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On the Uncertain Foundation of the Law that Entropy Increases I: The Egregious Error in Clausius' Principle of the Equivalence of Transformations

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Abstract

The conceptual inconsistencies lying at the core of Clausius' work leading to his principle of the equivalence of transformations, the name with which he originally designated the second main principle of the mechanical theory of heat, as well as those of the body of knowledge, namely current second law thermodynamics, which eventually replaced some of Clausius original notions are here located and their consequences discussed. At the light of our results the foundation of what is supposed to be the supreme law of nature appears to be not as firm as commonly believed. An experimental test is suggested for the notion on which the validity of the second law, as currently understood, is based, namely the zero total-entropy change for the reversible transformations of heat into work and vice versa.

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Many fail to grasp what they have seen,
And cannot judge what they have learned,
Although they tell themselves they know.
Heraclitus [Fragments, Penguin Classics, 2001, p. 5]

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Keywords: Heat engines; Clausius corrects Carnot's theorem; Clausius' flawed principle of the equivalence of transformations; Equivalence values; Entropy; The second law; Post-Clausius thermodynamics contradicts some of Clausius results.

1. Introduction

1.1. Antecedents: Carnot and the Motive Power of Heat

Carnot was perfectly aware that the increased availability of mechanical work made possible by the steam-engine (heat-engines) was the driving force propelling that period of rapid change in manufacturing processes as well as standards of living we now refer to as the industrial revolution. In his own words:

> *Nature, in providing us with combustibles on all sides, has given us the power to produce, at all times and in all places, heat and the impelling power that is the result of it...From this immense reservoir we may draw the moving force necessary for our purposes....To develop this power, to appropriate it to our uses, is the object of heat engines...Already the steam-engine works our mines, impels our ships, excavates our ports and our rivers, forges iron, grinds grains, spins and weaves our cloths, transport the heaviest burdens, etc....The study of these engines is of the greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world... If, some day, the steam-engine shall be so perfected that it can be set up and supplied with fuel at small cost, it will combine all desirable qualities, and will afford to the industrial arts a range the extent of which can scarcely be predicted. It is not merely that a powerful and convenient motor that can be procured and carried anywhere is substituted for the motors already in use, but that it causes rapid extension in the arts in which it is applied, and can even create entirely new arts."* This level of perfection was, at the time of Carnot, far from being a real possibility. The reason being that: *"Notwithstanding the work of all kinds done by steam engines, notwithstanding the satisfactory condition to which they have been brought today, their theory is very little understood, and the attempts to improve them are still directed almost by chance."* It was to the understanding of the *"...phenomenon of the production of motion by heat..."* and through it to the establishment of *"...principles applicable not only to steam-engines but to all imaginable heat-engines, whatever the working substance and whatever the method by which it is operated..."* what Carnot's efforts were directed to Carnot [1].

Carnot's work on these issues was indeed fruitful as he was capable of providing an almost complete characterization of the transformation of heat into work as it takes place in heat engines. Working within the confines of the caloric theory of heat he was capable of bringing forward the following principles: 1) "...the production of heat alone is not sufficient to give birth to the impelling power: it is necessary that there should also be cold...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 temperatures [1]." For Raman the previous statement represents "...the very first formulation of the second law of thermodynamics." [2] "Heat can evidently be

a cause of motion only on virtue of the changes of volume or of form which it produces in bodies...These changes are not caused by uniform temperature, but rather by alternations of heat and cold...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); 3) To his realization, made explicit in the previous quote, that continuous work output in heat engines demanded an also continuous succession of contradictions and dilatations of the variable body, is where the origin of his cycle of operations can be traced. Carnot's cycle, shown in Figure 3(*g*) as the closed path *ABCDA*, consists of four reversible processes: *AB* is an isothermal expansion at the temperature T_h of the hot reservoir; *BC* is an isentropic expansion decreasing the temperature of the variable body to that of the cold reservoir of magnitude T_c; *CD* is an isothermal compression at the temperature of the cold reservoir, and *DA*, closing the cycle, an isentropic compression taking the temperature of the gas back to that of the hot reservoir; 4) As to the condition required to be fulfilled for a heat engine to output the maximum of work he stated "The necessary condition of the maximum is, then, 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 that this condition is fulfilled the maximum will be attained" [1]; the reason for such a condition stemming from the fact that *"...*contact between bodies of different temperatures (cause) loss of motive power*"* [1]. Note that the presence of conductive dissipation, characterized by Carnot in terms of a diminished work output, produces what we now call an irreversible operation; 5) With the previous notions in place, Carnot went on to face an essential question related to the transformation of heat into work in heat-engines:

> *The question has often been raised whether the motive power of heat is unbounded, whether the possible improvements in steam-engines have an assignable limit –a limit which the nature of things will not allow to be passed by any means whatever; or whether, on the contrary, these improvements may be carried on indefinitely. We have long sought, and are seeking today, to ascertain whether there are in existence agents preferable to the vapor of water for developing the motive power of heat; whether atmospheric air, for example, would not present in this respect great advantages* [1].

Carnot's argument that was to lead to the required answers was centered on the concatenation of an optimally efficient engine with its equally efficient inverse, i.e. a refrigerator. In the former work was produced 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" [1] These two bodies were 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*"* [1]. 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* [1].

Let us first of all note that in his previous quote Carnot is referring to optimally efficient operations characterized by "...no loss of motive power...", i.e. to an engine outputting the maximum of motive power and, consequently, to a refrigerator demanding the minimum. It is then on optimally efficient operations –reversible operations- where his analysis is centered on.

The reversal of effects made possible in this coupling of two optimally efficient and inverse operations on reason of the identity in the amount of work generated by the first operation and that demanded by the second one led Carnot to the following conclusion

> *Now, if there existed any means of using heat preferable to those which we have employed, that is, if it were possible by any method whatever to make the caloric produce a quantity of motive power greater than we have made it produce by our first series of operations, it would suffice to divert a portion of this power in order by the method just indicated to make the caloric of the body B return to the body A from the refrigerator to the furnace, to restore the initial conditions, and thus be ready to commence again an operation precisely similar to the former, and so on: this would be not only perpetual motion, but an unlimited creation of motive power without the consumption either of caloric or of any other agent whatever. Such a creation is entirely contrary to the ideas now accepted, to the laws of mechanics and of sound physics. It is inadmissible.*
>
> *We should then conclude that...the motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of the caloric* [1].

Carnot's theorem, as this last statement is also known, explicit the answers to some of the questions previously advanced. This way, for a given amount of caloric and a given temperature difference no particularity introduced in

the design, or operation, or choice of working substance have any effect on the maximum amount of work obtainable from an optimally efficient heat engine. It is all a matter of the temperatures involved. In Carnot's theorem making evident the impossibility of different work outputs for two optimally efficient cycles working with the same amount of caloric between the same two sources of heat we find, on the other hand, the very first expressions of those versions of the second law of thermodynamics commonly expressed as *"...all reversible cycles which work between the same two sources of heat have equal efficiencies"* and "*...the efficiency of an irreversible cycle is smaller than that of a reversible cycle, when both operate between the same temperatures*" [3]. Let us finally note that in Carnot's 'neutralization' of effects between two optimally efficient and inverse operations we also find the very first definition of thermodynamic reversibility.

At this point in his analysis most of the foundation of the science of heat engines had been laid. All the pieces of the puzzle were there, except one: the functional relation between the efficiency of the operation and the temperature of the reservoirs. Even if he correctly asserted that higher work outputs require larger temperature differences [1] and also that *"...a given quantity of heat will develop more motive power in passing from a body kept at 1 degree to another maintained at zero, than if these two bodies were at the temperature of 101° and 100°"* [1] he was incapable of getting at the actual mathematical expression connecting efficiency and the said temperatures. In his own words *"We are not prepared to determine precisely, with no more experimental data than we now possess, the law according to which the motive power of heat varies at different points on the thermometric scale"* [1].

The accomplishment of this task: the mathematical definition of the reversible efficiency, among others, was reserved for Clausius. This is the matter of the following section.

2. Clausius Corrects and Extends Carnot's Work
2.1. Clausius Conclusion of Carnot's Work

In 1832, eight years after the publication of his book *Reflexions sur la Puisssance Motrice du Feu* (Chez Bachelier, Libraire, Paris, 1824) in which he consigned the results of his study on the transformation of heat into work taking place in heat-engines, Carnot dies at age thirty six. As Angrist and Hepler note, "Except for some attention from Émile Clapeyron, (Carnot's results) lay dormant for some twenty five years...*"* [4] until Clausius took over the analysis at the point Carnot had left it.

Clausius introduced two critical modifications into Carnot's work. He abandoned the caloric theory of heat underwriting Carnot's analysis, and chose a different basis of proof for his results. The first of these modifications brought Carnot's work in compliance with the results of Rumford, Mayer, Joule, and others regarding the interconversion between heat and work. The work of these scientists was essential to the final acceptance of the principle of the conservation of energy, or as Clausius would name it: The first fundamental principle of the mechanical theory of heat. From this perspective, Carnot's assumption that the production of work in heat-engines is not due "...to an actual consumption of the caloric, but to its transportation from a warm body to a cold body" [1] had to be abandoned and replaced with the newly adopted ideas about heat and work. In Clausius words:

> *This way of dealing with the question does not accord with our present views, inasmuch as we rather assume that in the production of work a corresponding quantity of heat is consumed, and that in consequence the quantity of heat given out to the surrounding space during the cyclical process is less than that received by it. Now, if for the production of work heat is consumed then...there is no ground for saying that the work is created out of nothing...Accordingly not only must the principle enunciated by Carnot receive some modification, but a different basis of proof from that used by him must be discovered* [5].

Clausius new basis of proof took form in that "statement of experimental truth" as Schmidt calls it [3], expressed by Clausius as "Heat cannot, of itself, pass from a colder to a hotter body" [5].

If the amount of heat made available per cycle of operation by the hot reservoir to the variable body is designated as Q_h; the one transferred by the variable body to the cold reservoir as Q_c, and the work output of the cycle as Q or, equivalently, as W, then Clausius correction to Carnot's position means that $Q_h = Q_c + Q = Q_c + W$. It is then understood that Q is the portion of Q_h that ends up as work in some mechanical reservoir. The amount of heat Q_c is the one, using Clausius words, being "carried over" to the cold reservoir.

Armed with these new notions Clausius was able, in 1850, first to reword and then to prove the correctness of Carnot's theorem in its new form. Clausius version of Carnot's theorem read as follows *"...the relation between the quantity of heat carried over, and that converted into work, is independent of the nature of the matter which forms the medium of the change...(and depends only) on the temperatures of the two bodies...which act as heat reservoirs"* [5]. The proof carried on by Clausius, identical in essence to the *reductio ad absurdum* proof previously used by Carnot [1], showed that denying the validity of the theorem implied the unassisted transference of heat from a colder to a hotter body, result that stands in direct contradiction with experience [5]. Even if in his theorem Clausius makes reference to the ratio Q_c/Q, the actual ratio he first determined was Q_h/Q_c, the reason being that this is the ratio the equations by him used lead to in a direct form. From this ratio, it should be noted, the other two ratios between the three heat-magnitudes here involved, namely Q/Q_h, and Q_c/Q can be determined by substituting in Q_h/Q_c the required form of $Q_h = Q_c + Q$. Clausius set his attention on $Q_h/Q_c = \phi(T_h, T_c)$ in which, as stated in his theorem

> $\phi(T_h, T_c)$ *is some function of the two temperatures, which is independent of the nature of the variable body."* The independence of ϕ on the nature of the variable body offered Clausius *"...a ready means of determining this function, since as soon as we know its form for any single body it is known for all bodies whatsoever...Of all classes of bodies the perfect gases are best adapted for*

such a determination, since their laws are the most accurately known. We will therefore consider the case of a perfect gas subjected to a cyclical process, similar to that ...here reproduced... [5].

The cyclical process Clausius is referring to in the previous quote corresponds to that represented in Figure 3(*g*).

Let us now agree that the work output of Carnot's reversible cycle, as represented in Figure 3, is the sole matter of isothermal processes *AB* and *CD* there taking place, and this is so on reason of the inverse relation existing between isentropic processes *BC* and *DA* which translates into the work produced by expansion *BC* being precisely that required to be spent in forcing compression *DA* to take place, or that produced by *AD* consumed by *CB* in an inverse Carnot cycle (a Carnot refrigerator). The proof of this is starts by recognizing that for isentropic processes the first law reduces to $\Delta U = -W$. For Clausius' cycle with a perfect gas as the variable body we can then write, for processes *BC* and *DA*, the following expressions $\Delta U_{BC} = -W_{BC} = C_v(T_c - T_h)$ and $\Delta U_{DA} = -W_{DA} = C_v(T_h - T_c)$ respectively, from which it follows that $\Delta U_{BC} + \Delta U_{DA} = 0$ and $W_{AB} + W_{DA} = 0$.

The determination of the function ϕ started with Clausius writing the laws relating the heat exchanged, the ratio of the volume changes, and the corresponding temperatures of isothermal processes *AB* and *CD* in the following manner $Q_h = RT_h ln(V_B/V_A)$ and $Q_c = RT_c ln(V_C/V_D)$. In the previous equations R stands for the ideal gas constant, T_h the temperature of the hot reservoir, T_c the temperature of the cold reservoir, V_A and V_B are the initial and final volumes of the ideal gas in isothermal expansion *AB*, and V_c and V_D the initial and final volumes of the gas in isothermal compression *CD*. Also available to Clausius were the laws for isentropic processes *BC* and *DA*. From these equations he obtained the following relation $V_B/V_A = V_C/V_D$. He then proceeded to combine the expression obtained by taking the ratio between the laws for the isothermal steps, namely $Q_h/Q_c = (T_h/T_c)[ln(V_B/V_A)/ln(V_C/V_D)]$ with the one obtained from the isentropic steps to obtain the following expression $Q_h/Q_c = T_h/T_c$ [5] The substitution in this last equation of $Q_h = Q_c + Q$ followed by some algebra leads to $Q_c/Q = T_c/(T_h - T_c)$, and, following the same procedure, the substitution of $Q_c = Q_h - Q$ led to that expression which evaded Carnot's efforts, namely the one relating work output and heat intake which is seen taking the following form $Q/Q_h = W/Q_h = (T_h - T_c)/T_h < 1$ In this last equation, it should be recognized, the quotient on the left hand side represents the reversible efficiency, $Q/Q_h = W/Q_h = \eta_{rev}$, and from it we learn that the possibility raised by Carnot to the effect that *"...the possible improvements in steam-engines have an assignable limit –a limit which the nature of things will not allow to be passed by any means whatever..."* [1] turned out to be a certainty; in other words the complete conversion of the intake heat into work is impossible in cyclical process. The fact that this conclusion is not contemplated, nor predicted, or subsumed in the first principle of the mechanical theory of heat indicates that this notion belongs to a new and separate parcel of knowledge of the mechanical theory of heat, and that in this new parcel of knowledge $Q_h/Q_c = T_h/T_c$ or any of its equivalent expressions plays a central role.

Two avenues of inquiry opened to Clausius, stemming both from this last equation. One was to lead to the entropy function, and the other to a new statement for the central principle of this new parcel of knowledge that was to become the second law of thermodynamics. This new statement turned out to be, however, independent of any consideration about the limited convertibility of heat into work in cyclical processes. We will consider them in the following two sections.

2.2. The Entropy Function

In order to assure himself that the expression $Q_h/Q_c = T_h/T_c$ or, equivalently $-(Q_h/T_h) + (Q_c/T_c) = 0$, was indeed a general principle and if so that equations of the same form applied to any reversible cyclical process whatsoever, Clausius extended his analysis to reversible cycles of different degrees of complexity. For those in which "*...the taking in of positive and negative quantities of heat takes place at more than two temperatures*" [5] he found that, just like simple cyclical processes in which heat is exchanged at two temperatures only,

...any other cyclical process, which can be represented by a figure consisting solely of isothermal and isentropic lines, and which has any given number of temperatures at which heat is taken in, may be made to yield an equation of the same form, viz. $(Q_1/T_1) + (Q_2/T_2) + (Q_3/T_3) + (Q_4/T_4) + \cdots = 0$, *or generally* $\sum(Q/T) = 0$. [5]

In the former equation the numerators are signed magnitudes, positive for heat taken in, negative for heat given out. For cyclical processes in which the taking in of heat is simultaneous with changes of temperature the result obtained took the following form $\int \frac{dQ}{T} = 0$. About this last expression he further stated:

This equation, which was first published by this author in 1854 (Pogg. Ann. Vol. 93, p. 500)...may be expressed as follows: If in a reversible Cyclical Process every element of heat taken in (positive or negative) be divided by the absolute temperature at which it is taken in, and the differential so formed be integrated for the whole course of the process, the integral so obtained is equal to zero.

If the integral $\int \frac{dQ}{T} = 0$, *corresponding to any given succession of variations of a body, be always equal to zero provided the body returns finally to its original condition, whatever the intervening conditions may be, then it follows that the expression e the integral sign, viz.* dQ/T, *must be a perfect differential of a quantity, which depends only on the present state of the body, and is altogether independent of the way in which it has been brought into that condition. If we denote this quantity by S, we may put* $dQ/T = dS$ *or* $dQ = TdS$, *an equation which forms another expression, very convenient in the case of certain investigations, for the second Main principle of the Mechanical Theory of Heat* [5]

This function *S* received from Clausius the name entropy, after the Greek word "τροπη" meaning transformation [5].

The familiar notion that at the conclusion of a reversible cycle, defined by the return of the variable body to its initial condition, only two changes remain, these being those sustained by the hot reservoir of temperature T_h in releasing the amount of heat Q_h and that of the cold reservoir of temperature T_c in taking in the amount of heat Q_c, means that the expression $-(Q_h/T_h) + (Q_c/T_c) = 0$, in representing the combination of all the entropy changes taking place in the said reversible cycle, is a total-entropy change. In this vein the message of the previous expression is that the total-entropy change for a simple reversible cyclical process is equal to zero.

2.3. Toward a Statement for the Second Main Principle of the Mechanical Theory of Heat

Let us now recognize, as Clausius originally did, that the effects of a reversible cyclical process are nothing more than the manifestation of the way the intake heat Q_h is partitioned into the heat carried over Q_c, and the one converted into work Q. This notion, it should be recalled, is at the center of Clausius' re-expression of Carnot's theorem and it is the one that, through the laws for isothermal and isentropic processes of ideal gases, led to $Q_h/Q_c = T_h/T_c$. This 'partition' notion is also found at the center of a new argument developed by Clausius with one identifiable objective in mind: to validate $Q_h/Q_c = T_h/T_c$ (or, equivalently, $-(Q_h/T_h) + (Q_c/T_c) = 0$) by getting at it through a path independent of the said equations governing the isothermal and isentropic evolutions of ideal gases in Carnot's cycle. To accomplish this goal he started, with the said partition of Q_h as guide, by recognizing a reversible cycle as a process constituted by two simpler processes or transformations, as he called them. Since these two transformations account for the totality of the effects of the cycle it should then be possible to reduce the 'measure of their effects' to an expression identical to that obtained when the cycle's effects are measured in terms of the changes experienced by the heat reservoirs, namely $Q_h/Q_c = T_h/T_c$. This 'measure of effects' referred to above was originally designated by Clausius as 'equivalent value', and eventually replaced by 'entropy change'. In terms of entropy what Clausius was set to prove was that the total-entropy change of a reversible cycle expressed as the summation of the entropy changes of the heat reservoirs is identical to that coming out of the summation of the entropy changes of the said two transformations. As important as the role played by this validation in Clausius' scheme of things, is the fact that it brought with it the knowledge of the entropy changes of some fundamental thermodynamic processes such as the transfer of heat between two bodies of different temperatures, the transformation of heat into work and that of work into heat; knowledge essential to the development of thermodynamics' conceptual frame regarding energy interconversions. At the conclusion of this new argument Clausius was ready to advance a statement for the second main principle of the mechanical theory of heat in the way it applies to reversible processes. This statement, made in terms of the combined 'equivalence values' of the transformations taking place in a reversible cyclical process, makes no reference at all to considerations of efficiency or the limited convertibility of heat into work in these processes, and as such it embodies the divide between Carnot's and Clausius' thermodynamics.

This alternative path to $Q_h/Q_c = T_h/T_c$ started with Clausius recognizing that

> *...in a Simple Cyclical Process two variations in respect to heat take place, viz. that a certain quantity of heat is converted into work (or generated out of work), and another quantity of heat passes from a hotter into a colder body (or vice versa)...For the former of these two variations we have already employed the word 'transformation,' inasmuch as we said, when work was expended and heat thereby produced, or conversely when heat was expended and work thereby produced, that the one has been 'transformed' into the other. We may use the word 'transformation' to express the second variation also (which consists in the passage of heat from one body into another, which may be colder or hotter than the first), inasmuch as we may say that heat of one temperature 'transforms' itself into heat of another temperature. On this principle we may describe the result of a simple cyclical process in the following terms: Two transformations are produced, a transformation from heat into work (or vice versa) and a transformation of heat from a higher temperature to heat of a lower (or vice versa). The relation between these transformations is therefore that which is to be expressed by the second Main Principle* [5].

For the sake of economy of expression the two transformations taking place in a reversible cyclical process will be represented, in the order mentioned by Clausius, via the following self-evident notation: For a heat engine $[Q(T_h) \to W]$, and $[Q_c(T_h) \to Q_c(T_c)]$; For a refrigerator $[W \to Q(T_h)]$ and $[Q_c(T_c) \to Q_c(T_h)]$.

With the transformations defined, the next step consisted in finding a new way to establish a connection between them that also provided a path to $Q_h/Q_c = T_h/T_c$. This 'new way' had of course to be different from the one connecting the heat carried over and that transformed into work through the isothermal and isentropic laws of ideal gases described in Section 2.1. The required connection was found by Clausius in a couple of processes, one involving a reversible heat-engine, and the other a reversible refrigerator. The study of these processes, to be described below, allowed him to find that the relation existing between the two transformations occurring in reversible cyclical process was one of equivalence. In Clausius' words:

> *Of the two transformations in a reversible (cyclical) process...either can replace the other, provided this latter be taken in the reverse direction: in other words, if a transformation of the one kind has taken place, this can be again reversed, and a transformation of the other kind substituted in its place, without the occurrence of any other permanent change. For example, let a quantity of heat Q be in any way generated out of work, and taken in by the (hotter) body; then by the cyclical process above described it can be again withdrawn from the (hotter) body and transformed back into work, but in so doing a quantity of heat Q_c will be transferred from the*

(hotter) body to the (colder) body. Again, if the quantity of heat Q_c has previously passed from (the hotter) to the (colder body), it can by performing the above process in the reverse order be transferred back again to (the hotter) body, whilst at the same time the quantity of heat Q, at the temperature (of the hotter) body, will be generated out of work. It is thus seen that these two kinds of transformation may be treated as processes of the same nature; and two such transformations, which may mutually replace each other in the way indicated, will be henceforth called 'Equivalent Transformations'... [5]

A number of small notation changes were introduced in the previous quote to make it compatible with the rest of this paper.

Given the importance of the argument that is to be based on these replacement schemes, the description provided by Clausius is nothing but sketchy. In order to clearly understand the meaning of Clausius' previous quote is that a detailed discussion of the 'how' these replacements take place will be provided in the next section. The knowledge obtained from this discussion, performed from the perspective of the entropy function, will be instrumental in pinpointing an egregious error at the center of Clausius' argument on this matter.

2.4. A Parenthesis to Provide a Detailed Account of Clausius Replacement Schemes

Let us center our attention on process (*a*) of Figure 1. In it the amount of heat Q_c is conductively transferred from a hot reservoir of temperature T_h to a cold reservoir of temperature T_c. The total entropy change for this process, calculated as the summation of the entropy changes experienced by the heat reservoirs, finds the following expression: $\Delta S_{tot} = -(Q_c/T_h) + (Q_c/T_c) = Q_c(T_h - T_c)/(T_hT_c) > 0$. The irreversible nature of this process stems from the fact that the only possible way to restore the initial condition i.e. the only way possible for Q_c to transit back from the cold to the hot reservoir without additional changes setting in is experimentally impossible as it demands the spontaneous –unaided- flow of heat from a colder to a hotter body. Any other way capable of producing this transit will inevitably leave behind, in the best of cases an entropy-equivalent change, and an increased-entropy change in all others.

The best of cases mentioned above, in which the transfer back of Q_c from the cold to the hot reservoir takes place at the expense of leaving behind an entropy-equivalent change, will be here illustrated via the coupling or concatenation of process (*a*) of Figure 1 with one cycle in the operation of the constant total-entropy Carnot reversible refrigerator represented in process (*b*). In other words, process (*b*) is to take place at the conclusion of process (*a*), and it is understood that the heat reservoirs in process (*b*) are the same reservoirs used in process (*a*)

In the reversible refrigerator shown in (*b*) the transfer back of Q_c from the cold to the hot reservoir is accomplished via the expenditure of an amount work $W = Q_c(T_h - T_c)/T_c$ [Fermi, p. 44]. The spent work W ends up in the form of an equivalent amount of heat Q in the hot reservoir. In agreement with Clausius previous statements we find that one cycle in the operation of refrigerator (*b*) produces two variations with respect to heat: the transfer of Q_c from the cold to the hot reservoir, and the dissipation of W into the equivalent amount of heat Q at the temperature of the hot reservoir. These two processes, as they occur in the said cycle and in accord with the notation previously introduced, are to be respectively represented as $[Q_c(T_c) \rightarrow Q_c(T_h)]$ and $[W \rightarrow Q(T_h)]$. As it is evident from Figure 1(*b*), of these two transformations it is $[Q_c(T_c) \rightarrow Q_c(T_h)]$ the one in charge of sending Q_c back to the hot reservoir and in doing so cancelling or neutralizing the initial (*a*) change, while the other one, $[W \rightarrow Q(T_h)]$, remains behind as its entropic-equivalent substitute, and as such it has been represented in 1(*c*). In order to understand how the said concatenation of processes (*a*) and (*b*) leads to the substitution of process (*a*) by process (*c*), and how is it that the latter ends up the bearer of an entropy change of identical magnitude to that of the former, let us start agreeing, in reference to process 1(*b*), that at the completion of a refrigerator's cycle, defined by the return of the working substance to its precise original condition, the entropic effects of the refrigerator must be localized in the only bodies having any say in this matter, namely, the heat reservoirs [6].

Figure-1. The concatenation of the irreversible heat transfer depicted in (*a*) with one cycle in the operation of the reversible Carnot refrigerator detailed in (*b*) leads to the replacement of the former with its entropy-equivalent substitute represented in (*c*), consisting in the transfer into the hot reservoir of the expended work W in the form of the equivalent amount of heat Q
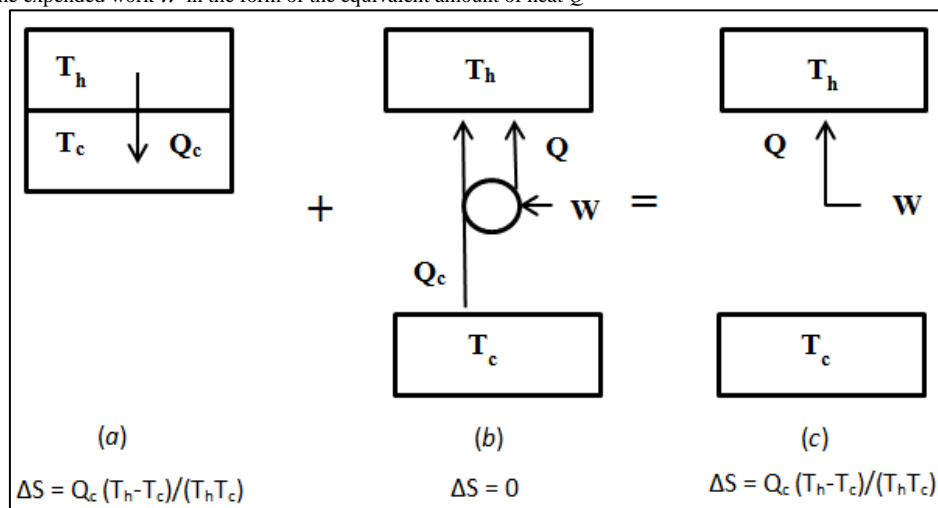
In regard to $[Q_c(T_c) \rightarrow Q_c(T_h)]$ these changes are: *i*) the release of the amount of heat Q_c by the cold reservoir of temperature T_c with an associated entropy change of $-Q_c/T_c$, and the absorption of the same amount of heat by the hot reservoir of temperature T_h with an associated entropy change of Q_c/T_h, for a combined or total entropy change of $\Delta S[Q_c(T_c) \rightarrow Q_c(T_h)] = -(Q_c/T_c) + (Q_c/T_h) = -[Q_c(T_h - T_c)/(T_h T_c)]$, of the same magnitude but opposite sign to the one associated to process (*a*). Note then that $[Q_c(T_c) \rightarrow Q_c(T_h)]$ cancels both: the effect of process (*a*) and also its associated entropy change. The result of this cancellation is that no trace remains of any of these two processes; it is as if they have never actually taken place; *ii*) Once the said cancellation complete, the only change remaining i.e. the only change left behind is process (*c*) and its associated entropy change. The absorption on the part of the hot reservoir of temperature T_h of the heat Q originating in the equivalent amount of work W expended in the refrigerator produces the following entropy change: $\Delta S[W \rightarrow Q(T_h)] = Q/T_h$. The fact that $Q = W = Q_c(T_h - T_c)/T_c$ allows us to write, previous substitution of the latter expression into the former, the following entropy change: $\Delta S[W \rightarrow Q(T_h)] = Q/T_h = Q_c(T_h - T_c)/(T_h T_c)$, identical to that of process (*a*), and of the same magnitude but opposite sign to that of $[Q_c(T_c) \rightarrow Q_c(T_h)]$, this last situation in agreement with the zero total-entropy condition imposed by the second law to the reversible refrigerator.

Figure-2. The concatenation of work-degrading process (*d*) with the reversible heat engine shown in (*e*) reverts both, the effects and entropy change of the former, leaving in its place its entropy-equivalent process (*f*)
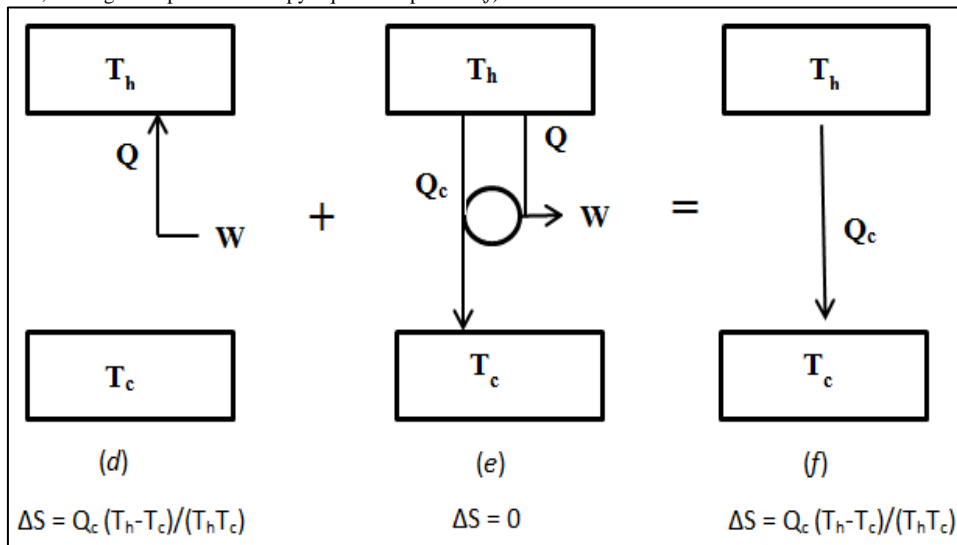
That the entropy change for the transfer of Q_c from the cold to the hot reservoir taking place in the refrigerator is of the same magnitude and opposite sign to that of process (*a*) is a result of the fact that opposite changes are left by one and the other in the only bodies affected by these transfers: the heat reservoirs, in a way such that the change left in anyone of these bodies by process (*a*) is undone by the corresponding change brought about by $[Q_c(T_c) \rightarrow Q_c(T_h)]$.

Let us now assume that, as shown in Figure 2(*d*), the irreversible, say frictional degradation of the amount of work W has taken place, with the equivalent amount of heat produced, Q, ending up in the hot reservoir of temperature T_h. The temperatures of the heat reservoirs as well as the magnitude of W (and if so also those of Q_h and Q_c) are assumed identical to those of Figure 1. The fact that process (*d*) is, like process (*a*), an irreversible process, means that also impossible is the restoration of its initial condition which, in the case at hand, means the transformation of an amount of heat Q of temperature T_h into an equivalent amount of work W without any other change taking place. As such, this transformation is not part of our experience, which is another way of saying that such a process never occurs in nature, i.e. it is an impossible process. This can be explained by the fact that the spontaneous occurrence of this process would make possible the known impossible spontaneous flow of heat from a colder to a hotter body. For suppose that

> ...*we could perform a transformation whose only final result would be to transform completely into work a definite amount of heat taken from a single source at the temperature t_1. By means of friction we could then transform this work into heat again and with this heat raise the temperature of a given body, regardless of what its initial temperature, t_2, might have been. In particular, we could take t_2 to be higher than t_1. Thus, the only final result of this process would be the transfer of heat from one body (the source) at the temperature t_1 to another body at a higher temperature, t_2.* [7]

Since restoration of the initial condition without changes left behind is impossible let us then try reverting process (*d*) by coupling or following it with one cycle in the operation of the reversible engine shown in (*e*). As known, the inverse of a reversible refrigerator is a reversible engine, and vice versa; the 'inverse' qualifier coming from the fact that the path traveled by the working substance in any one of them is the opposite of the other's; consequently their effects are also the inverses of one another. As already noted, while in refrigerator 1(*b*) the transference of an amount of heat Q_c from the cold reservoir of temperature T_c to the hot reservoir of temperature T_h is achieved via the consumption of an amount of work W quantified by $W = Q_c(T_h - T_c)/T_c$, with the spent work W ending up, alongside Q_c, in the hot reservoir in the form of the equivalent amount of heat $Q = W$; in engine (*e*), on

the other hand, an amount of work W, quantified as $W = (Q_c + Q)(T_h - T_c)/T_h$ is produced out the amount of heat $(Q_c + Q)$ received by the working substance from the hot reservoir. Their 'inverse' connection implies, as the interested reader can prove without difficulty, that $W = Q_c(T_h - T_c)/T_c = (Q_c + Q)(T_h - T_c)/T_h$. Once we recognize that the total entropy change for process 2(d), identical to that previously determined for 1(c), is given by $\Delta S_{tot}[2(d)] = Q/T_h$, we can proceed to identify the following two processes as those subsumed by one cycle in the operation of engine (e): 1) the transfer of the amount of heat Q_c from the hot to the cold reservoir, and 2) the transformation of the amount of heat Q of temperature T_h into an equivalent amount of work W. In accord with the notation previously introduced these processes, in the order given, will be represented as $[Q_c(T_h) \rightarrow Q_c(T_c)]$ and as $[Q(T_h) \rightarrow W]$. Their entropy changes will be determined following the procedure used in the previous example, that is, by linking their effects with the corresponding entropy changes of the heat reservoirs. In regard to $[Q_c(T_h) \rightarrow Q_c(T_c)]$ these changes are: *i*) the release of the amount of heat Q_c by the hot reservoir of temperature T_h, with an associated entropy change of $-Q_c/T_h$, and the absorption of the same amount of heat by the cold reservoir of temperature T_c, with an associated entropy change of Q_c/T_c, for a combined or total entropy change of $\Delta S[Q_c(T_h) \rightarrow Q_c(T_c)] = -(Q_c/T_h) + (Q_c/T_c) = Q_c(T_h - T_c)/(T_h T_c)$; *ii*) The fact that the only change taking place in regard to $[Q(T_h) \rightarrow W]$ is the release on the part of the hot reservoir of the amount of heat Q means that its total entropy change amounts $\Delta S[Q(T_h) \rightarrow W] = -Q/T_h$.

A close look at the entropy changes of the two processes brought forward by one cycle in the operation of engine (e) allows us to realize that the entropy change of $[Q(T_h) \rightarrow W]$ is of the same magnitude but opposite sign to the one associated to process (d). If so $[Q(T_h) \rightarrow W]$ cancels both, the effect of (d) and also its associated entropy change. The effect of this cancellation, aside of removing any trace of these two processes, is to leave behind process (f). The identity between the entropy change of process (f), of magnitude $\Delta S_{tot}[(f)] = Q_c(T_h - T_c)/(T_h T_c)$, with that of ($d$), given by $\Delta S_{tot}[(d)] = Q/T_h = W/T_h = Q_c(T_h - T_c)/(T_h T_c)$ confirms that the one left here behind, process (f), is the entropic-equivalent of process (d).

Clausius posits, without much explanation, that his replacement scheme evinces that an equivalence relation exists between the original transformation and the one replacing it. The previous detailed analysis of these replacement schemes confirms that the said equivalence exists and that it is an entropic equivalence. For a smooth transit between our previous arguments and those of Clausius on this same matter it should be kept in mind that what Clausius originally designated as "equivalence-value' became later on the 'entropy changes' of these transformations. Thus, the entropy change for process (a), and that of process (c) which is the one substituting (a) once the concatenation is complete, have identical entropy changes; likewise for processes (d) and (f). Apart from this we also see that the one staying behind is the opposite of the one that would have accompanied the original one in a reversible cycle. For example, the companion of (d) in a cycle would be $[Q_c(T_c) \rightarrow Q_c(T_h)]$ yet it is substituted by $[Q_c(T_h) \rightarrow Q_c(T_c)]$. This is what Clausius meant when saying

> *Of the two transformations in a reversible (cyclical) process...either can replace the other, provided this latter be taken in the reverse direction: in other words, if a transformation of the one kind has taken place, this can be again reversed, and a transformation of the other kind substituted in its place, without the occurrence of any other permanent change."* [5]

If the value of process (a) in Figure 1 is, to use Clausius terminology, represented as $V(a)$ and that of (c) as $V(c)$, then $V(a) = V(c)$. Since $V(c) = -V(-c)$, with ($-c$) representing the transformation coupled to (a) in refrigerator 1(b), it follows that $V(a) = -V(-c)$, and if so that $V(a) + V(-c) = V(process\ 1(b)) = 0$. A similar argument can be used to get to $V(d) + V(-f) = V(process\ 2e) = 0$. The previous results, expressed as the combined value of the transformations taking place in a reversible cyclical process is equal to zero is the knowledge made available by Clausius replacement-schemes.

The fact that in a reversible cyclical process no other change takes place but those represented by its associated transformations, combined with the fact that the entropy changes for these transformations take into account the contribution of each and every body in them involved, makes their combination a total entropy change. For the reversible refrigerator and engine of Figures 1 and 2 the values obtained were, respectively, $\Delta S[Q_c(T_c) \rightarrow Q_c(T_h)] = -(Q_c/T_c) + (Q_c/T_c)$, $\Delta S[W \rightarrow Q(T_h)] = Q/T_h$, and $\Delta S[Q_c(T_h) \rightarrow Q_c(T_c)] = (-Q_c/T_h) + (Q_c/T_c)$, $\Delta S[Q(T_h) \rightarrow W] = -Q/T_h$, which combine, in the order given, for the following total entropy change: $\Delta S_{total}[refrigerator] = -[-(Q_h/T_h) + (Q_c/T_c)] = 0$ and $\Delta S_{total}[engine] = -(Q_h/T_h) + (Q_c/T_c) = 0$. Clausius conceptualization of simple reversible cyclical processes as constituted by the previously referred transformations brought forward the validation of that equation originally obtained via the isothermal and isentropic laws of ideal gases. It is with base on this results that he was to forward, in the form of his Principle of the Equivalence of transformations, his very first statement of what we now understand as the second law of thermodynamics in the form it takes for reversible processes.

Clausius did not make available a graphic-based discussion on his replacement scheme such as the one presented above; had he, he would have produced an analysis identical to the one just given whose results, as will be seen in the next section, coincide *in toto* with those of the analysis which based on the said replacement scheme he did present. With this interlude concluded we are ready to resume our analysis of Clausius results which were to become the second law of thermodynamics.

2.5. Back to Clausius

Having inferred from his replacement scheme the existence of an equivalence relation between the transformations associated to a reversible cyclical process, Clausius proceeds to define, as stated in the quote below, the next step of that path that is to eventually led him to the second law in its zero total-entropy version.

We have now to find the law according to which the above transformations must be expressed mathematically, so that the equivalence of the two may appear from the equality of their values. The mathematical value of a transformation may be termed, thus determined, its 'Equivalence Value' [5].

As to the values of his equivalent transformations, Clausius reasoned as follows:

In regard to the magnitude of the equivalence-value, it is at once seen that the value of a change from work into heat must be proportional to the quantity of heat generated and that beyond this it can only depend on its temperature...Similarly the value of the passage of a quantity of heat Q from the temperature T_1 to the temperature T_2 must be proportional to the quantity of heat which passes, and beyond this can only depend on the two temperatures [5].

With these considerations as base he expressed the equivalence values by the formulas $\pm Q \, x \, f(T)$, and $\pm Q_c \, x \, F(T_1, T_2)$ where $f(T)$ is a function of the temperature of the heat either transforming into work or produced out of work; $F(T_1, T_2)$ a function of the two temperatures between which the transfer of heat takes place, with the positive sign applying, respectively, to the transformation of work into heat and the transformation of heat from a higher to a lower temperature, and the negative sign to their respective inverses. He then proceeded by saying

In order to compare these two expressions with each other, we have the condition that in every reversible process of the kind given above the two transformations that take place must be equal in magnitude but of opposite sign so that their algebraical sum is zero...Therefore the following equation must hold: $-Q \, x \, f(T_1) + Q_1 \, x \, F(T_1, T_2) = 0$... [5]

The previous equation refers to a reversible engine in which an amount of heat Q of temperature T_1 is transformed into an equivalent amount of work, while an amount of heat Q_1 is concurrently transferred from temperature T_1 to temperature T_2. The corresponding equation for a reversible refrigerator can be obtained via multiplication of the previous one by (-1). The values eventually obtained by Clausius for the transformations taking place in a reversible engine, written with notation used in the processes of Figures 1 and 2, were the following: $[Q_c(T_h) \rightarrow Q_c(T_c)] = -(Q_c/T_h) + (Q_c/T_c) = Q_c(T_h - T_c)/(T_h T_c)$ and $[Q(T_h) \rightarrow W] = -Q/T_h$. The negative of these values correspond to the transformations taking place in a reversible refrigerator. These values, when combined, reproduce and, if so, also validate Clausius previous result obtained from the isothermal and isentropic laws applying to processes *AB*, *BC CD*, and *DA* constituting the closed cycle of operations of the variable body in a reversible cycle, namely $-Q_h/T_h + Q_c/T_c = 0$, and in doing so also provide him with an alternative way of enunciating that new principle of the mechanical theory of heat which, originally centered on the limited convertibility of heat into work in cyclical process, was to be replaced with this new perspective centered on the equivalence values (entropy changes) of the transformations there taking place:

Hence the Second Main Principle of the Mechanical Theory of Heat, which in this form may perhaps be called the principle of the Equivalence of Transformations, can be expressed in the following terms: 'If we call two transformations which may cancel each other without requiring any other permanent change to take place, Equivalent Transformations, then the generation out of work of the quantity of heat Q of temperature τ has the equivalence value Q/τ ; and the transference of the quantity of heat Q from temperature T_1 to temperature T_2 has the Equivalence-value $Q[(1/\tau_2) - (1/\tau_1)]$; in which τ is a function of temperature independent of the kind of process by which the transformation is accomplished [5].

The temperature τ used by Clausius in the previous quote corresponds to the absolute temperature [5].

That the transformations combine to a value of zero was expressed by Clausius in the following form *"...in reversible cyclical processes the total value of all the transformations must be equal to nothing"* [5]. Replacement of 'value' for 'entropy change' will make clear that in his previous quote Clausius was forwarding a statement of the second law in the form it adopts for reversible processes. Further work in the realm of irreversible cyclical processes led him to the following conclusion *"The algebraic sum of all the transformations which occur in a cyclical process must always be positive or in the limit equal to zero"* [5]. Here he is stating second the law in its totality i.e. for reversible and irreversible cyclical process. Upon extension of his work to non-cyclical processes he was able to produce a general statement of the second law in the following form: "The theorem which...was enunciated in reference to circular processes only...has thus assumed a more general form, and may be enunciated thus:- The algebraic sum of all the transformations occurring in any alteration of condition whatever can only be positive, or, as an extreme case, equal to nothing*"* [8].

The central role played by the transformations in Clausius work leading to the law of increasing entropy can be properly gauged through the previous quotes.

Let me finally note here that Planck might very well have been the first to openly argue about the need to remove any anthropomorphism from physical science [9, 10] but it all appears to indicate that it was Clausius the one to take the first step in this direction when he eliminated any reference to the limited heat-to-work conversion in cyclical processes or their efficiency from his 'transformations-based' statements of the second law.

3. The Egregious Error in Clausius Argument About the Equivalence of Transformations

The equivalence existing between Clausius' analytical method just described and the one based on the concatenations of processes (*a*) and (*b*) in Figure 1, and (*d*) and (*e*) in Figure 2 is evinced by the identity of the transformations' entropy changes obtained from one and the other.

With this is mind let us start this argument by recognizing that the inverse of process (*a*) in Figure 1, to be here designated as process (−*a*), represents the impossible spontaneous transfer of heat from the cold to the hot reservoir, and as such it conveys the following total-entropy change: $\Delta S_{total}[(-a)] = -Q_c/T_c + Q_c/T_h = -Q_c(T_h - T_c)/T_h T_c$.

This equation evinces the fact that this impossible process involves no other bodies but the heat reservoirs. As a matter of fact it can be said that it is precisely on reason of the fact that no other bodies but the heat reservoirs are here involved that such a process is impossible. In other words, the transference of heat from a colder to a hotter body is perfectly possible when other bodies are involved in the process. Case at hand the use of reversible refrigerator (*b*) in Figure 1 to send Q_c back to the hot reservoir. It is precisely on reason of this evident fact (apparently not evident enough for Clausius), namely that the transfer of Q_c subsumed by process 1(*b*) is not a process taking place with the sole involvement of the reservoirs but with the added participation of the ideal gas acting as variable body which is the one actually absorbing this heat from the cold reservoir and eventually releasing it to the hot reservoir that the total entropy change for this heat transfer should include, in addition to the changes sustained by the reservoirs, those sustained by the variable body due to its participation in this task. This additional change makes the heat transfer taking place in the refrigerator an essentially different process from the spontaneous, unaided heat transfer we have designated as process (−*a*), so different in fact that while one is possible the other is not. This situation becomes clear once we realize that the transformations taking place in a cyclical process are not concomitant, but sequential, i.e. one takes place after the other. In reference to the reversible cycle represented in Figure 3 with starting point at *A* it is understood that it is along isothermal expansion *AB* that the ideal gas acting as variable body manages to transform the whole of the heat Q_h received from the hot reservoir into an equivalent amount of work W_h. At this point the work producing part of the cycle has concluded but the heat transfer part hasn't even started yet. It is along isothermal compression *CD* that the W_c portion of W_h is dissipated into an equivalent amount of heat Q_c and as such transferred from the gas to the cold reservoir. Just like it is true that at the end of a cycle the variable body returns to its initial condition and in doing so its total-entropy change is zero, also true is the fact that the role played by the variable body in each of the transformations is accomplished by transits representing part of its cycle, and if so, conveyors of non-zero entropy changes. Since the work effect of the cycle, *W*, is a fraction of the work W_h generated by the transit of the gas along *AB* it is obvious that its role in the production of *W* should be accomplished by its transit along a fraction of *AB* and it is precisely the entropy change sustained by the gas along this transit the one that should accompany the $-Q/T_h$ entropy change sustained by the hot reservoir in this transformation $[Q(T_h) \rightarrow W]$ to define its total entropy change. Similarly, the total entropy change for $[Q_c(T_h) \rightarrow Q_c(T_c)]$ should include, in addition to the $-(Q_c/T_h)$, and (Q_c/T_c) entropy changes sustained by the heat reservoirs, the entropy change associated to whatever transit the variable body experiences along this transformation. Not taking into account the entropy changes sustained by the variable body when determining the entropy changes of the transformations through the arguments based on Figures 1 and 2 of Section 2.4, arguments equivalent to the analytical one which described in Section 2.5 was forwarded by Clausius to this same end, is reason enough to reject these values and any conclusion, such as the Principle of the Equivalence of Transformations, based on them. At this point these values can be categorized as unknown. The imbroglio (embarrassing situation) represented by the previous realization finds perfect expression in the following quote from Truesdell and Bharatha: *"Thermodynamics was born in obscurity and disorder, not to say confusion, and there the common presentations of it have remained"* [11].

The definition of 'fallacy': "A failure in reasoning which renders an argument invalid." (Google Dictionary) allows us to qualify Clausius' Equivalence of Transformations' argument previously discussed as fallacious. In my opinion it couldn't have been otherwise, after all you need a fallacious argument to prove an equally fallacious statement such as that positing that 'the total-entropy change for a reversible cycle is given by $-(Q_h/T_h) + (Q_c/T_c) = 0$'. And where is the failure in reasoning, you might ask, making this last statement a fallacy? The answer is that such a statement assumes that only two changes remain at the conclusion of a cycle in the operation of a reversible cycle, these being the changes experienced by the heat reservoirs, when in reality we have three changes remaining: That of the mechanical reservoir, in addition to the two just mentioned concerning the heat reservoirs. I am certain that the said extra change was acknowledged, but neglected. If so, the fallacy (the failure in reasoning) can be located in the either perfunctory (An action carried out with a minimum of reflection) or calculated fashion in which it was decided that such a change had no entropy change associated with it. This particular issue is the matter of Section 5.

Let me insert here a most important clarification: Equation $-(Q_h/T_h) + (Q_c/T_c) = 0$ is indeed true for reversible cyclical processes. No doubt about it. It represents the fact that in those processes the entropy changes of the heat reservoirs are compensated, i.e. of equal magnitude but opposite sign; but also true is the fact that such an equation cannot be taken as the total-entropy change of such processes until proof is advanced that justifies the exclusion of that third change from the total-entropy change equation.

The reason for Clausius' egregiously incorrect analysis was eventually spotted, addressed, and 'corrected'. Who did it? When? Was this effort ever published? I do not know. This is a matter for historians of Thermodynamics. In view of this is that I have attributed the changes (surreptitiously) inserted into Clausius' argument with the purpose of correcting it to what I have called Post-Clausius Thermodynamics or *PCT*.

The following section proves that the total-entropy changes for Clausius' transformations supported by current thermodynamic wisdom are radically different from the incorrect values of Clausius.

4. Post-Clausius Thermodynamics (*PCT*) and a New Set of Values for the Transformations

Most students and studious of thermodynamics, the present reader no doubt included, believe that the thermodynamics of the second law as it is known, written about, and taught nowadays is essentially Clausius' work. Small changes here and there, no doubt; a lot extended, for certain; but all in all the thermodynamics Clausius constructed by correcting and extending Carnot's work on heat engines and the motive power of heat. This belief, however, bears no correspondence with reality. The body of knowledge that the present author and you the reader has been exposed to is actually a version whose essential or fundamental tenets are different from those constituting the conceptual foundation of Clausius work: Only the dome of Clausius' church –the results of Clausius' work known to be true or assumed as such- was retained; The walls on which Clausius supported the said dome were surreptitiously demolished and new and supposedly structurally sound walls were constructed in their place. By 'the dome' I refer to the equation for the total-entropy change of reversible cyclical processes $(-Q_h/T_h) + (Q_c/T_c) = 0$, to the entropy function, to the positive entropy changes produced by the irreversible transformation of work into heat, and heat from higher to lower temperature, and to the law of increasing entropy understood as $\Delta S_{tot} \geq 0$. The defective walls, understood as the entropy changes for Clausius' transformations, as quoted in his Principle of the Equivalence of Transformations were replaced, after *PCT's* takeover of Clausius' work with supposedly structurally sound walls –different magnitudes for the transformation's values. This is the matter of the following arguments.

In Figure 3(*g*) we find the common representation of Carnot's reversible cycle defined as two heat reservoirs of different temperatures thermally connected by the closed sequence of changes of the variable body. Since we have already described the nature of processes *AB*, *BC*, *CD,* and *DA* in a reversible engine, and that of *AD*, *DC*, *CB*, and *BA* in a reversible refrigerator, as well as the inverse nature of isentropic processes *BC/CB* and *DA/AD*, we will get into the matter of the discussion right away. Figure 3(*h*) is identical in all respects to 3(*g*) save the starting point. The rationale is the following. The fact that $Q_h > Q_c$ means that there exists some point *E* on isotherm *AB* such that in its transit *EB* the ideal gas takes from the hot reservoir an amount of heat Q_c identical in magnitude to that by it released to the cold reservoir along *CD*; the approximate location of this point in shown in Figure 3(*h*). The fact that the work W_c produced along *EB* out of the heat Q_c coming out of the hot reservoir is transformed back into heat along *CD* and as such transferred to the cold reservoir allows us to realize that the only effect produced by concatenation *EB-BC-CD-DA* is the reversible transit of Q_c from the hot to the cold reservoir. Process *DA* has been included in the said concatenation to assure that no other effect but the heat transfer remains once the gas reaches condition *A*. The reversible qualifier ascribed to the previously described heat transfer stems from the fact that if once at *A* the gas reverses course and transits along *AD-DC-CB-BE* each of the changes that had previously taken place will be precisely reverted so that at the end no trace remains of any change having ever taken place. Thus, along expansion *DC* the gas will take from the cold reservoir an amount of heat Q_c identical to the one it has previously received, and deliver it, through compression *BE,* to the hot reservoir from which it was originally taken. Similar descriptions of this reversible transfer of heat can be found in the literature [12-14].

Figure-3. Shown above are two equivalent graphical descriptions of Carnot's reversible cycle differing only in the starting point. While in (*g*) the cyclical path of the ideal gas acting as variable body is *A-B-C-D-A*, in (*h*) is *E-B-C-D-A-E*. The latter, described in detail in this section, will be used in the identification of the 'corrected' values or entropy changes for the two transformations there taking place. In these figures,

$$Q_h - Q_c = Q \; , \; W_h - W_c = W \; , \; Q = W$$
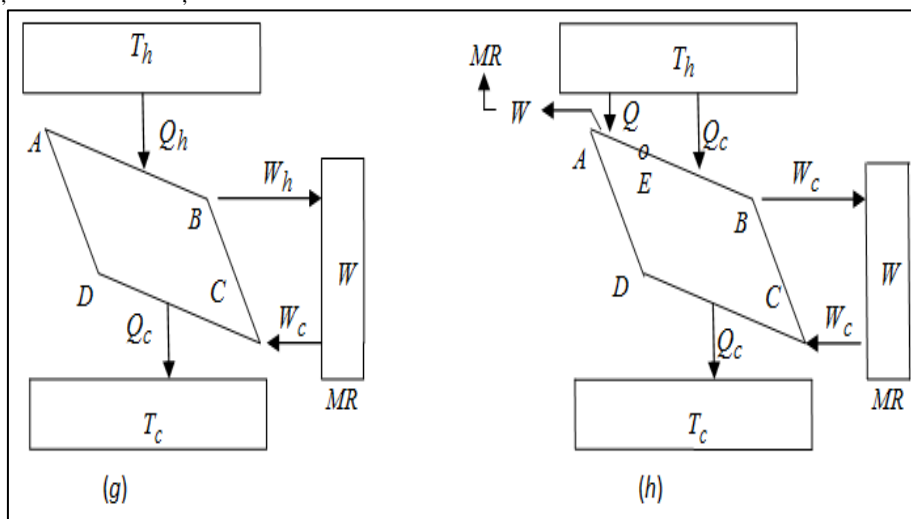
The total entropy change for the transfer of Q_c from the hot to the cold reservoir, as it takes place in a reversible cycle, can now be calculated as follows; In step *EB* in which the amount of heat Q_c is transferred from the hot reservoir to the gas, with both these bodies at temperature T_h, we recognize, in accord with current thermodynamic wisdom, two entropy changes: $-Q_c/T_h$ for the hot reservoir and Q_c/T_h for the ideal gas. In step *CD* in which the amount of heat Q_c is transferred from the gas to the cold reservoir, with both these bodies at temperature T_c we recognize, again in accord with current thermodynamic wisdom, another two entropy changes: $-Q_c/T_c$ for the ideal gas, and Q_c/T_c for the cold reservoir. The isentropic nature of processes *BC* and *DA* means that no other entropy

change but the ones previously described contribute to define the entropy change for this heat transfer. On reason of this we can then write its total entropy change in the following form $\Delta S_{tot}^*[Q_c(T_h) \to Q_c(T_c)] = -(Q_c/T_h) + (Q_c/T_h) - (Q_c/T_c) + (Q_c/T_c) = 0$. In the previous equation the first two terms on the right hand side correspond to process *EB* and the two last to process *CD*. The fact that each and every body contributing in any form to the entropy change of this process has been included, qualify this as a total entropy change. The star super-index attached to the previous entropy change distinguishes it from that assigned by Clausius to the same transformation of magnitude: $\Delta S_{tot}[Q_c(T_h) \to Q_c(T_c)] = -(Q_c/T_h) + (Q_c/T_h) = Q_c(T_h - T_c)/(T_h)(T_c)$.

Having started its cycle at *E*, the variable body, after managing to reversibly transfer an amount of heat Q_c from the hot to the cold reservoir, finds itself at point *A*. In its transit from *A* to *E* the ideal gas acting as working substance will absorb from the hot reservoir an amount of heat *Q* and transform it into an equivalent amount of work *W*. At the conclusion of this process the ideal gas will find itself in its initial condition *E*, bringing this way the cycle to its conclusion. The fact that no other effect but the transformation of *Q* into *W* can be associated to this *AE* isothermal expansion, means that this process is the one embodying the transformation of heat into work recognized by Clausius as one of the two taking place in a reversible engine. A similar analysis to that performed above leads us to writing the total entropy change for this process, in accord (again) with current thermodynamic wisdom, as the summation of the compensated entropy changes sustained by the hot reservoir and the gas due to the loss of the former and the gain of the latter, of the amount of heat *Q*, i.e. as: $\Delta S_{tot}^*[Q(T_h) \to W] = -(Q/T_h) + (Q/T_h) = 0$. The fact that these two entropy changes are the only ones occurring along *AE* confers to this entropy change the quality of 'total'. This zero-magnitude change should be compared to the one assigned by Clausius to the same transformation: $\Delta S_{tot}[Q(T_h) \to W] = -Q/T_h$. The fact that combined the zero total-entropy changes here obtained for each of the transformations define the total-entropy change for the reversible cycle confirms, if through a different path, Clausius conclusion that "...in a reversible Cyclical Process the total value of all the transformations must be equal to zero" [5].

Note now that the zero total-entropy changes ascribed by the previous argument to both of these transformations are in contradiction with the non-zero total-entropy changes produced by Clausius' argument. The remarkable thing to be noticed is that their combination, in both cases, amounts to zero. In other words, for Clausius the total-entropy change for a reversible cyclical process becomes identical with zero via the addition of two equal magnitudes of opposite sign; and in post-Clausius thermodynamics via the addition of two zeros. This is what we meant when we stated that Clausius' and *PCT* are two essentially different formulations of the second law.

The identification of the two transformations associated to a reversible engine with processes *EB-BC-CD-DA* and *AE* allows us to confirm our previous explanation regarding the origin of the incorrectness of the procedure described in Section 2.1 in regard to the processes of Figures 1 and 2, as well as the incorrectness of the necessarily equivalent procedure used by Clausius for the values of his transformations. Both of these last procedures assert, on reason of the return of the variable to its initial condition at the end of the cycle, that the only changes left behind were those sustained by the heat reservoirs and that in being this so only these bodies could determine the entropy changes of the transformations. This procedure is, however, incorrect. It is indeed true that at the end of a cycle no change remains in the variable body. This notion cannot, however, be used to determine the values of the transformations for the simple reason that, say, in its transit *EBCDA*, the one defining the reversible transformation of heat from the hot to the cold reservoir, the variable body is short of completing a cycle which means that its entropy change is not zero and if so cannot be left out of the calculation of the total entropy change of this process. The same goes for *AE*..

A question that deserves further consideration is how is it that the same result, namely a zero total entropy change for a reversible cyclical process can be the result of both, Clausius egregiously incorrect analysis, and the *supposedly* correct one just described based on current thermodynamic wisdom? To this author, as the following section will explain, the zero total entropy change produced by the latter approach appears to be no coincidence, no accident, but the result of fiat, decree, or purposeful design. For the present author the 'constant total-entropy property' of reversible process is not a reflection of nature's behavior, rather, it is the result of the willful desire to maintain the belief in the law of increasing entropy and its associated religious, political, social, economic, demographic, and eschatological notions. The following quote from Bazarov gives us a hint of what was at stake:

> The (second) *law has caught the attention of poets and philosophers and has been called the greatest achievement of the nineteenth century. Engels disliked it, for it supported opposition to Dialectical Materialism, while Pope Pius XII regarded it as proving the existence of a higher being* [15].

Conclusions for Part I

In our previous discussions we have shown that Clausius argument providing the proof for the second law of thermodynamics in its 'Principle of the Equivalence of Transformations' version, is a fallacious argument. We have also shown how the reasoning deficiency invalidating the said Clausius' argument was corrected by Post-Clausius Thermodynamics while keeping Clausius' original result –the total-entropy change for a reversible cyclical process is zero- intact.

In part II we will bring to light the fact that the previously described correction introduced by *PCT* subsumes what we consider an arbitrary, unproven assumption. The alternative to that assumption is introduced in the form of what I have called the 'Negentropic hypothesis' and through it we suggest an experimental test centered on Rayleigh-Bénard convection to ascertain which of the two approaches is sanctioned by nature.

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