and (37), read in accordance with the above treatment as well as Fig. 3 below on the basis of entropy growth potential, *entropy growth*, in association with entropy growth potential, [16] and [17], is not identical with the *dissipation of energy*. The entropy growth in both first terms plays, in fact, the opposite role: constructive production of useful work.

Helmholtz free energy and Gibbs free enthalpy, the first RHS terms of (36) and (37), are the driving forces for useful work in the Thomson-Clausius-Gibbs entropy narrative, or the *Thomson-Clausius-Gibbs energeia narrative*. The reversible manifestation of entropy growth in association with the Gibbs free enthalpy as a driving force for useful work has been constructed. The details can be found in a 1992 paper [20]. 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 3): an isentropic compression, $RO \rightarrow 1$; an isothermal process at peak temperature,

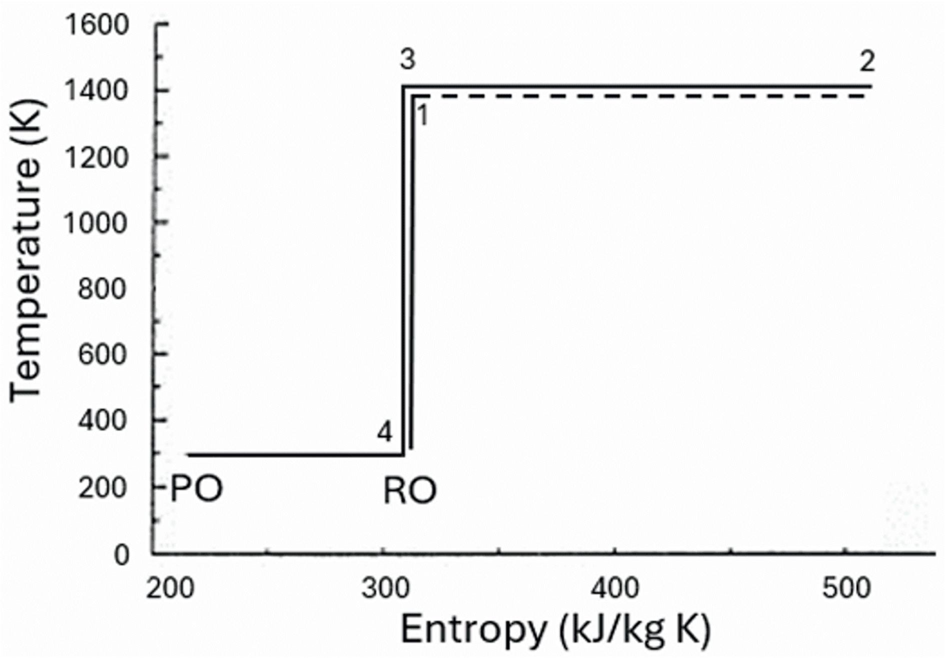

Figure 3. The reversible manifestation of Gibbs free enthalpy

1 → 2 → 3; an isentropic expansion, 3 → 4; and finally, an isothermal heat transfer process at T_0, 4 → $P0$. 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, such as $R0$→A in Fig. 2, the key step of the reversible engine cycle is the isothermal process at peak temperature, 1 → 2 → 3 (see also Figure 10 of [20] for examples of different peak temperatures).

The isothermal process at peak temperature is made up of two phases (see Figure 3 of [20]). 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), referring to Fig. 3 of [20]. 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, the 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. Note that heat rejection, which determines the thermal efficiency of the reversible heat engine, is independent of the peak temperature T_1. It is noted that a reversible combustion heat engine operating with different peak operating temperatures as shown in Figure 10 of [20] produces the same useful work equal to the Gibbs free enthalpy since the heat rejection remains the same. In addition to reference [20], more details can also be found in another easier-to-access reference [21].

5. "Extractable-heat," rather than "available energy," is the real discovery/invention

In our discussion, the following definitions are adopted:

unavailable energy—energy that is made unavailable for useful work by irreversible processes in accordance with the second law

entropy growth potential—the driver of every event in each Poincare range [[16]: 294] of both kinds: isolated systems and interactive systems referenced in the energeia physics version of the second law

reversible extractable-heat—reversible manifestation of harnessing entropy growth potential into mechanical energy of an amount equal to that of extracted heat

available energy—a derived concept defined as reversible extractable-heat subtracted by at least one unavailable energy; it is related to useful work as the upper bound of an inequality

bound energy—a derived concept defined as either internal energy or enthalpy subtracted by Helmholtz free energy or Gibbs free enthalpy, respectively

anergy—a derived concept defined as energy subtracted by exergy.

With entropy growth as the driving force, an inference of the heat-work equivalence theorem is that a reversible transformation requires a heat reservoir—the intrinsic role of such a reservoir is as a heat source for the extraction of heat powered by the management of entropy growth. If so, there will be no "irrevocable accumulations of waste heat." These happen only when phenomena of entropy growth involve chemical-affinity-driven combustion processes releasing heat at high temperatures, as shown in

Fig. 2. In these cases, entropy growth potential requires the heat reservoir to serve doubly as a heat sink for actualizing EGP ([16]; see also [17]: 338-340). The so-called waste heat includes in large part the "reversibly necessary" heat—for the classical Carnot cycle, heat by the amount of $Q_2 = Q_1\left(\frac{T_2}{T_1}\right)$, where T_2 is the temperature of the reservoir—to be disposed of to the heat sink.

As shown in Fig. 3, true reversible processes require no heat sink for actualizing EGP. Renewable energy sources are another example of entropy growth requiring no heat sink for actualizing EGP. Deployments of which do not lead to large waste heat; in fact, the opposite can happen in principle. [[16]: Section 8.7.2]

The role of a heat reservoir/sink can be clarified in reference to whether we are dealing with handling energy or harnessing entropy growth potential. Before EGP is harnessed into mechanical energy, it should not be treated as energy, which can be divided. This is the fundamental mistake of the JTM energy narrative. Consider again,

$$W_{rev} = [(A_H)_{R0} - (A_H)_{P0}]$$

Or

$$W_{rev} = [G_{R0} - G_{P0}]$$

As seen in Fig. 3, the transformation of $[G_{R0} - G_{P0}]$ into mechanical energy is a unitary process. Since the process cannot be subdivided, it should not be referred to as some kind of energy or available energy.

It is preferable to call it *reversible extractable-heat* for precision's sake and to define available energy in terms of this "virtual driving force" subtracted by "unavailable energy." That is,

$$available\ energy = reversible\ extractable \bullet heat - unavailable\ energy \tag{38}$$

That is, Zemansky's interpretation of the principle of the degradation of energy is an excellent take [18] [22]: that unavailable energy is the basic concept as based on the entropy principle. Based on this, available energy is to be defined in accordance with (38) as a derived concept. By this token, unlike unavailable energy, neither bound energy nor anergy are meaningful concepts, being the source of confusion to students of thermodynamics.

Since bound energy and anergy are themselves derived concepts, it makes no logical sense to define Helmholtz free energy and Gibbs free enthalpy on their bases, calling HFE and GFE some kind of energies or available energies, while $(U_A - U_B) - T_0\,(S_A - S_B)$ in Eq. (7) is properly called available energy.

6. Conclusion: available energy vs. extractable-heat

We call “energy phenomena” that are involved as the mutual action between matter facilitating thermodynamic transformations “energeia phenomena.” The word “energy” has been entrenched in the public mind as the capacity for performing work, thus depriving the second law of its full power. By resetting the topic that we study to be “energeia,” undergirded by both the law of conservation and the law of transformations, energeia physics offers a full understanding of thermodynamics that Carnot, Thomson, Clausius, Maxwell, and Gibbs bestowed upon us.

One major finding is the establishment of available energy and extractable-heat to be two distinctive concepts. It has been argued that reversible extractable-heat and unavailable energy are two definable terms, while available energy is related to the two terms by the equation,

$$\begin{aligned} W_{useful} \leq available\ energy \equiv rev.\ extractable \bullet heat \\ - \sum_{j=1}^{m} unavailable\ energy_{(Initial \rightarrow final)^j} \end{aligned} \tag{39}$$

We call (39) the *general expression for maximum useful work derived from energeia.*

What is the significance of making this distinction? Without the concept of extractable-heat, the entropy law is understood in terms of the principle of the degradation of energy, only as an *opposite force* to “energy” that makes the world go round. What is clear is that, in fact, behind the available energies that expediently make the world go round, the real driver powering all those available energies is the entropy growth-enabled “extractable-heat.” With the concept of extractable-heat, the entropy law, as the third version of the second law in the above surmises, exercises its *positive preeminent role*, the role that has been cast aside by the JTM energy narrative.

Machines that mankind has developed are basically fed by available energy involving at least one major irreversible process, that of combustion. This paper makes the case that the environmental impacts of industrialization are fundamentally the consequence of combustion, which is taken for granted as long as we view the issue as a problem of energy or available energy. To address the root causes of the aftermath of industrialization, we need to have a better understanding, instead of energy, of *energeia measured by energy and entropy* and *reversible-like extractable-heat.*

Available-energy-fed machines are like heterotrophs (available-energy-fed machines are “consumers”). Smil, the energy generalist, noted, “With agriculture humans ceased to be simple heterotrophs and became increasingly sophisticated manipulators of solar flows and builders of complex societies” [[23]:

372]. The time is also ripe to ask, “Are there different kinds of machines?” Will civilization be changed by totally different kinds of machines, autotroph-like machines that are connected as plants are? Will reversible-like extractable-heat be the underlying principle for autotroph-like machines, the author muses? Such thinking may be useful for understanding biology too. Not trained as a chemist or biologist, the author cannot answer the last question. Hopefully, other scientists, such as the author of reference [24], may provide an answer.

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