Qeios

Conceptual Differentiation of Heat: The Entropic Promise of a Post-Pyrocene World

Thermodynamics is thought to result from the conceptual differentiation (CD) of heat into energy, entropy, and heat. The form of CD that took place in the 19th century will be referred to as the CD of the "*energy-centric conception of entropy*" project. The conception is otherwise known as the concept of available energy, or free energy, or exergy. The defining goal of the project is the harvesting of free energy for the maintenance of all living organisms and all human institutions. This leads to a fundamental "free energy" conundrum of human existence: to thrive in style, we need abundant free energy; such pursuit of wellness for individuals increases the *speed* of the whole (of which individuals and their environment are parts) falling into the abyss of chaos. We argue that the free energy conundrum results from *imperfection*in the CD of the energy-centric project, imperfection due to the two laws failing to be demarcated as the law of energy and the law of entropy. This paper articulates a new thermodynamics (referred to as Unified Classical Thermodynamics [UCT]) under the masthead of "*entropy-centric conception of entropy*." An argument is put forward that the proposed entropy-centric project offers solutions to the fundamental conundrum of human existence.

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1. Introduction

In an address to the British Association in 1854, William Thomson declared that while physics has been the science of force, Joule's discovery of the conversion of heat into work is leading to "the greatest reform that physical science had experienced since the days of Newton," arguing that energy is becoming the primary concept on which physics is to be based [1: p. 58]. Physics is still the science of force, but Thomson had a point there: as a science of force, physics is not a complete theory of the microscopic and macroscopic worlds, missing a large part of macroscopic phenomena; to become that kind of theory, the primary concepts of physics need to be force *and* "energy as a generalized concept" [2: lines 539-541]. The missing part is the "energy consumption"-driven phenomena, the governing law of which is the first law of thermodynamics, "*energy can be neither created nor destroyed; only the form in which energy exists can be transformed from one form into another*" [3: p.44; 4]. The law statement is a sweepingly powerful statement evidencing that Thomson was correct that there was something new beyond force. But is it energy? More precisely, what does energy consumption mean? Since energy can be neither created nor destroyed, what is consumed is not energy but some form of energy, energy of one form is consumed to become

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energy of another form. So, the operative "part" of the above first law statement is "*the form in which energy exists can be transformed from one form into another.*" Since energy form and the direction of energy transformations are the purview of the second law of thermodynamics, this first law statement is not a statement of the first law per se but a statement of the combined first and second laws, with its essence being in fact the second law.

This paper begins with the assertion that thermodynamics has been led astray with "first law statements" and "statements concerning energy, and/or heat and work" that are really statements with core messages concerning entropy. Our focus on energy has been very much a misdirected project. The new physical idea discovered by Joule and Thomson was not energy, but entropy growth.

This assertion can be introduced from another viewpoint with a related example, a paper by Job and Lankau provocatively entitled "How harmful is the first law?" [[5]]. It turns out that Job/Lankau's critique is not directed at the first law if the law is defined strictly as a law of conservation of energy. Their critique is against the principle of *mechanical equivalent of heat* (MEH): "We are not questioning the principle of the conservation of energy, but its special formulation as part of the First Law of Thermodynamics—with the *equivalence of heat and work* as its central idea since 1850" [[5]: p.171]. That is, the first law is not the source of controversy if the law serves, strictly, as a *closure condition* for all thermodynamic processes or transformations. The title of the paper should have been "How harmful is the principle of the mechanical equivalent of heat?" MEH is the principle that motion and heat are mutually interchangeable and that a certain amount of work can produce the same amount of heat and vice versa. That is, whereas a first law can be defined as a closure condition without involving a causal relation of heat producing work, MEH is the principle claiming by default that a given amount of heat produces the same amount of work, a relation between cause and effect.

Now, it is important to get the timeline of *MEH* and the *first law* right. The corresponding issue is the origin of the concept of MEH: is it a consequence of some general idea (in this case, the principle of energy conservation [PEC]) or does the general idea derive from the establishment of MEH? In an influential 1959 article by Kuhn, "Energy conservation as an example of simultaneous discovery," Kuhn implies, as the title alludes to, that the 'formulation of PEC' conceptually preceded 'applications,' the principal example of which is MEH. Kipnis, in a masterful history of science study [[6]], contended otherwise with the conclusion:

> the development of the PEC process did not start with a formulation of a general principle of energy conservation which stimulated the development of particular concepts, such as the mechanical equivalent of heat. It will be shown that the opposite happened: it was the development of the mechanical equivalent of heat which led to the general principle of energy conservation (GPEC) [[6]: p.2026].

The existence of the Kipnis article itself bears out that the development of MEH was the gripping "confrontation" narrative deserving the detailed and balanced scholarship of Kipnis. Once the development of MEH between 1845 and 1872 (we shall refer to this as the 1845-1872 MEH revolution) was successfully completed, quite a few scientists, as witnesses to the captivating drama, were becoming receptive to the idea of energy conservation, as Kuhn observed, calling it an example of simultaneous discovery.

We may make the following observations at this point in the story. The setting of the MEH story should include Carnot's competing theory of steam engines, which we shall refer to as the *co-existence theorem* or *the second fundamental theorem*, while the MEH in a *refined* form will be referred to as the *equivalence theorem* or *the first fundamental theorem* (the latter names, "the first…" and "the second…," are names used by Clausius [[7]: p.111]). With this background setting, our story is better interpreted, rather than as the evolution of MEH into the first law, as the reconciliation of Carnot's and Joule's competing ideas or their synthesis into TWO laws of thermodynamics, [[8]: Ch. 16], the first law and the second law. One insightful way to describe the synthesis project is to consider the investigative object at the beginning of the project to be *caloric*, the original notion of heat. In terms of heat, the original heat, therefore, the synthesis has been identified by Tisza as a project of *conceptual differentiation* (or bifurcation or splitting) of caloric (the original heat) into energy, entropy, and heat (the modern heat as a disorganized form of energy). [[9]; [10]: p.22, pp.30-36] From the point of view of conceptual differentiation, heat in the MEH certainly in the early stage of the principle was caloric. But by the time of the first law's formulation, what we had referred to as heat or caloric became the modern heat, Q, whereas a part of the original caloric became in the modern first law something represented by the "thermal component of the internal energy U." Both the MEH that Job and Lankau rejected and the first law statement in Paragraph One failed to make the conceptual differentiation: the MEH failed as a reflection of the history of confrontation in real time (see Sect. 2), and the first law fails as a reflection that the conceptual differentiation is not in the DNA of thermodynamics even today.

The main object of the present paper is the assertion that, together with the two fundamental laws resulting from it, ***conceptual differentiation*** in itself is the cornerstone of the edifice of thermodynamics and that, as the two law-statements in orthodox thermodynamics are found not to adhere to the conceptual differentiation requirement, steps for correcting deficiencies in orthodox thermodynamics are given to transform it into a coherent system of Unified Classical Thermodynamics (UCT), with entropy and entropy growth as its centerpiece. With the entropy-centric foundation secured for UCT, the introduction of *entropic indeterminateness* is made in Sect. 3 to be its signature characteristic, differentiating thermodynamics, as the science of "energy consumption"-driven phenomena, from the mechanical sciences. Sect. 4 offers an example of UCT's new application, providing a sustainable path for real "reversible-like" approaches for a post-Pyrocene world.

2. Conceptual differentiation of caloric: energy, entropy, and heat in UCT

The foundation of energy physics was laid by Thomson in 1852 by introducing the concept of available energy, [[11]: pp.511-514], also known as free energy or exergy. It can be said that the centerpiece of orthodox thermodynamics is free energy. (Mechanical energy makes the heavenly bodies go round. But energy, once energy was introduced as a general concept with mechanical energy as one example of it, does not make the bodies on the Earth go round; for example, little of the humungous amount of energy in the oceans can serve for that purpose.) For the discussion of "energy consumption"-driven phenomena, therefore, the common saying of "energy makes the world go round," which is nonsensical, should be replaced with an improved version, "free energy makes the world go round."

Though the improved version is still problematic, free energy is based on the premise that only a part of energy is theoretically available for producing mechanical work; therefore, free energy should be by definition smaller than energy. The awkward fact is that this is not always true. [[2]: lines724-731]. We may refer to the free-energy-as-the-centerpiece thermodynamics as the thermodynamics based on an "energy-centric conception of entropy":

> 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, the energy-centric based entropy understanding: the idea that although the energy of a system (and all other parts that it interacts with) can never be destroyed, the free energy of the system (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 the dissymmetry and 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. [[2]: lines 1150-1159]

We now dive into the claim of the "centerpiece of orthodox thermodynamics being free energy" by first explaining what we mean by an "energy-centric" conception of entropy.

By "energy-centric," we mean that the premise of orthodox thermodynamics as a theoretical system, in accordance with the first law statement in Paragraph One, is that energy, or more precisely, free energy, is the driver for all "energy consumption"-driven phenomena or processes. By referring to free energy, it brings into focus the importance of entropy and the second law. This focus, however, highlights entropic processes only in terms of their impediments or hinderances to mechanical processes and other free-energy-driven processes. Free energy is the central quantity of thermodynamics, whereas entropy plays an important but secondary role in thermodynamics.

We now refer to Job and Lankan, together with the group of scientists with a similar position on this issue, as the Heat As Entropy school (HAEnt school) [[12]]. The HAEnt school has a very different take on the free-energy vs. entropy issue. Two recent papers, "Which Physical Quantity Deserves the Name 'Quantity of Heat'?" by Herrrmann and Pohlig [[13]], and "Entropy and the Experience of Heat" by Fuchs, D'Anna, and Corni [[14]], clarify the position of the HAEnt-school scientists. Foremost in their minds, they view the advent of MEH with regret; heat became heat energy, a disordered energy. With that, "the name of an existing quantity [heat] was taken away from this quantity and given to another one [Q]. However, the old quantity was not given a new name, resulting in its disappearance from the scene" [[13]: p.9]—the regret of the loss of the experience of the old quantity heat. The second important point made by the HAEnt school is the identification of entropy, rather than energy, for encapsulating the experience of heat (caloric). The second point is important because if the energy-centric approach of the MEH-based orthodox thermodynamics could encapsulate the experience of heat with the concepts of energy and free energy, the dissatisfaction of the HAEnt school would have dissipated. But the HAEnt school finds the energy-centric approach wanting.

The HAEnt school is right on both points, especially on the second point. But their solution to the first point by restoring the concept of caloric amounts to a counterrevolution of the 1845-1872 MEH revolution. The HAEnt solution by restoring the concept of caloric denies the merit of conceptual differentiation in the formulation(s) of the two laws of thermodynamics by Clausius and Thomson (though their treatments bear common features, they are by no means identical, as we see in the following). The denial does not prove that orthodox thermodynamics' conceptual differentiation is wrong but instead manifests that the orthodox thermodynamics developed by Thomson and his fellow North British physicists/engineers fails to carry out differentiation satisfactorily. While the development from Clausius' treatment became Gibbsian thermodynamics and the Berlin/Vienna/New-Haven microscopic molecular science with a defining problem different from that of energy physics, the latter development stops short of correcting deficiencies in energy physics.

We can correct this by taking the following steps.

The first step is the trimming down of the **first law statement** to become, "*Energy can be neither created nor destroyed; total energy stays the same in every transformation even though the energy of a system or subsystems may change."* Other than energy conservation and the fact that constant total energy is the closure condition for every transformation, the statement makes no mention of the nature of transformations.

The second step deals with the nature of transformations in accordance with Clausius' *Fourth Memoir* [[7]: pp.111-135]. That is, Clausius recognized that Joule's contribution and Carnot's contribution deal with two distinctive issues of transformations respectively: Joule's dealt with the equivalence of heat and work that became the closure condition of constant total energy for all transformations, whereas Carnot's contribution was that of dealing with the nature of transformations, what brought about the transformations. The "two distinctive issues" also were referred to as two (DisOrganized Energy) (DOE) questions [[2]: lines131-135].

There are two phases of the second step. The first phase is the refinement of *MEH*. We shall adopt the name *equivalence theorem* for the version of *equivalence of heat and work* without a commitment to how heat and work are interconverted into each other -- only the assertion that the appearance of heat is accompanied by the disappearance of work of equal amount and vice versa. The first phase of the step is the precondition for the second phase: preparing *equivalence theorem*and updating Carnot's idea of coexistence of heat transmission and the production of work into the *Second Fundamental Theorem* as the dual foundations of the *mechanical theory of heat* [[7]]. Carnot's idea on heat and work is described by Kipnis, "…neither Carnot and Clapeyron nor Holtzmann and Thomson thought before 1850 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" [[6]: p.2032, Sect. 9].

With the refinement of MEH into "equivalence theorem," it was possible for Clausius to formulate Carnot's idea of the coexistence of heat transmission and work production into his Second Fundamental Theorem, which we shall refer to as the *coexistence theorem*. The preamble of which is the assumption that there exist two kinds of dissymmetric or irreversible transformations in nature, transformations of natural direction or what Clausius referred to as positive direction, and those of unnatural direction or negative direction. The Second Fundamental Theorem, as stated by Clausius, is the assertion,

> *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* [[7]: p.364].

Clausius was clear that for every kind of dissymmetric transformation, a subdivision of each kind into two can be made in accordance with the directions of individual transformations. Those of positive direction can exist by themselves. But in the opposite (negative) direction, the transformation can take place only in coexistence with another transformation of positive direction, "they can only take place in such manner as to be compensated by simultaneously occurring positive transformations."

Clausius then considered the limiting case to investigate quantitatively the details of cyclic processes involving transformations in *reversible coexistence* in a six-step cycle (his invention of a modified Carnot cycle). [[7]:p.119] He was able to devise a system of assigning for each transformation its *equivalence-value* and referred to the condition of their coexistence as the condition of *equivalence*, the condition that "algebraical sum [of equivalence-values of the transformations of a reversible cyclical process] is zero" [[7]: pp.127-129]. This case of reversible cyclical process was appropriately referred to as the *theorem of the equivalence of transformations* [TET].

The second fundamental theorem and TET are two different theorems, the former asserts the idea of coexistence, first introduced by Carnot, and the latter the idea of equivalence, the quantitative expression of Carnot's idea that has been made to be consistent with the equivalence theorem.

Clausius' extraordinary insight was marred with one problem, he never used the terms, *coexistence*. This is reflected in the fact that he has not consistently been making clear the distinction between the second fundamental theorem and TET. In fact, while he introduced both terms in Fourth Memoir, the Memoir treated both theorems with the same theorem-statement, [[7]: p.125] the TET statement as a replacement statement as given in [[7]: pp.125-126]. Fourth Memoir is all about TET.

Only by Sixth Memoir, Clausius—there as he noted, "In a memoir published in the year 1854…I deduced a theorem which is closely allied to, but does not entirely coincide with, the one first deduced by S. Carnot… I have called it the Theorem of the Equivalence of Transformations. I did not, however, there communicate the entire theorem in the general form—began writing about the statement of the theorem in the general form [[7]: p.218] as a distinctive statement from the TET statement. Clausius then followed with the treatment of the second fundamental theorem in Seventh Memoir and Ninth Memoir, the last statement is one that is cited in the above.

In a nutshell, while TET is deservedly famous, it is the coexistence theorem that gives rise to the second law for engineering thermodynamics. Whereas TET, serving beautifully as the foundation for equilibrium thermodynamics, is not sufficient by itself to be the foundation for engineering thermodynamics. Because they highlighted TET over the role of coexistence theorem, Clausius himself and Gibbs who followed him did not carry out the obvious extension of their approach to make their theories applicable to energy physics and engineering thermodynamics. Nor did they attempt to unify the two separate sciences, engineering thermodynamics and Gibbsian equilibrium thermodynamics. The extension and unification have been attempted by stressing the role of coexistence theorem in a recent paper on UCT [[2]].

As reported, the centerpiece of UCT is entropy and entropy growth. The theory also introduced *entropy growth potential* [3]. A comparative summary of the three theoretical systems of thermodynamics is given in Table 1. In orthodox thermodynamics, free energy is the driver for all macroscopic processes, while entropy growth, in association with free energy, manifests the dissipation of entropy growth potentials and impediment of mechanical processes. In UCT, the driver and the dissipation agent are unified into a single agent, entropy growth. The **second law statement** is, "*Entropy always grows; 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*." The identification of entropy growth as the sole agent makes it possible to unify two branches of thermodynamics with their different defining problems, the "determination of the equilibrium states" and the "motive power of heat," by bringing engineering thermodynamics under the framework of equilibrium thermodynamics, see paper [2: Sects.6-7].

Details of the treatment of **heat** will be given elsewhere, except to say that any use of the term "heat" necessitates the concept of a heat reservoir and that the importance of heat reservoirs will also be touched upon in Sect. 4.

	Energy physics	**Experientially natural form of thermodynamics**	**Unified Classical Thermodynamics (UCT)**
Centerpiece	Free energy	Old heat (caloric)	Entropy & entropy growth
De facto centerpiece	Entropy	Entropy	Entropy
Background setting to 1845	Equivalence of heat and work	"Caloric fall-ing through a temperature difference"	Carnot: *coexistence* of heat transmission and work production Joule: *equivalence* of heat and work
The 1845-1872 MEH Revolution	Energy physics is the product of the Revolution	View the Revolution with regret	Confirm the Revolution for its cause but view its aftermath resulted from getting its true cause wrong
Conceptual differentiation (CD)	Yes: conceptual differentiation is the answer to the resolution of the Revolution; but Thomson's energy physics did not achieve *complete* CD (see reference to "free energy falling)	Scientists of the School view "caloric falling" as its central metaphor, which is not unlike energy physics' "free energy falling"	The good news is that Clausius/Gibbs have laid the foundational approach, which can be carried out to its logical completion to achieve the goal of *complete* CD

	Energy physics	Experientially natural form of thermodynamics	Unified Classical Thermodynamics (UCT)
Best way to characterize the center-pieces of the three systems	Energy-centric conception of entropy	Heat is a Force of Nature	Entropy-centric conception of entropy
What makes the world go round?	Free energy makes the world go round with entropy growth serving to be the hinderance to the going	Caloric makes the world go round	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

Table 1. Three theoretical systems of thermodynamics

An interim summary: It has been argued that in energy physics, UCT [2], and the experientially natural form of thermodynamics [14], the centerpieces of all three theoretical systems are de facto *entropy* (see Table 1). For energy physics, the situation is best described as, as a result of imperfection in achieving conceptual differentiation, its entropy conception is an energy-centric conception of entropy in the form of free energy. For the experientially natural form of thermodynamics, its attempt to deny the necessity of conceptual differentiation is mis-guarded, but its emphasis on entropy, or on heat as entropy (heat as a Force of Nature), serves a useful purpose for making thermodynamics a subject of greater attraction. We argue that by carrying out the logical completion of Carnot/Clausius' coexistence theorem and Gibbsian thermodynamics, we transform energy physics' centerpiece into an entropy-centric conception of entropy in UCT.

For problems to which energy physics is applicable, the shortcoming of energy physics is not that calculations based on free energy give the wrong answers, but that the energy-centric conception of entropy leads to the inference that "there is a *continuous* and *irrevocable* qualitative degradation of free energy into bound energy [underline added; bound energy is energy which is no longer available for the purpose of producing mechanical work]" ([15]: p.6). The entropy-centric conception of entropy, though it allows continuous degradation, does not infer an *irrevocable* degradation of free energy [2: lines502-506]. The concept that highlights this fundamental difference of UCT from energy physics, which still carries the *efficient-causation* (or *physical necessity*) tradition of Newtonianism, is introduced below as an integral part of UCT.

3. Entropic indeterminateness and innovation in reversible-like processes

Nicholas Georgescu-Roegen's, *The Entropy Law and the Economic Process* (TEL/TEP), [15], published in 1971, is a seminal work in the field of *ecological economics*, in which he offers a pessimistic analysis of the sustainability of human economic activities resulting in material and free-energy degradation as governed by the entropy law. We need to appreciate G-R's thinking with discretion: exercising critical evaluation of the "*irrevocable* degradation of free energy," which is squarely based on energy physics and is defective, while at the same time appreciating and embracing his inventiveness of thinking outside the (Newtonian) box.

His acceptance of "irrevocable degradation of free energy" is a mistake. But his thinking outside the box against Newtonianism can be invaluable for navigating a path away from the aftermath of the 1712 Newcomen's invention of steam engines, leading to the three-century practice of *third-fire* (see Sect. 4). What follows is a very brief discussion in this section and Sect. 4 on the aftermath and the entropic solution to which.

In a new review of the 1971 TEL/TEP by Greene [16], Greene summarizes G-R's contrasting entropic thinking from the mechanistic (Newtonian) thinking in four points [16: 376]. In the following, these four are grouped into three highlights (the second and third points are herewith combined into Highlight-2):

1. Two worlds: The mechanistic world is reversible, whereas the entropic world is directional or dissymmetric (though it has been emphasized in [2: lins1136-1140] that dissymmetric is not unidirectional).
2. "Locomotion" vs. "true happening": In the reversible world, mechanics knows only locomotion, whereas entropic changes in the dissymmetric world are true qualitative changes not reducible to locomotion.
3. Entropic indeterminateness: Mechanics describes locomotion as a physical necessity, i.e., deterministically, whereas the Entropy Law

   "determines neither *when* (by clock-time) the entropy of a closed system will reach a certain level nor exactly *what* will happen … All we can say about the process as time goes by [is that] its total energy remains constant while the distribution of this energy becomes more even … This leaves some substantial freedom to the actual path and time schedule of an entropic process … We may refer to it as entropic indeterminateness" [15: p.12].

   We may, therefore, refer to Highlight-3 as a contrast of physical necessity in mechanics vs. both physical necessity and causal necessity [3: Sects. 10.4 and 10.5] in thermodynamics because of entropic indeterminateness. In the UCT second law statement, the part "*the dissipation of entropy growth potentials and impediment of mechanical processes spontaneously*" is an example of physical necessity, while "*the production of reversible-like transformations interventionistically*" is an example of causal necessity. Note that for processes of physical necessity, we may refer to them as processes governed by laws, but for processes of causal necessity, they cannot be said to be governed by laws since laws in these latter cases do not determine, strictly speaking, these processes.

All three highlights are manifestations of how our entropic world differs, characteristically, from the mechanistic world, but only Highlight-3, entropic indeterminateness, represents the bringing-about of these characteristic differences into actionable possibilities rather than merely observational remarks. In the following, we consider the example of how mechanical engineers deal with these issues in their application of the second law.

In A Treatise [3: Chapter 10], a curious situation was noted: of the two general laws of thermodynamics, only the differential equation of the first law of thermodynamics is used as a *governing* differential equation. “The customary inclusion of the *second laws of thermodynamics* serves no concrete purpose” [3: p.277]. This is because when the first law serves as a governing differential equation, for example, for heat transfer problems, [3: Eq. (196); herewith labeled as Eq. (1)],

$$\rho c_p \left(\frac{\partial T}{\partial t} + \vec{V} \cdot \nabla T\right) = -\nabla \cdot \vec{q}'' + T\beta \frac{Dp}{Dt} + \left(\bar{\bar{\boldsymbol{\tau}}} : \vec{V}\right) + \dot{q}_{ext-heating} \tag{1}$$

the constitutive laws in the equation, Eq. (1), *ensure* that the processes described by the equation satisfy the second law. Here the constitutive laws are Fourier’s law of heat conduction, $\vec{q}'' = -k\nabla T$ and Stokes’ law of viscosity for $\bar{\bar{\boldsymbol{\tau}}}$. With these constitutive laws, Eq. (1), though customarily referred to as the energy equation, is in fact a governing differential equation – similar to the first law statement in Paragraph One – representing both the first law and the second law: the constitutive laws in (1) *are* the second law, which does not need to be included with a separate statement.

Correspondingly, starting with the first law in application to a control volume, mechanical engineers have been using, for <u>problems of reversible-like processes</u>, the following equation, [3: Eqn. (199/111); herewith labeled as Eq. (2)],

$$\dot{Q}_{cv} - \dot{W}_{shaft} - \dot{W}_{resistive} = \frac{\partial}{\partial t}\int_{cv} e\rho d\mathcal{V} + \int_{cs} \rho \left(h + \frac{V^2}{2} + gz\right)\vec{V} \cdot d\vec{A} \tag{2}$$

Note the work term, $\dot{W}_{resistive}$, is an example of a constitutive term in accordance with Joule resistive heating; however, the <u>shaft work</u>, $\dot{W}_{shaft}$, of a reversible-like process is not represented by any constitutive law. The theoretical foundations for problems of reversible-like processes include *both* general laws of thermodynamics, the first law and the second law (in a separate statement).

The second law in a separate statement is required for setting the maximum value for $\dot{W}_{shaft}$. However, **no law of nature, including the second law, can determine the *actual* value of the shaft work**; Eq. (2) is not a governing equation. In the case of mechanical engineering, human designers, generated the design of the real machine; not laws of nature, determines the shaft-work output.

Human design, in the context of the second law in accordance with the above considerations, is an example of a “higher principle” in the scheme of Polanyi’s dual control. [17] Poincaré made a similar observation,

> [These thermodynamic laws] can have only one significance, which is that there is a property common to all possibilities; but in the deterministic hypothesis, there is only a single possibility, and the laws no longer have any meaning. In the indeterministic hypothesis, on the other hand, they would have meaning, even if they were taken in an absolute sense; they would appear as a limitation imposed upon freedom [18: pp.122-123].

In which, Poincaré articulated his reading of the meaning of the second law to be human freedom exercised via entropic indeterminateness. Both Poincaré and Polanyi made a similar argument as G-R did, i.e., entropic thinking points to, in addition to spontaneous processes in the preferred positive direction, which are deterministic, the existence of indeterministic (indeterminate), reversible-like processes. The latter —which are novel or "true happenings" beyond the prediction or control of—though always compatible with—all constitutive laws.

4. The entropic promise of a post-Pyrocene world

The property that enables "energy consumption"-driven phenomena to transcend the second law while in fact obeying it, [[19]: xiv; Ch. 4], as Monod called the property of gratuity for living organisms to transcend the laws of chemistry, will be referred to as the entropic promise. Here, we offer an example of the entropic promise via UCT's application.

The story of fire and the myth of Prometheus are integral to the story of *Homo sapiens*. The fire historian Stephen Pyne structures his history of fire in three phases [[20]]: "first-fire" is the natural fire, a natural phenomenon that existed before the appearance of humans; "second-fire" is the anthropogenic fire; "third-fire" is the industrial fire. Pyne makes a compelling case that Earth is a fire planet, telling an epic history of the evolutionary and ecological roles of the first-fire. The term "Pyrocene" is proposed to provide a narrative of how humans, with the development of the anthropogenic second-fire, have been continuing in the second stage of this history, interacting with fire. At the very end of the second stage, a transition from the anthropogenic second-fire into the industrial third-fire phase emerges with the practice of burning fossil (lithic) biomass. Pyne prefers to use the term "industrial combustion" to describe the third-fire, to emphasize that the Enlightenment scientific approach to fire phenomena led to the disappearance of the phenomena with all their complexity into the neatly categorized processes (mixing, ignition, combustion) and components (fuel reactants, oxidizer, input chamber, furnace). The scientific approach to fire phenomena, turning it into combustion processes, made it possible to scale up third-fire into unsustainable industrial combustion.

We have suggested that the entropy law per se does not *determine* the impossibility of sustainable human economic activities. As a fire planet, Earth will continue to exist with the first-fire and the second-fire as necessary events for their evolutionary and ecological roles. What cannot continue is the continuation of human economic development based on industrial combustion.

There is indeed a broad consensus of necessity for energy transition, a reason for which is commonly given as that the resources for third-fire, fossil (lithic) biomass, are finite. We articulate here the same necessity for a different reason: instead of the unsustainability of the resources for third-fire, we argue that the phenomena themselves, the third-fire, are not sustainable. The continuation of third-fire will ultimately lead to the collapse of the fire planet, a failure to keep the planet *far from equilibrium*.

Following from the writings of Schrödinger (*What is Life*, 1944) and Prigogine (1977 Nobel Prize), there has been a vast literature on the necessity of keeping living organisms away from thermodynamic equilibrium by keeping their entropy low. Despite the second law, which asserts the inevitable growth of entropy for isolated systems, it is possible for individual living organisms to do so, because they are open systems, by exporting entropy that is produced in the interior of organisms to be disposed of in the environment.

Space considerations limit us from a satisfactory treatment of the topic in its full context, except to state that the main point of this section is to ask the question: What is the consequences of exported entropy by individual organisms? —by extension, the consequences of exported entropy by individual economic units. That is, not only do individual organisms need to be kept *far from equilibrium,* but also the whole ecosystem, to which the individual organisms belong, must be kept *far from equilibrium.*

Surprisingly, this question has never been addressed. We surmise that this is due to a lack of a true understanding of reversible processes. It is noted in paper [[2]: lines1030-1037],

> 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. Analysis in this paper, and particularly in this subsection, suggests, however, that the 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 involvement of heat release that is intrinsically irreversible. "Reversible" use of heat, such as the Carnot cycle or the Carnot-Clausius cycle, only idealizes the part involving heat transmission, leaving the irreversible heat release hidden from consideration.

Fire, both first-fire and second-fire, is a spontaneous, irreversible process. The invention of the third-fire was thought to be the invention of reversible processes. For the first time in human history, humans discovered a new way of using fire, a reversible way of using third-fire in addition to second-fire for heat, light and cooking. It turns out it was an imperfect new way. Thinking in terms of energy, there remains at its core a big part of the third-fire that is intrinsically irreversible.

The good news is: The theoretical understanding made by Carnot/Clausius/Gibbs, updated into UCT [[2]], shows that the essence of the 1712 invention was not the discovery of a new form of energy, heat as disorganized energy, but the discovery of dissymmetry, i.e., entropy growth potential (EGP), in heat and other transformations of positive direction. We find EGP in fossil fuels in the form of *stock* EGP, as well as in renewable phenomena in the form of *natural* or *ongoing* EGP. [[3]: Sect.8.7.2]

In the UCT theoretical system, a reversible event requires a heat reservoir. [[2]] Such an event necessitates coexistence between a transformation of positive direction and a "work production" transformation of negative direction (the two transformations are in equivalence, i.e., reversible coexistence, with each other). The event yields a reversible work,

$$W_{rev-event} = T_{res} \cdot EGP \tag{3}$$

where $W_{rev-event}$ is the work output of the reversible event, T_{res} is the temperature of the heat reservoir. For the case of the Carnot-Clausius cycle $T_{res} = T_0$, indicating that the heat reservoir is here used as both a reservoir for heat and a heat sink), Eq. (3) takes the form,

$$W_{rev-event} = T_0 \cdot EGP(T_0) \tag{4}$$

Note that in this case $EGP(T_0)$ is a function of $T_0(= T_2)$, and equals (see [[2]: line989]).

$$EGP(T_0) = \frac{-Q_1}{T_1} + \frac{Q_1}{T_2} = \frac{-Q_1}{T_1} + \frac{Q_1}{T_0} \tag{5}$$

It follows that $W_{rev-event}$ is,

$$W_{rev-event} = T_0 \cdot \frac{-Q_1}{T_1} + \frac{Q_1}{T_0}\left[= Q_1\left(1 - \frac{T_0}{T_1}\right)\right] \tag{6}$$

Instead of looking at $Q_1\left(1 - \frac{T_0}{T_1}\right)$, the demarcation of the two DOE questions—"*what*drives the reversible event?" in (5) and "what *closure condition* the transformations of the reversible event are subject to?" in $T_0\left(\frac{-Q_1}{T_1} + \frac{Q_1}{T_0}\right)$ — identifies the **dual roles** that the heat reservoir plays: as a heat sink for the EGP driving force, as shown by (5), and as a heat source-reservoir for the heat extract mechanism made possible by the driving force, as shown by (6). Note that EGP, due to the role of the reservoir as a heat sink, is a strongly increasing function of decreasing T_0; reversible work in this case has a complicated relationship with the temperature of the heat reservoir, T_0.

It should be emphasized that a large part of the low-temperature heat in association with this case is heat disposed to the reservoir serving as a heat sink—necessitated in this case as a result of the burning of fossil fuels, rather than an intrinsic role of the heat reservoir.

For other kinds of EGPs, as shown in examples in [2], and in renewable phenomena in the form of *natural* or *ongoing* EGP, however, the driving force EGPs do not need a heat sink, and the temperature of the reservoir can be any arbitrarily one, T_X (because *EGP* is not dependent on T_X: indicating that the heat reservoir is used as a reservoir for heat extraction only),

$$W_{rev-event} = T_X \cdot EGP \tag{7}$$

Unlike the above "reservoir as a heat sink" case, reversible work in (7) is simply proportional to the temperature of the heat reservoir.

In paper [2], we find many examples of heat reservoirs serving as sources for heat extraction only:

> "The reversible realization of all these cases represents 'transformations of heat into work' in which heat is extracted from the surroundings, rather than heat being discharged into them, is the dominant mechanism … Demand for a sizable heat sink is an option, resulted from the technological choice [of third-fire], rather than a necessity, in accordance with physics.
>
> "Calling heat discharged to heat sink *waste heat* may be misleading. [21] In the Carnot/Clausius account, the discharged heat is 'reversibly' necessary. That the equivalence theorem demands, cumulatively, 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 irreversibility of combustion heat release. Prodigious production of heat to be disposed, requiring **sizable heat sink**, is not demanded by the equivalence theorem but is the consequence of failing to achieve reversibility in the Carnot/Clausius account, as the philosophical accord of the Industrial Revolution" [2: lines1051-1066].

The philosophical accord of the 21st century is the Carnot/Clausius/Gibbs account [2] for achieving true reversible-like transformations driven by *natural* or *ongoing* EGP—progressing from the era of the third fire since Newcomen's steam engine of 1712 towards, in the 21st century, a post-Pyrocene world at far from equilibrium.

5. Conclusion

This year, 2024, is the bicentennial anniversary of the 1824 publication of Carnot's magnum opus, *Reflections on the Motive Power of Fire*, which eventually led to the introduction of entropy by Clausius in 1865. In the interim years, the introduction of energy was made by quite a few scientists and engineers. The standard account of these developments takes the shape of orthodox thermodynamics in terms of the conceptual centerpiece of "*energy-centric conception of entropy*," otherwise known as available energy, free energy, or exergy. We refer to this formulation also as energy physics, a theoretical system the defining goal of which is the harvesting of free energy for the maintenance of all living organisms and all human institutions. The pursuit of this goal leads to "a *continuous* and *irrevocable* qualitative degradation of free into bound energy" [15: p.6]. The entropic degradation, however, goes on by itself regardless of the presence of living activities or human/social activities. More precisely, therefore, the pursuit of this goal leads to *faster* degradation of free energy.

This is the fundamental conundrum of human existence. To exist, we need free energy, and to thrive in style, we need abundant free energy. Such pursuit of wellness for individuals increases the speed of the whole (of which individuals and their environment are parts) falling into the abyss of chaos.

This paper articulates a new thermodynamics in terms of the conceptual centerpiece of "*entropy-centric conception of entropy*." We refer to this formulation as Unified Classical Thermodynamics (UCT), the unification of engineering thermodynamics into a framework generalized from the basic equilibrium thermodynamics framework [2: Sects.6-7]. The signature characteristic of UCT is entropic indeterminateness, which differentiates UCT from the determinist mechanical science offering beauty and grandeur in the thermodynamic view of our world, instead of entropic pessimism, of entropic possibilism. This entropy-centric conception offers better understanding of the true nature of reversibility (Sect. 4): free from the conversion of heat into work, reversibility is instead achieved through the extraction of heat from a heat reservoir. The heat reservoir is no longer used, by intrinsic necessity, as a heat sink as its dominant purpose. These innovations and conceptual tools free us from irrevocable degradation of free energy. We can have free energy derived from natural or ongoing EGP: the use of free energy does not lead to faster degradation of total planetary-wide free energy but instead may, in fact, slow down entropy growth from their natural, i.e., ongoing, growth rate. The Earth will be reset to the path of a Gaian Earth—under human stewardship.

References and Notes

[1] Harman, P M (1982). Energy, Force, and Matter: The Conceptual Development of Nineteenth-Century Physics (Cambridge Univ. Press)

[2] Wang L-S (2024). "Unified Classical Thermodynamics," Qeios. doi:10.32388/9RYDVV.2 [Please be sure that you are accessing **Version 2** of the paper, which is substantially revised from the original.]

[3] Wang L-S (2020). A Treatise of Heat and Energy

[4] Moskowitz C (Aug 5, 2014). "Fact or Fiction?: Energy Can Neither Be Created Nor Destroyed," *Scientific American* The exact excerpt from the piece is:

> The law of conservation of energy, also known as the first law of thermodynamics, states that the energy of a closed system must remain constant—it can neither increase nor decrease without interference from outside. The universe itself is a closed system, so the total amount of energy in existence has always been the same. The forms that energy takes, however, are constantly changing. Potential and kinetic energy are two of the most basic forms, familiar from high school physics class: Gravitational potential is the stored energy of a boulder pushed up a hill, poised to roll down. Kinetic energy is the energy of its motion when it starts rolling. The sum of these is called mechanical energy. The heat in a hot object is the mechanical energy of its atoms and molecules in motion. In the 19th century, physicists realized that the heat produced by a moving machine was the machine's gross mechanical energy converted into the microscopic mechanical energy of atoms. Chemical energy is another form of potential energy stored in molecular chemical bonds. It is this energy, stockpiled in your bodily cells, that allows you to run and jump. Other forms of energy include electromagnetic energy, or light, and nuclear energy—the potential energy of the nuclear forces in atoms. There are many more. Even mass is a form of energy, as Albert Einstein's famous $E = mc^2$ showed. Fire is a conversion of chemical energy into thermal and electromagnetic energy via a chemical reaction that combines the molecules in fuel (wood, say) with oxygen from the air to create water and carbon dioxide. It releases energy in the form of heat and light. A battery converts chemical energy into electrical energy. A nuclear bomb converts nuclear energy into thermal, electromagnetic, and kinetic energy. As scientists have better understood the forms of energy, they have revealed new ways for energy to convert from one form to another.

[5] Job G and Lankau T (2003). "How harmful is the First Law?" *Annals of the New York Academy of Sciences*, ***988***:171-181

[6] Kipnis N (2014). "Thermodynamics and Mechanical Equivalent of Heat," *Sci & Educ* ***23***:2007–2044

[7] Clausius, R. *The Mechanical Theory of Heat, with Its Applications to the Steam-Engine and to the Physical Properties of Bodies*. (John van Voorst: London, UK, 1867): pp. 1-374: (Fourth Memoir, 111–135; Sixth Memoir, 215–256; Ninth Memoir, 327–374).

[8] Coppersmith J (2015). *Energy, the Subtle Concept* (Oxford Univ. Press)

[9] Tisza L. "The logical structure of physics," *Synthese* ***14*** (1962): 110-131

[10] Tisza L (1966; 1977 paperback edition) *Generalized Thermodynamics* (The MIT Press)

[11] Thomson W (Lord Kelvin) (1911) *Mathematical and Physical Papers of William Thomson* ***1***:1–571. Cambridge Univ Press

[12] Wang L-S (2022). "Triadic relations in thermodynamics," *Energy Conversion and Management: X* ***15*** (2022) 100233

[13] Herrmann F and Pohlig M (2021). "Which Physical Quantity Deserves the Name 'Quantity of Heat'?" *Entropy* (Basel. 2021 Aug 19) ***23***(8):1078.

[14] Fuchs H U, D'Anna M, and Corni F (2022). "Entropy and the Experience of Heat," *Entropy* 2022, ***24***, 646.

[15] Georgescu-Roegen N (1971) The Entropy Law and the Economic Process

[16] Greene H (2018). "Nicholas Georgescu-Roegen, The Entropy Law and the Economic Process," *The Ecozoic Journal* (No. 5, 2018): The Ecozoic Way

[17] Polanyi M (1968) "Life's irreducible structure," *Science*

[18] Poincaré H (1913) Science and Hypothesis. The Science Press, Lancaster, PA (pp. 122–123)

[19] Monod J (1971). *Chance and Necessity* (Penguin Books)

[20] Pyne S J (2021) The Pyrocene: How We Created an Age of Fire, and What Happens Next (Univ. of Calif. Press)

[21] Kostic M (2024) "2024 Key Reflections on the 1824 Sadi Carnot's "Réflexions," preprints202402.0605.v1.pdf