

# A Rational Approach to Reversibility via Carnot's Lost-Work

JoséC. Íñiguez

Correspondence: JoséC. Íñiguez, Retired instructor of science and mathematics: 1227 21<sup>st</sup> Street, Douglas AZ 85607, USA.

Received: August 12, 2019 Accepted: October 8, 2019 Online Published: October 10, 2019

doi:10.5539/ijc.v12n1p1

URL: <https://doi.org/10.5539/ijc.v12n1p1>

## Abstract

The reversibility definition emerging from Carnot's 'lost-work' notion or, equivalently, from considerations of optimal efficiency and lack of dissipation is here qualified as a rational alternative to that which based on Planck's constant total-entropy criterion resorts to either a sequence of equilibrium states or the action of infinitesimal forces for the definition of the reversible path.

**Keywords:** reversibility, equilibrium, quasistaticity, efficiency, lost-work, driving forces

## *Thermodynamics is too important to be left to the thermodynamicists*

(Angrist & Hepler, 1967, p. v)

### 1. Reversibility According to Planck

A process which can in no way be completely reversed is termed irreversible, all other processes reversible. That a process may be irreversible, it is not sufficient that it cannot be directly reversed...The full requirement is, that it be impossible, even with the assistance of all agents in nature, to restore everywhere the exact initial state when the process has once taken place...The significance of the second law of thermodynamics depends on the fact that it supplies a necessary and far reaching criterion as to whether a definite process which occurs in nature is reversible or irreversible. Since the decision as to whether a particular process is irreversible or reversible depends only on whether the process can in any manner whatsoever be completely reversed or not, the nature of the initial and final states, and not the intermediate steps of the process settle it...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. (Planck, 1990, pp. 84, 86, 87,103)

Planck's entropy-based criterion for determining the reversibility, or lack of it, of any given process taking a system from an initial equilibrium state  $A$  to a final equilibrium state  $B$  finds formal representation in the following expression:  $\Delta S_{tot}[A \rightarrow B] = S_{tot,B} - S_{tot,A} \geq 0$ , where the equality applies to reversible processes and the inequality to all others. The sub-index *tot*, short for 'total', indicates that the entropies of all the bodies taking any part in the process have been included in the quantification of the magnitudes to which it is attached. In reversible changes the total entropy at any given point along the process is identical in magnitude to that of the initial state. In irreversible changes the total entropy increases along the process acquiring a maximum value at the final equilibrium state.

### 2. The Entropy Change for Irreversible Processes

The fact that the entropy finds definition in terms of reversible heat ( $dS = dQ_{rev}/T$ ) requires us, when determining the entropy change for the irreversible evolution of a given system between initial and final equilibrium conditions  $A$  and  $B$ , respectively, to find an alternative reversible path for the said transit with which to evaluate the corresponding entropy change. Since the entropy is a state function and the initial and final states of the system in the original irreversible process and in the alternative reversible one are identical, the entropy change evaluated for the latter will be identical to that of the former.

The previously stated procedure has a notable exception: heat reservoirs. As known, heat reservoirs are assumed to be

constant volume and constant composition bodies with large thermal capacity [thermal capacity = (mass)·(specific heat)], and large thermal conductivity. These last two characteristics allow a heat reservoir to maintain a constant and uniform temperature throughout its mass under exchanges of finite amounts of heat. The constant volume and constant composition conditions prevent heat reservoirs from any exchange of energy in the form of work, and in these conditions, in accord with the first law, the heat given up or taken in by any of these bodies is equal to the change of its internal energy, i.e.  $dU = dQ$ , and if so, it is also independent of the path. This fact means that the defining equation for the entropy, namely  $dS = dQ_{rev}/T$  can be re-expressed, for the case of a heat reservoir in which the path-restriction imposed to the heat is inoperative, as  $dS = dQ/T$ . The constant temperature condition of any of these bodies allows writing the following integrated version of the previous differential equation as  $\Delta S = Q/T$  which makes reference the heat  $Q$  exchanged by any of these bodies at the temperature  $T$  (Denbigh, 1968, p. 40; Smith & Van Ness, 1965, pp. 186-187)

### 3. Work as the Essential Notion of Thermodynamic Reversibility

As explicitly stated by Planck, the reversibility condition hinges on the possibility of restoring the universe of the process (the totality of the bodies involved, or, equivalently, the system and its surroundings) to its precise initial condition once the said process has taken place. In this perspective, the proof of reversibility passes through the said restoration, and this restoration implies, in turn, a cycle (Denbigh, 1968, p. 41) i.e. the concatenation of the original process, which will be henceforth referred to as the ‘forward’ process, with the reversible version of its inverse, which will be further referred as the ‘inverse’ process. The reason for this is the following: being the condition of the forward process the one to be ascertained, it then follows that its inverse has to be necessarily conducted in a reversible fashion. If this weren’t so, no knowledge about the condition of the forward process would be possible, since we would never be able to know whether the source of irreversibility, if any is present, is the forward process, the inverse process, or both.

It should here be obvious that in any forward-inverse cycle while one of the two processes is spontaneous, the other is not. In other words, if one of those two processes is capable of producing work, the occurrence of the other will demand its expenditure, or vice versa. As to the amounts of work involved in one and the other and the connection existing between them in the case of a reversible cycle, the following is known: The work outputted by the system along its spontaneous and reversible  $A \rightarrow B$  transit corresponds to the maximum output possible when compared to the amounts of work coming out of the system when the said transit proceeds along any of the irreversible counterparts of the original process. Likewise, the amount of work that needs to be spent to force the non-spontaneous and reversible  $B \rightarrow A$  transit of the system corresponds to the minimum demand possible when compared to that required when the said transit proceeds along any of the irreversible counterparts of the original process. In the case of a reversible cycle, where these two processes are the reversible inverses of one another, the said maximum and minimum amounts are of identical magnitude which means that along the spontaneous leg the system will output the precise amount of work required to push it back to its original condition along the non-spontaneous one. The previous situation corresponds to the fact that in a reversible cycle  $A \rightarrow B \rightarrow A$  “...the reverse process is an exact ‘mirror image’ of the forward process” (Kestin, 1966, p. 129), or to the fact that “if we transform a system reversibly from an initial state A to a final state B, we can then take the system by means of the reverse transformation from B to A through the same succession of intermediate steps but in the reverse order” (Fermi, 1956, p. 4).

Even if in our own description as well as in that of Fermi reference is made to the system, we should be aware of the fact that what is returning to its initial condition is the universe, i.e. the system of interest plus any other body or bodies involved in the process. Consider for example the isothermal and reversible expansion of an ideal gas as the spontaneous forward leg. Here the universe is composed of three bodies: the gas, a heat reservoir, and a mechanical reservoir. In this process the heat reservoir transfers an amount of heat  $Q$  to the gas which through its expansion transforms this heat into an equivalent amount of work  $W$  which ends up increasing the potential energy of a weight-in-pulley coupling acting as mechanical reservoir. The amount of work deposited in the mechanical reservoir by the expansion of the gas corresponds to the precise amount required to be spent to push the system to its initial condition through the non-spontaneous, isothermal and reversible compression constituting the inverse leg. Once its task completed, the spent work ends up in the form of heat in the heat reservoir. At the end of the cycle the gas and the two reservoirs, and with them the universe of this process, will be found in their respective initial conditions: 1) the gas because it was forced to do so; 2) the mechanical reservoir because along the compression it released an amount of work identical to the one it had previously received along the expansion; and 3) the heat reservoir because along the compression it recuperated the amount of heat it initially released along the expansion. This is the meaning of restoring the initial condition through a reversible cycle. Just like a line can be drawn with a pencil, it can be erased when its

inverse, the eraser, travels the same path in reverse in a way such that at the end (some latitude allowed) no evidence remains of a line ever being traced. In this case the pencil's trace representing the set of changes produced by the forward reversible leg will be reversed, i.e. erased by the inverse reversible process.

Let us also note in this regard that the only difference between a reversible process and its irreversible counterparts is the absence in the former and the presence in the latter of dissipative forces; and that the difference between any two irreversible counterparts is the magnitude of the dissipative forces operating in one and the other. Dissipative forces such as friction, convection, electrical resistance, irreversible mixing, etc. have the effect of decreasing the work output of spontaneous processes and increasing the demand of those non-spontaneous. They are responsible for the work-production/work-consumption inefficiency displayed by irreversible processes when compared to the optimal efficiency characteristic of their reversible counterparts in which those dissipative forces are absent.

With the previous antecedents in place let us now consider the two possibilities arising in reference to the problem stated above of using a cycle with a reversible inverse to ascertain the nature of the forward process. First, if the amount of work made available by the forward process along its transit between states  $A$  and  $B$  is insufficient to produce the transit of the system from  $B$  to  $A$  through the reversible inverse then the final condition will correspond to some state  $C$  different from the initial one  $A$ , an indication of the fact that the initial condition was not restored and that the forward process took place in an irreversible fashion. In the other case, if the work spent by that body selected to force the occurrence of the forward process from  $A$  to  $B$  is only partially recuperated by that outputted by the  $B$  to  $A$  transit of the system along the reversible inverse, then the final condition will not correspond to the initial one on reason of the fact that even if the system completed its  $A \rightarrow B \rightarrow A$  cycle, the same did not happen with the work supplying body which at the end is found in a condition different from the one it initially had. The fact that initial condition was not restored serves as proof for the irreversibility of the forward process.

The conclusion is straightforward: restoration of the initial condition is possible if and only if the forward and reverse processes are optimally efficient. The reason behind the failure to achieve restoration of the initial condition can always be traced to the inefficient process: when the forward process is spontaneous and inefficient its work output is lesser than that demanded by the reversible inverse; when non-spontaneous and inefficient the work by it demanded is larger than the one the reversible inverse is capable of paying back. Inefficiency, the reason and source of irreversibility, can be traced to the action of dissipative agents whose role is to waste available work production potential or to degrade actual work into heat. The previous considerations evince the fact that reversibility requires of no other condition than that represented by optimal work production and/or optimal work utilization. Optimal efficiency appears at this light as both: a necessary as well as sufficient condition for thermodynamic reversibility.

#### 4. A Heat Transfer Through a Finite Temperature Gradient

In that process represented by the direct, conductive transfer of an amount of heat  $Q$  from a hot reservoir ( $h$ ) of temperature  $T_h$  to a cold reservoir ( $c$ ) of temperature  $T_c$  the only bodies affected are the heat reservoirs. If so, the total-entropy change for this process will be given by the summation of the entropy changes of these bodies. According then to that stated in Section 2, the total entropy change takes the following form:  $\Delta S_{tot} = \Delta S_h + \Delta S_c = (-Q/T_h) + (Q/T_c) = Q(T_h - T_c)/(T_h T_c) > 0$ . The irreversible nature of this transfer, evinced by its positive total entropy change, is a consequence of the fact that the only way open to restore the initial condition once the irreversible heat transfer has taken place is represented by the unassisted or spontaneous flow of  $Q$  from the cold to the hot reservoir. This possibility is, however, denied by "(that) statement of experimental truth" expressed as "Heat cannot pass spontaneously from a body of lower temperature to a body of higher temperature" (Schmidt, 1966, p. 92). Surely,  $Q$  might be transferred back from the cold to the hot reservoir when a reversible Carnot refrigerator is inserted between the reservoirs. To run this refrigerator we need, however, an amount of work of magnitude  $W = Q[(T_h - T_c)/T_c]$  (Fermi, 1956, p. 44) that we don't have as none was generated in the irreversible heat transfer. This problem can be solved by bringing in a work-supplying body. Even if this procedure allows for the transfer back of  $Q$  from the cold to the hot reservoir it is incapable of restoring the initial condition, this on reason of the fact that it leaves two changes behind: A work-supplying body depleted of an amount of energy  $W$ , and a hot reservoir taking back an amount of heat  $W$  in excess of that it originally released.

#### 5. A Process That Should Be Reversible But Isn't

The following argument was originally uploaded to the Chemistry Preprint Server (Íñiguez & Íñiguez, 2004).

As the following quote illustrates, current thermodynamic wisdom posits that any process taking place under the action of infinitesimal gradients is a reversible process: "The reversible path must be one for which the internal forces of the system differ only infinitesimally from the external forces, and for which all heat transfers take place over temperature differences which are only infinitesimal" (Denbigh, 1968, p. 41). The following discussion prove that this is not so.

In order to ascertain the truthfulness of our previous statement let us consider the heat transfer process represented in Figure 1(a). In it a series of heat reservoirs have been arranged in descending temperature order, with the temperatures of these reservoirs complying with the following condition:

$$T_h - T_1 = T_1 - T_2 = \dots = T_i - T_j = \dots = T_{c-1} - T_c = dT$$

In the previous expression  $dT > 0$  represents a positive infinitesimal temperature gradient, with  $T_h$  and  $T_c$  representing two absolute temperatures fulfilling the condition  $T_h > T_c$ . All the heat reservoirs taking part in the process, identical to one another, share the characteristics outlined in Section 2.

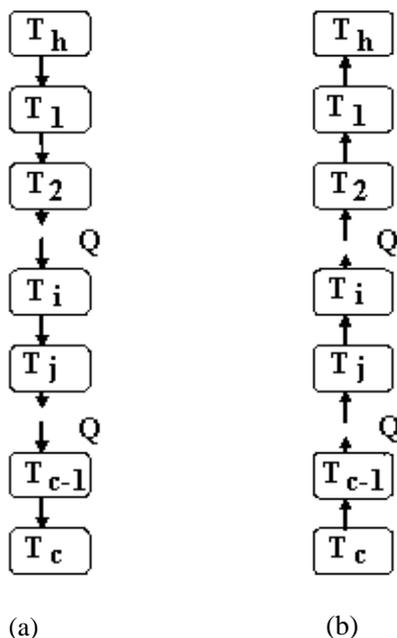


Figure 1. The transfer of an amount of heat  $Q$  from a hot to a cold reservoir through a series of intermediate heat reservoirs differing only infinitesimally in temperature is shown in (a). The reverse of this process is shown in (b). Even if propelled by infinitesimal gradients, its null work output makes process (a) irreversible, and this in turn makes process (b) impossible

As soon as  $Q$  has reached the cold reservoir of temperature  $T_c$  through the cascade of intermediate reservoirs depicted in 1(a) we will be facing the problem that the accomplishment of the reverse, non-spontaneous process, demands the expenditure of work and that none at all was produced in the forward process. In such a situation, the return to the precise original condition without changes in other bodies remaining means, plain and simple, that the transfer of the said amount of heat from  $T_c$  to  $T_h$  has to take place by itself. This, however, is not about to happen. As already noted, experience shows us that heat cannot, of itself, pass from a colder to a hotter body. The impossibility of restoring the initial condition once 1(a) has taken place proves its irreversibility. Let us emphasize in regard to process 1(b) that unless work is spent,  $Q$  will remain in the cold reservoir for the simple reason that the flow of heat against an adverse temperature gradient requires the expenditure of work. If the adverse gradient is infinitesimal the amount of work required will be correspondingly infinitesimal, but not certainly zero. Process 1(a) could have accessed the condition of ‘reversible’ had it generated the amount of work required to be spent in 1(b) to restore  $Q$ , and in doing so recuperate the initial condition. Claiming that work-less (no work output) process 1(a) is reversible implies the spontaneity of the flow of heat against adverse gradients and this, in turn, implies that 1(b) will take place without the expenditure of work. If this were to be so the second law wouldn’t exist

The previously annotated fact that the heat transfers in 1(a) take place under infinitesimal temperature gradients, i.e.  $T_h - T_1 = T_1 - T_2 = T_i - T_j = T_{c-1} - T_c = dT > 0$ , allows us to write their corresponding infinitesimal entropy

changes in the following manner:  $dS_{h,1} = Q(T_h - T_1)/(T_h T_1) = QdT/(T_h T_1) > 0$   $dS_{1,2} = Q(T_1 - T_2)/T_1 T_2 = QdT/(T_1 T_2) > 0$  ...  $dS_{i,j} = Q(T_i - T_j)/T_i T_j = QdT/(T_i T_j) > 0$  ,  $dS_{c-1,c} = Q(T_{c-1} - T_c)/T_{c-1} T_c = QdT/(T_{c-1} T_c) > 0$ . The total entropy change for process 1(a) will then be given by the summation of the infinitesimal entropy changes of the infinitude of heat transfers there taking place. This infinite summation process can be reduced to a single operation as soon as we realize that the pair of entropy changes experienced by each and every one of the intermediate heat reservoirs combines for a total of zero. To understand this let us note that every 'i' intermediate reservoir of temperature  $T_i$  experiences two compensated entropy changes:  $Q/T_i$  due to the absorption of the amount of heat  $Q$ , and  $-Q/T_i$  due to the release of this same amount of heat, in a way such that the total entropy change for each and every one of these intermediate reservoirs is equal to zero. The situation with the extreme-positioned reservoirs is different. Here the entropy changes are not compensated. This way the total entropy change for process 1(a) can be alternatively evaluated by the combination of the uncompensated entropy changes of the extreme heat reservoirs:  $\Delta S_{tot}[process\ 1(a)] = -Q/T_h + Q/T_c = Q(T_h - T_c)/(T_h T_c) > 0$ . This result shows that the process under consideration, propelled by infinitesimal gradients, is not, as some of current thermodynamic ideas would lead us to believe, reversible. Using the same extreme-positioned reservoirs approach we can determine the total entropy change for process 1(b) as follows:

$\Delta S_{tot}[process\ 1(b)] = -Q/T_c + Q/T_h = -Q(T_h - T_c)/(T_h T_c) < 0$ . The negative total entropy change confirms that this is an impossible heat transfer process. The *universal* statement positing that all processes driven by infinitesimal gradients are reversible needs only one counter-example to be proven false. Process 1(a) is such a counter-example.

The identical nature of process 1(a) and the one discussed in Section 4 is made evident by the fact that the effects of one and the other reduce to the changes experienced by the heat reservoirs origin and destiny of  $Q$ . As a matter of fact, under the assumption that  $Q$ ,  $T_h$ , and  $T_c$  have identical magnitudes, these two processes become identical.

According to Planck's total-entropy criterion for reversibility quoted in Section 1, reversible process  $A \rightarrow B$  takes place with  $\Delta S_{tot}[A \rightarrow B] = 0$ . For the inverse of this process it necessarily follows that  $\Delta S_{tot}[B \rightarrow A] = 0$ . If this weren't so then, contrary to Planck's definition, restoration wouldn't be accompanied by a zero total-entropy change. If so, then  $\Delta S_{tot}[Rev.\ Cycle] = \Delta S_{tot}[A \rightarrow B] + \Delta S_{tot}[B \rightarrow A] = 0 + 0 = 0$ . If we now use the previously determined total-entropy changes for 1(a) and 1(b) to calculate the total entropy-change for the impossible cycle defined by 1(a) + 1(b) we would get:

$$\Delta S_{tot}[Impossible\ Cycle] = \Delta S_{tot}[1(a)] + \Delta S_{tot}[1(b)] = -Q/T_h + Q/T_c - Q/T_c + Q/T_h = 0.$$

Note then that here the total-entropy criterion fails to discriminate between the reversible and the impossible cycles. If we were believers in the notion that all processes propelled by infinitesimal gradients are reversible, we could take the previous result as proof of it. The fact is that even if from the reversibility of the cycle's forward and inverse processes the zero-total entropy of the cycle follows, the converse is not necessarily true.

Had we inserted minuscule reversible heat engines between the reservoirs shown in 1(a) in order to harness for purposes of work production the infinitesimal gradients there operating, we would have secured the work required to be spent in 1(b) to restore the initial condition i.e. to restore  $Q$  to the hot reservoir without changes being left behind. In this 'minuscule-engines-mediated' heat transfer process even if the heat reservoir at  $T_h$  releases the amount of heat  $Q$ , only the smaller amount  $Q_c$  reaches the cold reservoir of temperature  $T_c$ , with the difference  $Q - Q_c$  defining the combined work output of the said set of minuscule engines. The truth of this last statement is the matter of the following argument in which  $W_h, W_1, \dots, W_i, \dots, W_{c-1}$  represent the respective work output of the engines working between  $(T_h, T_1), (T_1, T_2), \dots, (T_i, T_j), \dots, (T_{c-1}, T_c)$ . Here, for any intermediate ( $i$ ) heat reservoir  $Q_i$  represents, on reason of their identical magnitudes, either the heat received or the heat released by it. If so, the engine working between  $(T_h, T_1)$  receives  $Q$  and releases  $Q_1$ , while that working between  $(T_1, T_2)$  receives  $Q_1$  and releases  $Q_2$  and in being this so their respective work outputs are  $Q - Q_1$  and  $Q_1 - Q_2$ . Note now that engine 1 will consume –as do all engines in the inverse leg– an amount of work identical to that it generated in the forward leg i.e.,  $Q_1 - Q_2$ , to extract  $Q_2$  from reservoir 2 and deliver  $Q_2 + (Q_1 - Q_2) = Q_1$  to reservoir 1; engine  $h$  will in turn consume an amount work  $Q - Q_1$  to

extract  $Q_1$  from reservoir 1 and deliver to the hot reservoir of temperature  $T_h$  an amount of heat  $Q_1 + (Q - Q_1) = Q$ . Our previous considerations allow us to write the total work output  $W$  of these minuscule engines as follows:  $W = Q - Q_1 + Q_1 - Q_2 + Q_2 \dots + Q_i - Q_j + \dots - Q_{c-1} + Q_{c-1} - Q_c = Q - Q_c$ . This work output is, it should be noted, identical to that coming out of a single reversible engine working between the extreme reservoirs of temperatures  $T_h$  and  $T_c$ . At the light of these results the infinitude of combined minuscule engines behaves just like a single engine. The work output of any of these two reversible engines is also given by  $W_{rev\ eng} = Q(T_h - T_c)/T_h$ , and its magnitude is, as can be easily proved, identical to that required to be spent on the reversible inverse of any of these two engines, namely  $W_{rev\ ref} = Q_c(T_h - T_c)/T_c$  (Fermi, 1956, p. 44), to produce the transfer of  $Q$  from  $T_c$  to  $T_h$ . In the previous expressions for  $W$  the sub-indexes *rev, eng*, and *ref*, stand, respectively, for reversible, engine, and refrigerator.

An alternative path for the reversible transfer of heat between two heat reservoirs in which, at difference of the one just discussed, the amount of heat reaching the cold reservoir corresponds to the amount of heat released by the hot reservoir, can be found in the literature (Dickerson, 1969, pp. 162-163; Moore, 1972, p. 88; Klotz & Rosenberg, 1986, p. 139).

## 6. Carnot and the Origin of the Reversibility Concept

Working within the confines of the caloric theory of heat and in an attempt to improve the efficiency of the heat-to-work conversion carried on in heat engines, Carnot set himself to identify the essential principles governing the operation of these devices; in his own words: "Notwithstanding the work of all kinds done by steam-engines, notwithstanding the satisfactory condition to which they have been brought today, their theory is little understood, and the attempts to improve them are still directed almost by chance" (Carnot, 1960, p. 5). In his way to bring these principles to light, he started recognizing a number of facts:

The production of motion in steam engines is always accompanied by a circumstance on which we should fix our attention. This circumstance is (the) passage (of the caloric) from a body in which the temperature is more or less elevated to another in which it is lower. (Carnot, 1960, p. 6)

Heat can evidently be a cause of motion on virtue of the change of volume or of form which it produces on bodies. These changes are not caused by uniform temperature, but rather by the alternations of heat and cold. Now to heat any substance whatever requires a body warmer than the one to be heated; to cool it requires a cooler body. We supply caloric to the first of these bodies that we may transmit to the second by means of the intermediary substance ... Steam is a means of realizing this power, but it is not the only one. All substances in nature can be employed for this purpose, all are susceptible of changes of volume, of successive contradictions and dilatations, through the alternation of heat and cold. All are capable of overcoming in their changes of volume certain resistances, and of thus developing the impelling power. (Carnot, 1960, pp. 8, 9)

We have already remarked upon this self-evident fact, or fact that at least appears evident as soon as we reflect on the changes of volume occasioned by heat: wherever there exists a difference of temperature, motive power can be produced. Reciprocally, wherever we can consume this power, it is possible to produce a difference of temperature. (Carnot, 1960, p. 9)

According to established principles at the present time, we can compare with sufficient accuracy the motive power of heat to that of a waterfall. Each has a maximum that we cannot exceed, whatever may be, on the one hand, the machine which is acted upon by the water, and whatever, on the other hand, the substance acted upon by the heat. The motive power of a waterfall depends on its height and on the quantity of the liquid; the motive power of heat depends also on the quantity of caloric used, and on what in fact we will call the height of its fall, that is to say, the difference of temperature of the bodies between which the exchange of caloric is made. (Carnot, 1960, p. 15)

The previous considerations allowed him to recognize the essential components of a heat engine, these being a hot body thermally connected to a colder body through a closed sequence of contradictions and dilatations of the intermediary substance or variable body. This closed sequence, now known as Carnot's cycle, even if described in detail by Carnot (1960, pp. 17-18), had to wait for the work of Clapeyron to receive graphical representation in  $P$ - $V$  coordinates in 1834 (Carnot, 1960, p. 75)

Even if armed with these notions Carnot went on to consider a number of essential questions/issues about the work producing capability of heat engines, we will only consider here the ones related to the operating conditions required for any given engine to output the maximum of motive power as well as its closely related issue concerning, using Planck's terminology, restoration of the initial condition. This is done in the following three paragraphs:

The necessary condition of the maximum is...that in the bodies employed to realize the motive power of heat

there should not occur any change of temperature which may not be due to a change of volume. Reciprocally, every time this condition is fulfilled the maximum will be attained. This principle should never be lost sight in the construction of heat engines; it is its fundamental basis. If it cannot be strictly observed, it should at least be departed from as little as possible...Every change of temperature which is not due to a change of volume...is necessarily due to the direct passage of the caloric from a more or less heated body to a colder body. This passage occurs mainly by the contact of bodies of different temperatures; hence such contact should be avoided as much as possible (because it brings)...loss of motive power...It cannot probably be avoided entirely, but it should at least be so managed that the bodies brought into contact with each other differ as little as possible in temperature. (Carnot, 1960, pp. 13, 14)

Carnot's argument that was to unveil the notion we call reversibility as well as its associated concept of restoration starts with him considering a first operation consisting in the production of work via the transfer of a given amount of caloric between "two bodies *A* and *B*, kept each at a constant temperature, that of *A* being higher than that of *B*" (Carnot, 1960, p. 10). These two bodies are also assumed of being capable of exchanging heat without change in their respective temperatures, and in doing so exercising "the functions of two unlimited reservoirs of caloric" (Carnot, 1960, p. 10). The conclusion of the first operation is then followed by the expenditure of the motive power just generated in order to produce, via the inverse sequence of changes of the variable body, the transfer of caloric from the body *B* to the body *A*. In his own words:

By our first operations there would have been at the same time production of motive power and transfer of caloric from the body *A* to the body *B*. By the inverse operations there is at the same time expenditure of motive power and return of caloric from the body *B* to the body *A*. But if we have acted in each case on the same quantity of vapor, if there is produced no loss of either motive power or caloric, the quantity of motive power produced in the first place will be equal to that which would have expended in the second, and the quantity of caloric passed in the first case from the body *A* to the body *B* would be equal to the quantity which passes back again in the second from the body *B* to the body *A*; so that an indefinite number of alternative operations of this sort could be carried on without in the end having either produced motive power or transferred caloric from one body to the other...so that these two series of operations annul each other, after a fashion, one neutralizing the other. (Carnot, 1960, pp. 11, 19)

The reader should note the correspondence existing between Carnot's previous quote and our discussion presented in Section 3.

Between Planck and Carnot's positions on reversibility we find coincidences and differences. If we compare Planck's statement transcribed in Section 1, with Carnot's quote immediately above, we will realize that the situation which Planck's describes as 'the restoration of the initial condition' is equivalent to that which in Carnot's argument is achieved by the said 'neutralization of effects'. This equivalence could not be possible, however, without the existence of a similar equivalence between their respective premises, i.e. between the notions giving sustenance to one and the other, these being the zero total-entropy changes of the forward and inverse processes on which restoration depends in Planck's criterion, and the optimal efficiency or the absence of lost work in both of these processes which is the requirement for Carnot's 'neutralization of effects' to take place. That this is so is proved in the next section.

The identification of their differences, on the other hand, starts with Planck's explicit recognition in his quote from Section 1 that the reversibility, or lack of it, of any given process requires a detailed knowledge about the initial and final *equilibrium states* of the transformation but not about the nature of the intermediate steps. Carnot, on the other hand, makes the reversibility or irreversibility of a given process dependent on the nature of *the forces at play* along its evolution. In other words, while the essential notion behind Planck's reversibility is '*the equilibrium state*', those of Carnot are the inter-related concepts of '*force*', '*efficiency*', and '*lost-work*'. This distinction, at the light of the coincidences above noted, might appear superficial when in reality it marks what is an essential separation between Planck's and Carnot's approaches. This distinction will make itself evident when trying to use Planck's essential notion, the equilibrium state, to explain the nature of the intermediate steps of thermodynamic processes.

### 7. An Optimally Efficient Process Is a Constant Total-Entropy Process

Let us start by bringing here, in the form it is commonly written, the equation with which Clausius established the second law of thermodynamics (Clausius, 1879, p. 83), namely

$$\left(-\frac{Q_h}{T_h} + \frac{Q_c}{T_c}\right)_{rev} = 0 \quad (1)$$

The previous equation gives the total entropy change for one cycle in the operation of a reversible heat engine. In it the first term of the left hand side represents the entropy change sustained by the hot reservoir of temperature  $T_h$  in

transferring the amount of heat  $Q_h$  to the cycle's working substance. The second term represents, on its part, the entropy change of the cold reservoir of temperature  $T_c$  upon absorption of an amount of heat  $Q_c$  released to it by the working substance. The fact that these two entropy changes, the only ones taking place in the universe of this heat engine, combine to a total of zero, is usually expressed by saying that the total entropy change for a reversible engine is equal to zero ( $\Delta S_{tot,rev} = 0$ )

For non-reversible (*nr*) heat engines the previous equation becomes:

$$\left(-\frac{Q_h}{T_h} + \frac{Q_c}{T_c}\right)_{nr} > 0 \quad (2)$$

The message conveyed by the previous equation is usually stated by saying that the total entropy change for any non-reversible engine is always positive ( $\Delta S_{tot,nr} > 0$ ). In both of the previous equations it is true that  $T_h > T_c$ ,  $Q_h > Q_c$ , and  $Q_h - Q_c = W$ , with  $W$  representing the work output of the cycle.

Let us then take equation (1), the one expressing the zero total entropy change for the reversible operation, and in it replace  $Q_c$  with  $Q_c = Q_h - W$ . In doing this we get

$$-\frac{Q_h}{T_h} + \frac{Q_h}{T_c} - \frac{W}{T_c} = 0 \quad (3)$$

The previous equation has been written omitting the *rev* sub-index. Factorization of  $Q_h$  and further solution of the resulting expression for  $W/Q_h$  leads us to

$$\frac{W}{Q_h} = \frac{T_h - T_c}{T_h} \quad (4)$$

Recognition of the fact that the quotient  $W/Q_h$  is the efficiency of this reversible engine,  $\eta_{rev}$ , allows us to write equation (4) as follows

$$\eta_{rev} = \frac{T_h - T_c}{T_h} \quad (5)$$

The fact evinced by this simple argument that equation (1) –the one positing the zero total entropy change for reversible engines– finds re-expression in the form of equation (5) means that these two equations are equivalent, and if so, that also equivalent are their respective messages. This way, constant total entropy becomes synonymous with reversible efficiency. Efficiency is not, however, a property or a characteristic of the initial and final equilibrium states of a process, but of the process itself. Work-production requires displacement or change, something alien to any equilibrium state. As expressed in equation (4) efficiency is a measure of the ability of the processes subsumed by what we call a heat engine to produce work out of heat. The fact that a heat engine working at the reversible efficiency is capable of producing the maximum possible amount of work at its conditions of operation means plain and simple that such an operation takes place in the absence of dissipative processes, and if so, also in the absence of any loss of work. At the light of the previous considerations a reversible heat engine can be recognized either by its zero total-entropy change or by its optimal work production efficiency, as these two descriptions, as proved above, are equivalent.

Let us now center our attention on inequality (2) which is the form the law of increasing entropy takes for non-reversible heat engines. When the substitution  $Q_c = Q_h - W$  is in it performed, followed by factorization and rearrangement, we get  $(W/Q_h) < \eta_{rev}$ . Recognition of the fact that in the case being considered the quotient  $W/Q_h$  is  $\eta_{nr}$  allows us to write the previous inequality as follows:

$$\eta_{nr} < \eta_{rev} \quad (6)$$

Again, the reduction of inequality (2) to that given in (6) evinces their equivalence. This way, entropy production becomes synonymous with inefficiency. In line with what was said in regard to equation (5), we can say that inequality (2) is nothing more than a re-expression of the message of equation (6). That all the non-reversible counterparts of a given reversible heat engine are entropic finds then final explanation in the always finite difference existing between their respective efficiencies i.e. in the fact that  $\eta_{rev} - \eta_{nr} > 0$ .

In order to bring this argument to its clear conclusion, we will develop two equivalent equations for the total entropy change of heat engines, reversible or not. One will be given in terms of  $\eta_{rev}$ ,  $\eta_{nr}$ , and  $T_c$ ; the other in terms of the 'lost-work', magnitude to be defined below, and its associated temperature  $T_c$ .

Let us start by comparing the reversible (*rev*) with the non-reversible (*nr*) operations of a given heat engine taking place between heat reservoirs of temperatures  $T_h$  and  $T_c$  where  $T_h > T_c$ , with the working substance in each of these

operations receiving the same amount of heat  $Q_h$  from its hot reservoir. Let us then take equations (1) and (2) and combine them in the following form:

$$\left[-\frac{Q_h}{T_h} + \frac{Q_c}{T_c}\right]_{nr} > \left[-\frac{Q_h}{T_h} + \frac{Q_c}{T_c}\right]_{rev} \quad (7)$$

The previous inequality is a statement of the fact that the total entropy change for the non-reversible operation is larger than that of its reversible counterpart. The already mentioned fact that in each of these operations the same amount of heat is transferred from the hot reservoir to the working substance allows us to write the following simplified version of equation (7)

$$\frac{Q_{c,nr}}{T_c} > \frac{Q_{c,rev}}{T_c} \quad (8)$$

The previous equation can also be written as:

$$\frac{Q_{c,nr} - Q_{c,rev}}{T_c} > 0 \quad (9)$$

The simple argument producing equations (8) and (9) out of (7) allows us to explain the larger entropy change of the non-reversible engine in terms of the larger amount of heat by it transferred to the cold reservoir in comparison to that transferred in the reversible operation. Even if this notion is easily understandable we will, for the purpose of this argument, re-express equation (9) in terms of work. This task starts by recalling the following two facts: 1) that  $Q_h = Q_c + W$ , and 2) that the magnitude of  $Q_h$  is the same for both operations. These two conditions combine to produce the following expression:

$$(Q_c + W)_{nr} = (Q_c + W)_{rev} \quad (10)$$

or equivalently

$$Q_{c,nr} - Q_{c,rev} = W_{rev} - W_{nr} \quad (11)$$

Equation (11) shows that the difference in heat outputs between the non-reversible and reversible heat engines (heat output is heat discarded in the cold reservoir) translates into an equal difference between the reversible and non-reversible work outputs. Thus  $Q_{c,nr} > Q_{c,rev}$  implies that  $W_{nr} < W_{rev}$ . In the reversible engine all of the heat coming out of the hot reservoir ( $Q_h$ ) goes through the work-producing cycle of the variable body and in doing so delivers an amount of work equal to  $W_{rev} = \eta_{rev}Q_h$ . In the non-reversible engine this is not so; in it a portion  $Q_i$  of the heat coming out of the hot reservoir manages -due to, say, lack of proper insulation- to bypass the work-producing circuit of the engine's working substance and ends up, with its work-producing potential untapped, in the cold reservoir. The work output of the non-reversible operation can be calculated either as  $W_{nr} = \eta_{nr}Q_h$  or as  $W_{nr} = \eta_{rev}Q'_h$ . This last expression, in which  $Q'_h$  represents the amount of heat actually subject to the work-producing cycle, allows us to quantify the amount of heat passing directly from the hot to the cold reservoir as  $Q_i = Q_h - Q'_h$ . The work-producing potential of this heat, in the amount  $\eta_{rev}Q_i = \eta_{rev}(Q_h - Q'_h) = W_{rev} - W_{nr} = W_{lost}$ , instead of reaching the engine's mechanical reservoir ends up being wasted as cold heat in the cold reservoir. This is the 'lost work' quantifying the difference in work-outputs between a reversible engine and any of its non-reversible counterparts. If we now combine equations (9) and (11) we will get

$$\frac{W_{rev} - W_{nr}}{T_c} > 0 \quad (12)$$

The difference in total entropy changes evident in equation (7) finds explanation in equation (12) in terms of the different work outputs between these two operations. The previously introduced concept of lost-work ( $W_{lost} = W_{rev} - W_{nr}$ ) allows us to write inequality (12) in the following form

$$\frac{W_{lost}}{T_c} > 0 \quad (13)$$

Let us now bring here the already introduced fact that in heat engines work-output is given as the product of heat intake times the efficiency of the operation, i.e.  $W = \eta Q_h$ . If this notion is used in equation (12) we will get

$$[(\eta_{rev} - \eta_{nr})Q_h/T_c] > 0 \quad (14)$$

Let us now recall that the equation origin of this argument, equation (7), is a re-expression of the statement  $\Delta S_{tot,nr} > \Delta S_{tot,rev}$ . In equations (9), (12), (13) and (14) this statement has transformed into  $\Delta S_{tot,nr} - \Delta S_{tot,rev} > 0$  same which on recognition of the fact that  $\Delta S_{tot,rev} = 0$  becomes  $\Delta S_{tot,nr} > 0$ . If so, the actual messages of equations (13) and

(14) are:  $\Delta S_{tot,nr} = (W_{lost}/T_c) > 0$  and  $\Delta S_{tot,nr} = [(\eta_{rev} - \eta_{nr})Q_h/T_c] > 0$ . The fact, however, that a non-reversible process morphs into a reversible one when  $\eta_{rev} = \eta_{nr}$  allows for the following two general expressions for the total entropy change; one in terms of lost-work, the other in terms of efficiency:

$$\Delta S_{tot} = W_{lost}/T_c \quad (15)$$

And

$$\Delta S_{tot} = [(\eta_{rev} - \eta_{nr})Q_h/T_c] \quad (16)$$

In equations (15) and (16),  $\Delta S_{tot}$  represents the total entropy change of any given heat engine, reversible or not. That it subsumes the zero total-entropy change for reversible engines can be proved by substituting in equation (15) their essential operational characteristic expressed as  $(W_{lost})_{rev} = 0$ ; and in equation (16) the fact that when the efficiency of any given engine becomes identical to the corresponding reversible efficiency it will be true that  $\eta_{rev} - \eta_{nr} = 0$ .

The previous argument proves our earlier statement that the evident equivalence existing between Planck's 'restoration of the initial condition' and Carnot's 'neutralization of effects' was the result of a similar equivalence existing between the notions giving sustenance to one and the other. We also stated there that beyond these coincidences these two perspectives to reversibility differ. While Carnot's lost-work approach is capable of providing a rational and commonsensical description/explanation of the reversible process, Planck's isn't. This is the matter of the following sections.

### 8. Carnot and the Reversible Process

Let us start recognizing that the word 'process' subsumes the notions of change, transformation, evolution, etc., and that none of these characteristics can arise without the action of a force. The fact that forces can be either conservative or dissipative combined with the fact that Carnot's no-lost-work condition for reversibility requires the absence of the latter kind means that any process, finite or infinitesimal, propelled solely or exclusively by conservative forces will comply with the no-lost-work-condition. The absence of dissipative forces means no-lost-work, and no-lost work means optimal efficiency in regard to both, work production and work consumption. Nothing else needs to be added to Carnot's original insight: reversible processes are those taking place in the absence of dissipation and the fact that the complete elimination of dissipation from any natural process is impossible is the reason why these processes are also impossible. Going a little deeper it can be said that the impossibility of reversible processes stems from the fact that dissipative forces cannot be uncoupled from conservative forces. In the words of O'Connell and Haile:

Even though a quasi-static process is driven differentially, the driving forces may still contain dissipative components. These components may arise because some properties have finite differences across boundaries or they may arise from differential effects accumulated over a finite process. If we could remove all dissipative components...so the process would be driven only by conservative forces, then the change of state would be reversible. (2005, p. 22)

That Carnot's perspective of reversibility in terms of lost-work and associated notions encompasses the whole of the process i.e. the initial and final equilibrium states in addition to the intermediate steps, can be understood by realizing that no work can be lost if none can in principle be generated, situation arising in the absence of any driving force, i.e. at equilibrium.

The following quotes not only characterize the state of equilibrium they also bring out in a clear way the connection between equilibrium and work. Pitzer and Brewer understand the state of equilibrium as "a state of rest" (1961, p.16); for Reiss "equilibrium precludes change" (1965, p. 9), while for Hill "...there are no net processes taking place inside the system or between the system and its surroundings" (1966, p.2). On this same issue Weber and Meissner tells us that spontaneous processes occur:

...because of the action of unbalanced potentials...If an unbalanced potential does exist in a system, it can always somehow be harnessed so that, during the occurrence of the spontaneous process, work may be done on the surroundings. Therefore, an alternative test for equilibrium in a system is to determine whether, during any conceivable change, the system would do net work on the surroundings. If work could be done, the system is not in equilibrium. (1957, pp. 35-36)

A similar statement is advanced by Maron and Prutton:

All changes in nature are due to a tendency on the part of the system to reach a condition of maximum stability commensurate with the state of each system, i.e. equilibrium. Once equilibrium has been reached, the propensity toward further change disappears...As long as a system is away from equilibrium, it will experience a tendency to reach that state...Work results when the tendency to attain equilibrium is harnessed in some way.

From a system in equilibrium no work can be obtained, but a system on the way to equilibrium may be made to yield useful work. (1965, p.189)

The fact that work demands, by definition, the action of a force means plain and simple that in the absence of a driving force no work can be generated and if so, no work can be lost. The power of Carnot's approach to reversibility, or lack of it, in terms of lost-work finds manifestation in that both, 'the thermodynamic process' –no lost-work due the sole action of conservative forces- as well as 'the state of equilibrium' –no lost-work because no work can in principle be generated- can be precisely characterized by it.

### 9. The Nature of the Intermediate Steps of a Process From Planck's Perspective

Disregard of Carnot's position on this issue leads to a completely different conceptualization of the reversible path. To exemplify it let us start noticing that in the equation for the total-entropy change for the irreversible heat transfer depicted in Figure 1(a), namely  $\Delta S_{tot}[1(a)] = Q(T_h - T_c)/(T_h T_c)$ , we will have  $\Delta S_{tot}[1(a)] = 0$  for a temperature gradient of zero, i.e. for  $T_h = T_c$ , or in other words, at equilibrium. The fact that in Planck's perspective the zero total-entropy change characterizes the whole of the reversible path brings forth the inescapable conclusion that such a path is nothing more than a succession of equilibrium states. The problem here is that none of these equilibrium states is capable of any work output, situation that stands in direct opposition to the notion that (spontaneous) reversible processes are optimally efficient in regard to work production.

From the second law it is learned that all natural change is accompanied by a total-entropy increase; that negative total-entropy changes indicate impossible processes, and that, as previously exemplified via a heat transfer process, zero-total entropy changes are characteristic of the equilibrium condition. These notions should make clear from the start the logical difficulties accompanying Planck's total-entropy perspective when attempting to describe/define the 'reversible process' given the fact that while reversible means equilibrium, and equilibrium in turn means 'inability to change'; 'process', on the other hand, means change, transformation, evolution. When considered within Planck's conceptual frame, the phrase 'reversible process' becomes an oxymoron.

### 10. Reversible Processes as a Succession of Equilibrium States

The desire on the part of Planck's disciples to know the details of the intermediate steps of reversible processes was not deterred by the master's disregard for this part of the process. This will to know led to a number of descriptions/definitions of the thermodynamic path involving the concept of 'quasi-static' process as well as the already introduced notion of a path constituted by a sequence of equilibrium states.

In reference to reversible processes Kestin states that:

...when such a process was performed, the system remained in equilibrium at every stage; it consisted of a continuous sequence of states of equilibrium. An ideal process of this type is said to be reversible. (1966, p. 127)

On this same issue Barrow tells us that "A process or reaction for which there is no tendency to proceed in either direction has been described as balanced, or reversible" (1973, p. 168).

Smith, on his part, posits that:

If a change occurs so that the system is always in equilibrium, then the change will proceed infinitely slowly and will be capable of doing the maximum amount of work. Such a change we call 'reversible'. The conditions that must be satisfied for a reversible change are the same conditions that must be satisfied if the system is to be in a state of equilibrium. (1973, p. 21)

Having learned that all actual change in nature is accompanied by a total-entropy increase and that total-entropy decreasing processes are forbidden by the second law, it can only be concluded that if any change is to be experienced by a system in equilibrium it will have to be accompanied by a zero-total entropy change, which is another way of saying that changes taking place with a zero total-entropy change, so-called reversible changes, change nothing. If in a reversible process the system, as Kestin states, is to remain in an equilibrium state at every stage of the process one cannot help but to ask how is it that the transit from one equilibrium state to the next one is to take place. Miracles aside, a system in equilibrium will remain in that state unless there is a gradient or imbalance of potentials to propel the system's change, the problem is that a gradient, however small, is impossible in a state of thermodynamic equilibrium. This is the conceptual contradiction inherent to all those explanations of reversible processes in terms of a sequence of equilibrium states. The said contradiction leads to the paradoxical notion advanced by Koyré of "a change without change." (Quoted by Prigogine 1980, p. 2)

Note that in his quote, Smith's goes as far as to link work-production with systems in equilibrium, when, as we know, no such thing is possible. We have to accept that, again, magic aside, the transit of the system from one equilibrium state

to the next is unexplainable without the concurrence of a force. In the absence of such a force the system will never actually abandon its original condition and no process will take place. This move to include 'forces' in the explanation of the reversible transit, it should be agreed, is a move away from Planck's position –to which 'force' is an alien concept- and in the direction of Carnot's perspective to reversibility. A number of definitions of 'reversible process', in which the just noted inconsistency is removed, are given below:

The reversible path must be one for which the internal forces of the system differ only infinitesimally from the external forces, and for which all heat transfers take place over temperature differences which are only infinitesimal. (Denbigh, 1968, p. 41)

Any process, which is so conducted that at every stage the driving force is only infinitesimally greater than the opposing force, and which can be reversed by increasing the opposing force by an infinitesimal amount, is called reversible. (Maron & Prutton, 1965, pp. 109-110)

Particularly important among the thermodynamic states of a system are the states of equilibrium. These states have the property of not varying so long as the external conditions remain unchanged...Very often we shall have to consider transformations of a system from an initial state to a final state through a continuous succession of intermediate states...A transformation is said to be reversible when the successive states of the transformation differ by infinitesimals from equilibrium states. (Fermi, 1956, p. 4)

A reversible process consists of a series of states of equilibrium which follow one another; the direction in which the process will proceed from any one state of equilibrium to another depends on the sign of an infinitely small force, both directions being equally possible. (Schmidt, 1966, p. 91)

It is only logical to infer that any process propelled by an infinitely small force will take an infinite amount of time to occur or, equivalently, that any such process will unfold at an infinitely small rate. It is precisely on reason of this that these processes have also been called 'quasi-static processes'. In concordance with the meaning of the prefix quasi = almost, we find the following definitions for quasi-static in the thermodynamic literature: for Callen "The infinite-slowness of the process is, roughly, the essential feature of a quasi-static process" (1985, p. 19); For Pauli a quasi-static process is a "slowly occurring" process (1973, p. 7); For Kestin "quasistatically" means "infinitely slowly" (1966, p. 110); for Fast: "Strictly speaking, only processes which occur infinitely slowly can be completely reversible, since more rapid change requires finite forces and temperature differences." (1970, p. 12). The connection between quasistaticity and reversibility can be learned from the following quotes. For Pauli: "A quasi-static process is always reversible" (1973, p. 17); while for Haase: "quasistatic equals reversible" (1969, p.3).

Apart from the fact that the variable 'time' is not a member of the catalog of variables of classical thermodynamics and if so, neither is the rate at which thermodynamic processes evolve, field this last one constituting the subject matter of kinetics, the previous definitions imply that when a particular small rate of occurrence is reached –the rate that justifies referring to any such process as quasi-static- the process somehow becomes reversible. At this light the reversibility of a process appears to be a sole function of its rate of occurrence, and not as Carnot and Planck respectively claim, of the absence of lost-work or of the total-entropy change, situation this that effectively makes of classical thermodynamic a section of kinetics.

An important notion either explicit or implied by these definitions in terms of infinitesimal forces is the one asserting that in these infinitesimal paths the process can be made to evolve in the opposite direction by the simple expedient of, as expressed in Maron and Prutton's previous quote "...increasing the opposing force by an infinitesimal amount"; or by Waser "A reversible path is one that may be followed in either direction. At any point the direction may reversed by a small change in a variable such as temperature or pressure" (1966, p. 13), and also by Pitzer and Brewer for whom reversible is a "...process so conducted that at every stage an infinitesimal change in the external conditions would cause a reversal in the direction of the process..." (1961, p. 77). What these authors appear to forget is that no change takes place without a reason, without a cause, or without a price. Reversing a spontaneous process such as the heat transfer depicted in Figure 1(a) means plain and simple that heat has to flow from the colder to the hotter body against the temperature gradients operating between consecutive intermediate heat reservoirs and for this to happen work has to be expended; even so, work is not even mentioned in the previous quotes. If we apply to process 1(a) Waser's prescription of introducing what he calls a "...small change..." in temperature to produce the flow of heat in the opposite direction we would have to change the temperature of the cold reservoir from  $T_c$  to  $T_h$ , that of the hot reservoir from  $T_h$  to  $T_c$  and the temperatures of the intermediate reservoirs as required, or even more simply, to shift the position of these reservoirs accordingly. Once we do this we will realize that we haven't reversed the process as in the new setting heat will still be flowing from the hotter to the colder body.

The previous considerations, even if limited in extent, convey some of the bizarre ideas –to say it mildly- that current thermodynamics has to depend on to try to make sense of the reversibility concept when looked from Planck's

total-entropy perspective. Accepting them implies the rejection of what might very well be a cardinal notion of our discipline: “That thermodynamics is an experimental science, and not a branch of metaphysics” [McGlashan, 1979, Preface]. The quote perfectly fits the divide between Carnot’s and Planck’s perspective to reversibility. While the former takes form in terms of notions –lost-work and efficiency– concepts that lie within the realm of our experience; notions that are susceptible of quantification, even of sensible identification –I doubt there is a reader who hasn’t felt the heat coming out of the dissipation of mechanical work taking place in an electric motor, or that radiating from the motor of an automobile originating in the inevitable friction between piston and cylinder, or benefited from the heat coming out of an electrical resistor-heater. The said concepts form part of our physical reality and can be subject to experimentation, say, for efficiency determination purposes, or directed at finding better lubricants, better insulators, etc. Compare the previous statements with the perspective based on Planck’s total-entropy criterion which requires, as in the previous quote by Kestin, a reversible process to be composed of a succession of equilibrium states. Given that an equilibrium state is, as previously noted, a state of rest, and that the action of a physical force is not contemplated in this scenario, it is only by accepting that change can take actually place without a cause, or by accepting the intervention of a metaphysical agency (either miracle or magic) that the transit from one equilibrium state to the next can be explained. In the absence of this agent the system would remain for ever in its initial equilibrium condition as there is no cause, no reason for it to abandon it. The same situation arises when stating that a reversible process is composed by a succession of states only infinitesimally away from equilibrium. Serves well to remind us here that either a system is in equilibrium, or it is not. If not, the system will inevitably experience change –the rate at which it does it being immaterial. But change, according to the second law, leads inevitably to the production of entropy, and if this is true then the systems evolving infinitesimally away from equilibrium are producing infinitesimal amounts of entropy and on reason of this they turn out to be irreversible, not reversible as assumed. Accepting the previous notion requires, again, the concurrence of a metaphysical agency capable of bending up a little bit the laws of nature in a way such that the said irreversible processes can pass for reversible.

The contrast between Carnot’s and Planck’s perspectives take this way the form of the contrast between the pragmatic, experimental view of nature of the former, and the metaphysical, idealist view of the nature of the latter which deep at its core assumes that nature behaves according to our ideas and pre-conceptions.

Let us note here that Pitzer and Brewer, even if subscribing the notion of reversibility in terms of infinitesimal forces, they also recognize reversibility in terms of the lack of dissipation:

When we speak of an actual process as being always irreversible, we have in mind a distinction between such a process and an ideal process which, although never occurring in nature, is nevertheless imaginable. Such an ideal process, which we shall call reversible, is one in which all friction, electrical resistance, or other such sources of dissipation are eliminated. (1961, p. 77)

This appears to be the proper place to introduce the following quote from Truesdell who in reference to quasistaticity states the following:

Just here, I think, is where the tradition of the late nineteenth century stumbled into the dismal grimpen of obscurity. It refused to recognize the concept of constitutive relation, which the pioneers had used fluently, informally, and correctly. It gave up the concreteness of the pioneers, who usually spoke of air, carbonic acid gas, steam, water, and such materials; after the oracling of Clausius it turned away from engines and other applications to the visible, palpable circumstances of man, instead it grew portentous about the universe, which man cannot experience, let alone subject to experiment; seeing the breadth of Gibbs thermostatics, it claimed by fiat that thermodynamics existed only for nearly static circumstances; it took ‘quasi-static’ as primitive, explained only by psychic and rhetorical exclamation, ungraced by mathematical definition or logical hygiene of any kind. (1984, p. 32)

In turning away from Carnot’s interpretation of reversibility in terms of the human-experience-accessible concept of lost-work and dissipative forces, and adopting instead, indiscriminately, the ones making use of a succession of equilibrium states or the quasi-static concept, thermodynamics found itself, either by accident or design, complying with Planck’s *Magister Dixit* requiring the removal of any trace of anthropomorphism from physical theory (Planck, 1998, p. ix-x). It is in this senseless practice of defining the essential notions of classical thermodynamics in terms alien to human experience where this author finds the ultimate reason for the neglect of Carnot’s ideas on this matter. This state of affairs finds illustration in the following quote, also by Truesdell, which makes reference to Caratheodory’s principle:

A student bursts into the study of his professor and calls out: ‘Dear Professor, dear professor. I have discovered a perpetual motion machine of the second kind!’ The professor scarcely takes his eyes of his book and curtly replies: ‘Come back when you have found a neighborhood  $U$  of a state  $x_0$  of such kind that every  $x \in U$  is

connected with  $x_0$  by an adiabat.’

Contrast this demand with ‘Show me a cyclic heat-engine that works with an efficiency greater than  $1 - T_{\min}/T_{\max}$ ’ or ‘Show me a cyclic heat-engine that does positive work yet emits as much heat it absorbs’. (1986, p. 118)

## 11. Discussion

Two are, apparently, the ways available to approach the reversibility issue: One, based on Carnot’s approach, is that of exclusion, i.e. excluding from real, irreversible processes all that which separates them from the ideal situation, even if the separation is in practice impossible. Case in point that of separating or uncoupling dissipative from conservative forces to stress the fact that any process driven exclusively by the latter kind is a reversible process. The other way, the one based on Planck’s perspective, also the most popular among thermodynamic authors, is that of delusion (An unshakable...belief in something false and impossible, despite evidence to the contrary: <https://psychcentral.com/encyclopedia/delusion/>), which in the case at hand takes the form of trying to pass an irreversible process as reversible, or, equivalently, trying to pass the impossible as possible. Case in point the use of infinitesimal gradients or infinitesimal forces as drivers of reversible processes even if aware that any gradient, however small, is bound to produce entropy. The following quote is illustrative in this regard:

The reversible path must be one for which the internal forces of the system differ only infinitesimally from the external forces, and for which all heat transfers take place over temperature differences which are only infinitesimal. (Denbigh, 1968, p. 41)

Instead of telling us that reversibility requires any heat transfer to take place with a *zero* temperature gradient and that it is precisely because of this that such a process is impossible, Denbigh chooses to illustrate reversibility with an irreversible heat transfer process. The delusional attitude of thermodynamic authors takes form in the implied message found in text-books as well as in the classroom that the impossibility of reversible processes is not absolute, not total, but almost total, or only a little bit away from total, and that in being this so a reversible process, as posited by Denbigh, can be produced with an almost zero temperature gradient. If we bring here the equation for the total entropy change of process 1(a), namely  $\Delta S_{tot} = Q(T_h - T_c)/(T_h T_c)$  we will realize that  $\Delta S_{tot} = 0$  if and only if  $T_h = T_c$ . In any other situation, even if the difference is infinitesimal, i.e. even if  $T_h - T_c = dT > 0$  we will have  $\Delta S_{tot} = QdT/(T_h T_c) > 0$ , and Denbigh process, assumed reversible, turns out to be irreversible.

The requirement for the restoration of the initial condition is not that the final state of the inverse path be close, or somewhat close, or really close, or really, really close to the initial state of the forward path. Those are cook-book-like specifications, not scientific statements; either the values of the relevant thermodynamics variables  $T$ ,  $P$ ,  $x_i \dots$  (temperature, pressure, compositions, etc.) coincide or they do not; either the final state is identical to the initial state or it is not. If not, restoration has not been accomplished and the process is irreversible.

## 12. Conclusion

The reversibility definition originating in Carnot’s lost-work notion which makes reversible any process evolving in the absence of dissipative forces turns out to be a simpler and controversy-free way to discriminate reversible from irreversible processes. The dissipative, work-losing effects of friction, electrical resistance, conduction, etc., are well known to most of us; not only that, the fact that those effects just cannot be eliminated is either known or suspected also by most of us, thermodynamicist or not. In view of this it is just unexplainable how this avenue to the discussion/definition of reversibility can be sidelined for that which sees the reversible process as a sequence of equilibrium states, or quasi-static processes.

The faithful of thermodynamics orthodoxy may object, it isn’t easy after all to accept new ideas (not really new, Carnot wrote his memoir in 1824) even if correct, when these ideas contradict long held beliefs, even if incorrect. A similar statement has been previously expressed by Leo Tolstoy (1899, p. 124).

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