An Unusually Efficient Coupling of Carnot Engines

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The heat engine, or related mechanisms, appears as an essential component in most models for self-organizing phenomena. Following the autopoietic-allopoietic classification used in Prigogine's dissipative structures paradigm to discriminate heat engines in terms of the final use of the work by they produced, we introduce here an autopoietic coupling of heat engines as a possible model for the energy inter-conversions sustaining the dissipative structure known as Bénard convection. A thermodynamic analysis shows that it can access efficiencies larger than those allowed by the second law.

Keywords: Thermodynamics, coupled Carnot engines, ultra-reversible efficiencies, self-organizing phenomena, Bénard convection, negentropy.

Introduction

An important role is played by heat engines in some of the paradigms for self-organization. In Smith's paradigm for life and evolution, directed to "…understand at an aggregate level what the biosphere is doing as it constructs and maintains itself, and what limits may exist to how well and how far it can do this…" [1], the chemical Carnot cycle – the chemical counterpart to the thermal Carnot cycle [2] – becomes a key element in the description of metabolic processes that transfer energy and entropy [3]. The construction of Muller and Schulze-Makuch uses, on its part, sorption heat engines – simple negative entropy generators driven by thermal cycling and working on alternating adsorption and desorption – to model, among other systems, "the self organization of matter that resulted in the origin of life" [4]. For Chaisson, on the other hand, "the origin of Nature's many varied structures is closely synonymous with the origin of free energy" [5]. In Chaisson's construction the universe is modeled not as a "mechanical device running with Newtonian precision, but as a global engine capable of potentially doing work as local emergent systems interact with their environments – especially those systems able to take advantage of increasing flows of free energy resulting from cosmic expansion and its naturally growing gradients" [6]. In his quest for the law governing the biosphere's unfolding, Kauffman introduces, on his part, the notion of autonomous agent as "a self-reproducing system able to perform at least one thermodynamic work cycle" [7].

The Dissipative Structures paradigm pioneered by Prigogine and collaborators [8] can also be understood from the heat engine perspective. A dissipative structure has been defined as a far from equilibrium system that "efficiently dissipates the heat generated to sustain it, and has the capacity of changing to higher levels of orderliness" [9]. Efficient heat transfer, as well as the ability to perform the work required to bring about and sustain a new and higher level of order appear as the essential characteristics of these far from equilibrium systems. This perspective has led some author's to establish a parallel between the mechanism sustaining dissipative structures and that of energy-transforming engines "the dissipative structure is a kind of energy-transforming engine which uses part of the energy inflow to produce a new form of energy which is of higher thermodynamic value (what means lower entropy): examples…the mechanical energy in Bénard cells, the electrical energy in nerve membranes and the concentration gradients (activity gradients) in chemical dissipative structures" [10]. Still another perspective to dissipative structures is offered by Jantsch through the contrast of the notions autopoiesis and allopoiesis. Autopoiesis (self-reproduction, self-renewal) refers to systems "not concerned with the production of any given output but with its own self renewal in the same process structure" [11]. Allopoiesis, on the other hand, "refers to a function given from outside, such as the production of a specific output" [12].

The previously documented continued use of the heat engine as a model for a number of aspects of self-organizing systems, a testament to its usefulness and versatility, prompted this author to consider adopting such a perspective for the thermodynamic modeling and analysis of the self-structuring process known as Bénard convection [13]. The fact that in this system the far from equilibrium condition is sustained by the temperature difference existing between the heat source and the sink, combined with the fact that the higher level of order here arising, represented by the cells themselves, is sustained by mechanical work, was the deciding argument to associate the inner-workings of this phenomenon with those of a heat engine. This effort lead, in turn, to the exploration of the thermodynamic features of a number of Carnot engines couplings. Of these, the one here reported shows the unusual behaviour of accessing efficiencies beyond those permitted by second law thermodynamics.

Two different couplings

The coupling of interest, to be referred also as the complex coupling, appears depicted in Figure 1(b). The simple coupling depicted in Figure 1(a) is to be used as reference in the efficiency calculations. They were developed, in the order mentioned, following the defining lines of autopoitic, and allopoietic systems given above by Jantsch. As should be noted from this figure, the following operational conditions hold for both of these couplings:

1. The temperatures of the outer, or limit heat reservoirs are T_h and T_c , with $T_h \rangle T_c$

2. A number ($n \geq 2$) of reversible Carnot's engines and their associated heat reservoirs have been fitted between the outer heat reservoirs.

3. These engines have been arranged in a way such that the cold reservoir of any of them acts also as the hot reservoir of the engine down below.

4. The temperatures of the reservoirs are ordered in the following fashion

$$T_h \rangle T_1 \rangle T_2 ... \rangle T_c \tag{1}$$

Furthermore, these temperatures have been chosen in such a way that all the engines are equally efficient. This condition, introduced with the purpose of simplifying the analysis, in no way implies that a different set of efficiencies could not lead to similar results.

5. An amount of heat Q_h delivered by the source enters both of these couplings.

6. Common to both couplings is also the restriction imposed by the second law of thermodynamics which states "No engine can be more efficient than a reversible engine operating between the same temperature limits" [14].

As should also be noted from the figure, the conditions that set these operations apart are the following:

7. In the simple coupling the work generated by any given engine is directed to a mechanical reservoir. Because of this, each engine down the line receives a smaller amount of heat, and outputs a smaller amount of work than the previous one.

8. The simple, allopoietic coupling of reversible engines is, as a whole, a reversible process. When the work stored in the mechanical reservoir is used to feed each of the individual engines – in a sequence opposite to that shown in Figure 1(a) – with an amount of work identical to that by them previously generated, it is possible to reverse the flows of heat that originally took place, returning this way the universe of this process to its original condition, without changes in other bodies remaining.

9. In the complex coupling the work generated by any given engine ends up, alongside the heat passing through, as heat at the temperature of its cold reservoir, and from here fed to the next engine down below. This way each engine receives the same amount of heat as any other, and as a consequence of the fact that all of them have the same efficiency, we have that they all output the same amount of work.

10. Notwithstanding that each and every one of the engines constituting the complex coupling is reversible, the fact that the work-to-heat transformations accompanying their operation are irreversible, makes the complex coupling as a whole, irreversible. That this is so can be understood by realizing that the reversal of the flows of heat shown in Figure 1(b) demands an amount of work that can only come from a foreign body. Being this so it follows that the reversal of the universe of the complex coupling to its original condition can only be achieved at the expense of changes remaining in the said body.

With the previous considerations in place, the goals of the analysis to be here performed can be stated as follows: Given T_h, T_c, Q_h, and the definition of efficiency as total work divided by the heat entering the coupling:

A. Produce an expression for the efficiency of the complex coupling in terms of T_h and T_c.

B. Compare it with the maximum efficiency predicted by the second law of thermodynamics for any engine working between T_h and T_c.

The common efficiency

As previously stated, the efficiency of any engine in any of the couplings is equal to that of any other. If this common efficiency is represented as η, then

$$\eta_1 = \eta_2 = \eta_3 = ... = \eta_n = \eta \tag{2}$$

In the previous equation η_1, η_2, η_3, η_n respectively represent the efficiencies of engines 1, 2, 3, *n*, of any of the couplings depicted in Figure 1.

Let us now recognize that in terms of the temperatures of the reservoirs, equation (2) leads to the following series of equations

$$(T_h - T_1)/T_h = (T_1 - T_2)/T_1 = (T_2 - T_3)/T_2 =$$

$$(T_{n-1} - T_c)/T_{n-1} = \eta \tag{3}$$

When these equations are respectively solved for T_1, T_2, … , T_c, the following results are obtained

$$T_1 = T_h(1-\eta),\ T_2 = T_1(1-\eta),\ T_3 = T_2(1-\eta) \dots\ T_c = T_{n-1}(1-\eta) \tag{4}$$

Substitution of the first of these equations in the second, of the second in the third, and so on leads, in turn, to the following results

$$T_1 = T_h(1-\eta),\ T_2 = T_h(1-\eta)^2,\ T_3 = T_h(1-\eta)^3,\ T_c = T_h(1-\eta)^n \quad (5)$$

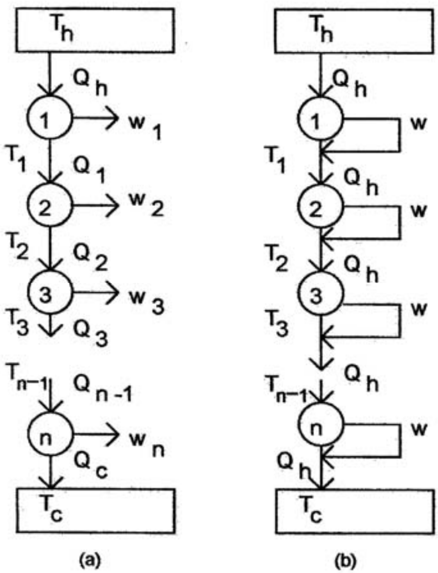

Figure 1: In the simple coupling shown in (a) the work produced by every engine is directed to a mechanical reservoir. The complex coupling shown in (b) includes a 'feed-forward' or work recycling step. After having performed the function of maintaining the order in the dissipative structure, the work output of every engine is fed as heat, alongside that passing through, to the next engine down below. The reader should note the parallel existing between the defining characteristics of these couplings, in the order presented, with those of allopoietic and autopoietic systems.

The limit efficiency predicted by the second law of thermodynamics, η^*, equal to that of a single reversible engine working between T_h and T_c, can now be introduced through the following equation

$$\eta^* = (T_h - T_c)/T_h\ ,\ 0\langle \eta^* \langle 1 \tag{6}$$

Taking now the last member of the string of equations represented in (5), and equating it with the one produced when equation (6) is solved for T_c, produces the following result

$$T_h(1-\eta)^n = T_h(1-\eta^*) \tag{7}$$

Solving this last equation for η leads to

$$\eta = 1 - \sqrt[n]{1-\eta^*} = 1 - \sqrt[n]{T_c/T_h} \tag{8}$$

The previous equation, it should be pointed out, subsumes the information required to set up these couplings. When the given values for T_h, T_c, as well as a selected value for *n* are substituted in this equation, the common efficiency becomes known. This piece of information alongside T_h fixes, through the series of equations shown in (5), the temperatures of the reservoirs. Conversely, if it is the common efficiency the one that is provided, then the number of engines required can also be determined through (8). As before η, alongside T_h, will determine the temperature of the required reservoirs.

The simple coupling

Let us now define the efficiency of the simple coupling (η_{sc}) of Figure 1(a) as follows

$$\eta_{sc} = W^*/Q_h \tag{9}$$

Here W^* represents the total work output of the simple coupling. In other words

$$W^* = w_1 + w_2 + w_3 + ... + w_n \tag{10}$$

Therefore

$$\eta_{sc} = (1/Q_h)(w_1 + w_2 + w_3 + ... + w_n) \tag{11}$$

A simple energy balance around each of this coupling's engines leads to the following series of equations

$$w_1 = Q_h - Q_1,\ w_2 = Q_1 - Q_2,\ w_3 = Q_2 - Q_3 \dots w_n = Q_{n-1} - Q_c \tag{12}$$

Substitution of (12) in (11) produces

$$\eta_{sc} = (1/Q_h)(Q_h - Q_1 + Q_1 - Q_2 + Q_2 ... - Q_{n-1} + Q_{n-1} - Q_c) \tag{13}$$

After simplification, equation (13) transforms into

$$\eta_{sc} = (Q_h - Q_c)/Q_h \tag{14}$$

The cancellation pattern arising in equation (13) allows us to realize that the combined operation of all these engines collapses, i.e. reduces to that of a single engine which in taking in an amount of heat Q_h from the heat reservoir of temperature T_h, and discarding an amount of heat Q_c to the cold reservoir of temperature T_c, transforms into work the difference $Q_h - Q_c$. In terms of the amounts of heat involved, the efficiency of the operation of this reversible engine is given by equation (14). But as equation (8) clearly shows, any single reversible engine ($n = 1$) working between the outer heat reservoirs do so with an efficiency equal to $(T_h - T_c)/T_h$. Therefore

$$\eta_{sc} = \eta^* = (Q_h - Q_c)/Q_h = (T_h - T_c)/T_h \tag{15}$$

The previous result allows us to conclude that the particular organization existing among the engines constituting the simple coupling works within the bounds of the second law.

The complex coupling

Let us start our analysis of the complex coupling by recognizing that its efficiency (η_{cc}) can be written as follows

$$\eta_{cc} = W/Q_h \tag{16}$$

In the previous equation Q_h represents the amount of heat entering the coupling. W represents, on its part, the coupling's total work output, and as such is given by the following expression

$$W = nw \tag{17}$$

The fact that the work output of a heat engine is determined by the product of its efficiency times the incoming heat, allows us to write equation (17) in the following form

$$W = n\eta Q_h \tag{18}$$

The combination of equations (16) and (18) leads to

$$\eta_{cc} = n\eta \tag{19}$$

The substitution of equation (8) in the previous result permits writing the following equation for the efficiency of the complex coupling

$$\eta_{cc} = n\left(1 - \sqrt[n]{1-\eta^*}\right) = n\left(1 - \sqrt[n]{T_c/T_h}\right) \tag{20}$$

Equation (20) embodies, it should be recognized, the first of the stated goals of this analysis. It is worth noticing that for the case of a single engine ($n = 1$) this equation, as expected, reduces to $\eta_{cc} = \eta^*$.

Beyond the thermodynamic limit

A comparison between η_{sc} and η_{cc} will be now performed through equations (9) and (16), as follows

$$\eta_{cc}/\eta_{sc} = W/W^* = \left(w + w + w + ... + w\right)/\left(w_1 + w_2 + w_3 + ... + w_n\right) \quad (21)$$

For the different work terms appearing in equation (21) the following apply

$$w = \eta Q_h\,,\ w_1 = \eta Q_h\,,\ w_2 = \eta Q_1\,,\ w_3 = \eta Q_2\,,\ldots, w_n = \eta Q_{n-1} \quad (22)$$

We know that the work produced by every engine of the simple coupling is directed to a mechanical reservoir. As a consequence of this each engine down the line receives a smaller amount of heat than the previous engine. This fact can be represented as follows

$$Q_h \rangle Q_1 \rangle Q_2 \rangle Q_3 \rangle ... \rangle Q_{n-1} \quad (23)$$

Combination of (22) and (23) leads, in turn, to the following set of relations between the constant amount of work *w* produced by the engines of the complex coupling, and the different amounts of work produced by the engines of the simple coupling

$$w = w_1\,,\ w \rangle w_2\,,\ w \rangle w_3, \ldots,\ w \rangle w_n \quad (24)$$

From (24) we realize that with the exception of the work output of the very first engine, for all the others the work output of a given engine in the complex coupling surpasses that of its corresponding engine in the simple coupling. This consideration allows the writing of the following inequality

$$nw \geq w + w_2 + w_3 + ... + w_n \quad (25)$$

Note that if the coupling were to reduce to a single engine, equation (25) would produce the trivial result of $w = w$. Once a coupling is in place with two or more engines, the inequality shown in (25) would hold. In this situation it will be true that

$$W \rangle W^*, \ \forall n \geq 2 \tag{26}$$

Substitution of this result in equation (21) allows us to conclude that

$$\eta_{cc} \rangle \eta_{sc}, \ \forall n \geq 2 \tag{27}$$

And on reason of (15), that

$$\eta_{cc} \rangle \left(T_h - T_c\right)/T_h, \ \forall n \geq 2 \tag{28}$$

As expressed by equation (28), as long as $n \geq 2$, the engine of engines represented in Figure 1(b) will exhibit efficiencies beyond that allowed by the second law of thermodynamics. The origin of this situation cannot certainly be traced to the individual efficiencies of the engines constituting the complex coupling – each and every one of them is a simple reversible engine – but to the way they happen to be coupled to one another i.e. to their organization. The coupling under consideration expresses this way what has been taken to be an essential characteristic of self-organizing phenomena: that the whole is more than the sum of its parts.

It seems necessary to point out that the work produced by the complex coupling is used first to form and then maintain the self-organizing structure, and because of this no possibility exists – as a superficial and naive reading of this coupling might suggest – of it being used for purposes related to perpetual motion machines or the production of unlimited ‘ordered energy’. The moment an attempt to harness this work is carried on, the same moment the structure – the cells in Bénard’s convection – and its associated energy transforming mechanism, disappears. The reason is simple; directing the work output of the engines for outside use will reduce or transform the complex coupling into a simple coupling, with the concomitant destruction of the organization upon which its particular behaviour rests. It should be kept in mind that when taken by itself, any engine of the complex coupling will output no more work than that allowed by the second law of thermodynamics, quantified by the product of its efficiency and the amount of incoming heat. These *caveats* are here presented in order to emphasize that this coupling has no possible existence outside the confines of a self-organizing structure.

In what follows we will take a closer look at the thermodynamics of this complex coupling. This will be done by investigating the behaviour of its efficiency in a number of situations.

Further considerations on the efficiency of the complex coupling

Let us analyze the behavior of η_{cc} as given by equation (20), at the limit values of η^*, this is, as $\eta^* \to 0$ and as $\eta^* \to 1$. For the former situation we will have that

$$\lim_{\eta^* \to 0} \eta_{cc} = n\left(1 - \sqrt[n]{1-0}\right) = 0 \qquad (29)$$

The previous result, valid for $n \geq 1$, is the reflection of the fact that no engine operation is possible in the absence of a temperature gradient. The efficiency of the complex coupling, alongside the efficiency of its constituent engines, will collapse to zero when $T_h = T_c$.

A simple inspection of equation (15) shows that under this condition the same result applies for the efficiency of the simple coupling.

For the latter of the situations noted above we will have that

$$\lim_{\eta^* \to 1} \eta_{cc} = n\left(1 - \sqrt[n]{1-1}\right) = n \qquad (30)$$

The previous result, subsuming the physically unrealizable condition of $T_c = 0$, sheds light on the fact that the difference between the efficiencies of these couplings becomes larger at larger temperature gradients.

The behaviour of η_{cc} between these limits will be ascertained by taking its partial derivative with respect to $\eta *$, at constant *n*. By doing this we get

$$\left(\partial \eta_{cc} / \partial \eta *\right) = 1 \Big/ \left(1 - \eta *\right)^{1-(1/n)} \tag{31}$$

With regard to the right hand side of equation (31), it should be noted that on reason of $0 \langle \eta * \langle 1$, it follows that $0 \langle 1 - \eta * \langle 1$; and that on reason of $2 \leq n \langle \infty$, it follows that $0 \langle 1 - (1/n) \langle 1$. Being this so, then

$$0 \langle \left(1 - \eta *\right)^{1-(1/n)} \langle 1 \tag{32}$$

Consequently

$$1 \Big/ \left(1 - \eta *\right)^{1-(1/n)} \rangle 1 \tag{33}$$

Therefore

$$\left(\partial \eta_{cc} / \partial \eta *\right)_n \rangle 1, \; n \geq 2 \tag{34}$$

The fact that the partial derivative came out positive indicates that η_{cc} is an increasing function of $\eta *$. This means that as $\eta *$ increases, so does η_{cc}. For any given *n*, and starting with a value of $\eta * = 0$, η_{cc} will increase its value alongside that of $\eta *$, until at the limit $\eta * = 1$ it will acquire the value $\eta_{cc} = n$ shown by equation (30).

The previous considerations had to do with the effect that changes in $\eta *$ produce in η_{cc}. In what follows we will inquire at the effect that

n has on η_{cc}, at a given value of η^*. Let us then consider the following limit

$$\lim_{n\to\infty} \eta_{cc} = \lim_{n\to\infty} n\left(1-\sqrt[n]{1-\eta^*}\right) = -\ln\left(1-\eta^*\right) \qquad (35)$$

The previous result tells us that for $\eta^*=0$ no number of engines will be capable of producing a coupling's efficiency different from zero. For $\eta^*=1$ on the other hand, and in accordance with equation (30), an infinite efficiency will accompany the operation of an infinite number of engines.

The omnipresence of the law of increasing entropy

Notwithstanding the different vantage points embraced by the different approaches to the study of self-organizing phenomena, their different analytical tools, or the different degrees of success they might have achieved in describing nature's behaviour, a common thread runs through all of them: compliance with the dictates of the second law of thermodynamics. For Smith "The limits on the biosphere's ability to reject disorder will then derive from limits on energy flow and limits on the *efficiency* with which energy flow can reject entropy. Whereas different biological processes may approximate their limits to different degrees, the limits themselves derive ultimately from the second law of thermodynamics" [1] Mahulikar and Herwig state, on their part, that "creation of order is always in conjunction with disorder (to satisfy the second law)" [15]. For Prigogine "a system could organize (decrease its entropy), as long as the net change in the universe was positive" [16]. For Chaisson "All structures, whether galaxies, stars, planets, or life forms, are demonstrably open, non-equilibrated systems, with flows of energy in and out…and it is this energy, the so called 'free energy', that goes to work and help build structure…whether it's electricity powering a laser, sunlight shinning on a plant, or food consumed by humans, energy flows do play a key role on the creation, ordering, maintenance, and fate of complex systems – all in quantitative accord with thermodynamics' celebrated second law. None of nature's ordered structures not even life, is a violation (nor even a circumvention) of this law. For both, ordered systems as well as their surrounding environments, we find good agreement with modern, non-equilibrium thermodynamics. No new science is needed" [17].

A breakdown on the power of description of the second law

Let us now contrast from a number of perspectives, the operations of the simple and complex reversible couplings.

1. According to Planck "Every physical or chemical process in nature takes place in such a way as to increase the sum of the entropies of all the bodies taking any part in the process. In the limit, i.e. for reversible processes, the sum of the entropies remains unchanged. This is the most general statement of the second law of thermodynamics" [18]

Let us now write, with the aid of figure 1, the following equation for the entropy change of the simple coupling

$$\Delta S_{sc} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} \tag{36}$$

From the combination of equations (9) and (14) we get

$$W^* = Q_h - Q_c \tag{37}$$

Where, as previously defined, W^* stands for the total work output of this coupling. When Q_c is isolated from equation (37), substituted in equation (36), and the result simplified making use of equation (15), we get

$$\Delta S_{sc} = \frac{\eta_{sc} Q_h}{T_c} - \frac{W^*}{T_c} \tag{38}$$

Recognition of the fact that

$$W^* = \eta_{sc} Q_h \tag{39}$$

Leads to

$$\Delta S_{sc} = 0 \tag{40}$$

This result, in line with the conclusion represented by equation (15), shows that the simple reversible coupling is a well behaved process, complying with the dictates of the second law expressed in Planck's quote offered above.

Let us now, also with the help of Figure 1, write the following expression for the entropy change of the complex coupling

$$\Delta S_{cc} = -\frac{Q_h}{T_h} + \frac{Q_h}{T_c} \tag{41}$$

The simple rearrangement of this equation shown below makes it clear that the complex coupling, an irreversible process when considered as a whole, proceeds with an increase in the entropy of its universe, complying also with that established in the previous quote

$$\Delta S_{cc} = Q_h \left(\frac{T_h - T_c}{T_h T_c} \right) \rangle 0 \tag{42}$$

2. Another statement of the second law has been previously offered via a quote from Bevan-Ott and Boerio-Goates "No engine can be more efficient than a reversible engine operating between the same temperature limits, and all reversible engines operating between the same temperature limits have the same efficiency" [14].

The result shown by equation (28) stating the fact that the irreversible engine of engines we have called the complex coupling is actually more efficient than the reversible engine of engines we have called the simple coupling – both operating between the same reservoirs – contradicts this statement.

3. Consider the side by side operation of a simple reversible engine – such as the simple reversible coupling – and its irreversible counterpart, both operating between the same two heat reservoirs of temperatures T_h and T_c, with $T_h \rangle T_c$, and receiving the same amount of heat Q_h from the hot reservoir. As known, the frictional dissipative processes taking place in the irreversible process produce as consequence a diminished work output for this process and consequently, the rejection to the cold reservoir of a larger amount of heat than its reversible counterpart. In what follows the irreversible operation will be identified with the sub index '*irr*'. The previous considerations can also be expressed as follows

$$W^* \rangle W_{irr} \tag{43}$$

$$Q_h = W^* + Q_c \tag{44}$$

$$Q_h = W_{irr} + Q_{c,irr} \tag{45}$$

Furthermore, combination of equations (44) and (45) leads to

$$W^* - W_{irr} = Q_{c,irr} - Q_c \tag{46}$$

From which it follows that

$$Q_{c,irr} = W^* - W_{irr} + Q_c \tag{47}$$

The entropy change for the universe of the irreversible operation will now be written as follows

$$\Delta S_{irr} = -\frac{Q_h}{T_h} + \frac{Q_{c,irr}}{T_c} \tag{48}$$

Substitution of equation (47) in (48) produces

$$\Delta S_{irr} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} + \frac{W^* - W_{irr}}{T_c} \tag{49}$$

Combination of equations (40) and (49) leads finally, to the following result

$$\Delta S_{irr} = \frac{W^* - W_{irr}}{T_c} = \frac{W_{lost}}{T_c} \tag{50}$$

In the previous equation W_{lost} has been used in place of the difference between the reversible and irreversible outputs $W^* - W_{irr}$, to emphasize that this difference represents the work lost due to the dissipative processes taking place in the irreversible operation. As equation (46) shows, this lost work appears as heat in the cold reservoir.

Equation (50) is an expression of the fact that entropy, as Weber and Meissner have recognized [19], is a measuring rod or gauge of the work lost in irreversible processes.

Let us now bring here the fact, expressed by equation (26), that the complex coupling produces a larger amount of work than the simple coupling. The effect of the complex coupling is thus diametrically opposed to that expected from an irreversible process working between the same reservoirs. In the logic of the connection shown in equation (50) associating an entropy increase to any process were work is lost, it would be only natural to think of associating a negentropic effect to those – like the complex coupling – were work is *gained* or produced beyond the limits of the second law. In other words, if the opposition of effects between a simple irreversible coupling and the complex irreversible coupling could be expressed algebraically, it would have to be through some relationship of the form

$$W_{lost} = -W_{gained} \tag{51}$$

The corresponding substitution of equation (51) in (50) produces the previously mentioned result.

Notwithstanding the fact that the complex coupling has been constructed within the boundaries of the second law, it appears to be beyond its domain. Two out of three different approaches to its entropy change – all within the accepted wisdom of this law – produce different, even contradictory results. According to equation (42) the complex coupling is entropic, and according to the combination of equations (50) and (51), negentropic. According to equation (42) and Planck's statement, the complex coupling is within the domain of the second law, but according to equation (28) and the statement of Bevan Ott and Boerio-Goates, it is not.

4. In statistical mechanics, Boltzmann principle is given by

$$S = k \ln P \tag{52}$$

Where S is the entropy, k the Boltzmann constant, and P the total number of complexions compatible with the macroscopic state of the system [20] Through it, it is possible to obtain Boltzmann's basic formula for the probability, P_i, of the occupation of a given energy level, E_i

$$P_i = e^{-E_i/kT} \tag{53}$$

In which T is the temperature, and E_i the energy of the chosen level [21]. According to Prigogine this last equation, referred by him as Boltzmann's order principle, "…constitutes the basic principle that governs the structure of equilibrium states… It is of paramount importance as it is capable of describing an enormous variety of structures including, for example, some as complex and delicately beautiful as snow crystals" [22]. When confronted with self organizing phenomena however, the situation radically changes as the equation in question "would assign almost zero probability to the occurrence of Bénard convection. Whenever new coherent states occur far from equilibrium, the application of probability theory, as implied in the counting of number of complexions, breaks down" [23]. An interesting discussion on thermodynamics and its laws can be found in [24].

Final comment

The previous considerations are a clear indication that unconditional faith on the second law might not be warranted, and that as other have foreseen – among them Caillois "Clausius and Darwin cannot both be right" [25]; Farmer "I'd like to believe (life) is described by some counterpart of the second law of thermodynamics – some law that would describe the tendency of matter to organize itself, and that would predict the general properties of organization we'd expect to see in the universe"[26]; Kauffman "Could there possibly be a fourth law of thermodynamics for open thermodynamic systems, some law that governs biospheres anywhere in the cosmos or the cosmos itself?" [27]; Teilhard de Chardin "In order to completely encompass the evolutionary economy of the universe (life included), a third principle must be added, the principle of the reflection of energy, to those already in place about the conservation, and degradation of energy" [28]; and from other quarters Cápek and Sheehan [29], and Engels [30] – the times are calling for a larger formulation of the second law capable of dealing with those processes, like the complex coupling previously discussed, where order prevails over disorder.

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