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A thermodynamic impasse: A constant entropy irreversible process

José Íñiguez

1227 21st Street, Douglas, Arizona 85607, (USA)

E-mail: iniguez.jose@gmail.com; iniguezj@cochise.edu

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ABSTRACT

When the work produced by a reversible Carnot engine is subsequently degraded through a frictional mechanism into an equivalent amount of heat at the temperature of the cold reservoir, the universe of this reversible engine becomes identical to that of the commonly studied direct, irreversible transfer of heat from a hot to a cold body. The identity qualifier rests on the fact that in these two processes the changes experienced by the only two bodies affected -the heat reservoirs- are identical; situation that leads to the same entropy change for one process and the other. These coincidences notwithstanding, an essential difference separating these two processes is here identified: the fact that in the work-producing/work-degrading combination, the entropy change is determined not by the whole of the heat flowing from the hot to the cold body, as it happens in the direct transfer of heat, but by a fraction of it; with the remaining of the heat flowing irreversibly at constant entropy. The identification of this constant entropy irreversible process leads, in turn, to the unveiling of a contradiction between second law thermodynamics' reversibility criterion, and it's supposedly empirical counterpart embodied by the principle: Heat cannot, of itself, pass from a colder to a hotter body.

KEYWORDS

Coupling of Carnot's reversible cycle with a work degrading process;
Irreversible heat transfer;
Planck's and Clausius's reversibility criterions;
Constant entropy irreversible process.

INTRODUCTION

According to Planck[1]

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…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 second law of thermodynamics states that there exists in nature for each system of bodies a quantity, which by all changes of the system either remains constant (in reversible processes) or increases in value (in irreversible processes). This quantity is called, following Clausius, the entropy…

The thermodynamic analysis herein presented leads, however, to a contradiction with the previous statement.

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The contradiction takes form in an irreversible heat transfer taking place at constant entropy. This paper limits itself to the presentation of the thermodynamic analysis leading to such a result.

CARNOT'S REVERSIBLE ENGINE, THE TRANSFORMATIONS PRODUCED BY IT, AND THEIR ENTROPY CHANGES

The essential constitutive elements of a reversible Carnot engine, such as that represented in Figure 1(a) are the following:

1 A hot reservoir of temperature T_h
2 A cold reservoir of temperature T_c, where $T_h \rangle T_c$
3 A working substance, which for the purpose of this discussion will be taken to be an ideal gas, and
4 A mechanical reservoir acting as depository of the work produced in the operation.

One cycle in the operation of this engine may be described in terms of the following concatenation of processes:

AB: An isothermal and reversible expansion at the temperature of the hot reservoir T_h. Here an amount of heat Q_h absorbed by the ideal gas from the hot reservoir, is transformed into an equivalent amount of work W_h.

BC: An adiabatic and reversible expansion. Due to the adiabatic nature of the process, here the ideal gas manages to produce an amount of work W' out of its own internal energy and in doing so its temperature drops from T_h to T_c.

CD: An isothermal and reversible compression at the temperature of the cold reservoir T_c. Here a portion W_c of the work previously produced is utilized in order to carry on this compression. The spent work is absorbed as an equivalent amount of heat Q_c by the cold reservoir ($Q_c \rangle Q_h$).

DA: An adiabatic and reversible compression that returns the variable body to its initial condition, closing thus one cycle in the operation of this engine. This process demands the expenditure of an amount of work W' identical to that produced by process BC. Due to the adiabatic nature of the process, here the work expended ends up increasing the internal energy of the ideal gas, thus raising its temperature from T_c to T_h.

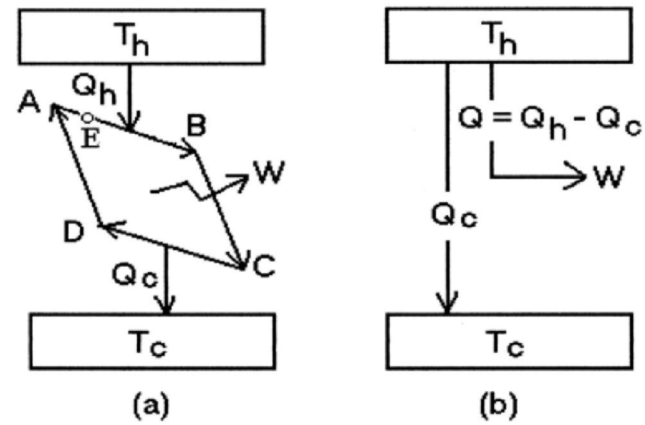

Figure 1 : Two representations of a reversible heat engine. The cyclical evolution defined in (a) by the concatenation of processes AB-BC-CD-DA produces, out of the amount of heat Q_h released by the hot reservoir, the two changes or transformations depicted in (b), these being the transfer of an amount of heat Q_c to the cold reservoir, and the transformation of the amount of heat Q into an equivalent amount of work W. Point E is used below in the argument directed to the identification and evaluation of the entropy changes of these two transformations

The fact that at the completion of one cycle the working substance returns to its original condition, reduces the changes produced by the engine to those experienced by the heat and mechanical reservoirs, consisting in the transfer of an amount of heat Q_c from the hot to the cold reservoir, and the transformation of an amount of heat Q, $Q = Q_h - Q_c$, into an equivalent amount of work W, $W = W_h - W_c$. These two changes or transformations, depicted in Figure 1(b), will be respectively represented by the following self-evident notation$[Q_c(T_h) \to Q_c(T_c)]_{rev}$, and $[Q(T_h) \to W]_{rev}$. As components of a reversible process, these transformations are reversible themselves. This fact has been indicated by the sub index 'rev'.

At the light of second law thermodynamics' constant-entropy reversibility criterion, as expressed in Planck's previous quote, the entropy change for the universe of the reversible Carnot engine under consideration can be written as

$$\Delta S[Q_c(T_h) \to Q_c(T_c)]_{rev} + \Delta S[Q(T_h) \to W]_{rev} = 0 \qquad (1)$$

The identification of the individual values for the entropy changes shown in eq. 1 starts by recognizing that, as previously described in reference to Figure 1, the heat taken in by the ideal gas from the hot reservoir along AB is larger than that it gives out to the cold reservoir along CD. This fact allows us to realize that there exists some point E on isotherm AB that allows the ideal gas in its transit along EB, to take from the hot reservoir an amount of heat Q_c identical to that given out to the cold reservoir along CD. The approximate location of point E is shown in Figure 1. Assuming that the operation of the cycle is to start at point E, consideration will be given to the effect of the concatenation of processes EB-BC-CD-DA. Actually, on reason of the fact that the effect of the adiabatic and reversible process BC is precisely cancelled by the adiabatic and reversible process DA, the effect of the said concatenation reduces to that produced by the combination of processes EB and CD. Along EB the hot reservoir transfers to the ideal gas an amount of heat Q_c. The ideal gas, on its part, transforms this heat into an equivalent amount of work W_c. Along CD, on the other hand, an amount of work W_c is transformed into an equivalent amount of heat Q_c. This heat ends up being absorbed by the cold reservoir. The fact that an identical amount of work as that produced along EB is consumed along CD, allows us to realize that what this concatenation manages to effect is the transfer of Q_c from the hot to the cold reservoir. Recognition of the facts that processes BC and DA are by definition isentropic, and that the entropy change for isothermal and reversible expansion EB as well as isothermal and reversible compression CD is zero on reason of the fact that in each of them the entropy changes for the reservoir and the ideal gas are of the same magnitude but opposite sign, leads to

$$\Delta S[Q_c(T_h) \rightarrow Q_c(T_c)]_{rev} = 0 \quad (2)$$

Let us now recognize that the process AE needed to bring the cycle to its conclusion is an isothermal and reversible expansion at the temperature of the hot reservoir. Through it the ideal gas absorbs an amount of heat Q from the hot reservoir and transforms it into an equivalent amount of work W. Since no other effect but this can be associated to this expansion, it follows that it is AE the one responsible for the net work output of the cycle, or in other words, for bringing forward the transformation of Q into W. For the reason previously given, the entropy change for isothermal and reversible expansion AE is zero. Therefore

$$\Delta S[Q(T_h) \rightarrow W]_{rev} = 0 \quad (3)$$

The entropy changes of equations 2 and 3 are found not only in compliance with equation 1, actually any pair of equal magnitude but opposite sign entropy changes could have also complied with it; what is most important is that they also comply individually with the constant-entropy reversibility criterion. The necessity of this individual compliance comes from the fact that each of those transformations is a universe in itself (or a sub-universe of the heat engine), and as such their respective entropy change calculations involved each and every body taking any part on them.

AN IRREVERSIBLE HEAT TRANSFER

The essential characteristic of the direct, irreversible transfer of a given amount of heat from a hot to a cold reservoir is that through it no work is at all produced. The fact that the transfer back of this heat from the cold to the hot reservoir demands the expenditure of work, combined with the fact that none was generated in the original process, leads to the realization that this reversion can only be accomplished with the concourse of a work-supplying body. This impossibility of recuperating the original universe without changes remaining in other bodies is what qualifies it as irreversible. The fact made evident by Figure 2, that such a process involves no other bodies but the heat reservoirs means that once the transfer has taken place the only changes left in the universe are those experienced by these bodies. Under the assumption that the initial condition of the hot and cold reservoirs involved in this

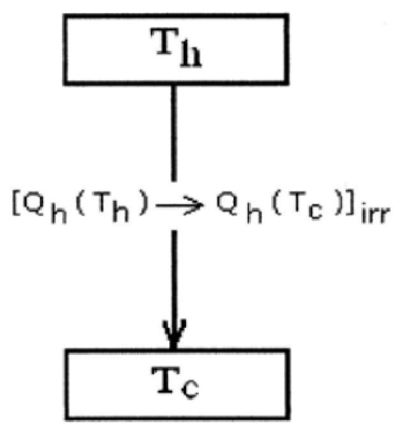

Figure 2 : The figure depicts the irreversible transfer of an amount of heat Q_h from a hot reservoir of temperature T_h to a cold reservoir of temperature T_c. The fact that no work is generated in this process makes it irreversible, as the transfer back of Q_h from the cold reservoir can only be achieved by leaving a permanent change on that body supplying the work demanded by such a transfer.

process are respectively identical to those used in the cyclical process of Figure 1, we can specify the changes experienced by these bodies in the process represented in Figure 2 as follows: The final condition of the hot reservoir equals its initial condition minus an amount of heat Q_h; The final condition of the cold reservoir equals its initial condition plus an amount of heat Q_h.

The entropy change for this irreversible process can be calculated through the expedient of finding a reversible path connecting the same initial and final states. This procedure finds explanation in the fact that the entropy function is defined in terms of reversible heat. With this alternate reversible path in place the reversible heat can be quantified for the specified change and the entropy change evaluated. Since the entropy is a state function, as long as the original irreversible process and its reversible counterpart link the same initial and final states, the entropy change will be one and the same.

For the irreversible heat transfer depicted in Figure 2, this procedure produces the following result[2]

$$\Delta S[Q_h(T_h) \rightarrow Q_h(T_c)]_{irr} = -(Q_h / T_h) + (Q_h / T_c) \qquad (4)$$

The re-expression of the previous equation in the following form

$$\Delta S[Q_h(T_h) \rightarrow Q_h(T_c)]_{irr} = Q_h(T_h - T_c)/(T_h T_c) \qquad (5)$$

makes clear that in this process each and every unit of heat contained in Q_h makes a contribution to the total entropy change in the amount of $(T_h - T_c)/(T_h T_c)$. Let us now recognize that in the previous equation the term $(T_h - T_c)/T_h$ can be identified as the maximum efficiency possible (η_{max}) for any heat engine working between those two reservoirs. On this perspective the product $Q_h((T_h - T_c)/T_h)$ represents the maximum possible amount of work (W) this engine could have outputted had Q_h been fed to it. The fact that Q_h was not fed to this engine, but instead it was transferred in a direct, irreversible fashion to the cold reservoir, allows us to realize that in this situation the said product quantifies the wasted work-producing potential i.e. the 'lost work' that Q_h carries with it to the cold reservoir. This last consideration is made explicit in the following re-expression of equation 5

$$\Delta S[Q_h(T_h) \rightarrow Q_h(T_c)]_{irr} = Q_h \eta_{max}/T_c = W/T_c \qquad (6)$$

This last equation sheds light on the fact that the entropy change produced by the irreversible transit of Q_h units of heat from the hot to the cold reservoir, is of equal magnitude to that associated to the absorption of an amount of heat $Q_h\eta_{max}$ by the cold reservoir.

AN EQUIVALENT IRREVERSIBLE HEAT TRANSFER

The workless label previously mentioned as the essential characteristic of an irreversible heat transfer opens up the possibility of producing a direct irreversible transfer of heat from a hot to a cold reservoir via the combination of a first step represented by one cycle in the operation of the reversible cyclical process represented in Figure 1, with a second step represented by the frictional degradation of the work previously produced by the cycle.

As shown in Figure 3(a), and as previously discussed, one cycle in the operation of this reversible engine brings forward the transfer of the amount of heat Q_c from the hot to the cold reservoir, as well as the transformation into work of the amount of heat Q of temperature T_h. Both of these reversible changes or transformations take place, as shown by equations 2 and 3, with zero entropy changes. We will take now the work generated by the engine and as shown in 3(b), degrade it via a frictional process, into an equivalent amount of heat (Q) that will end up in the cold reservoir. Once this work-degrading process is finished we find, as can be seen from 3(c), that all the changes brought about by this concatenation reside solely in the heat reservoirs. No change remains in the variable body of process 3(a) as at the end of one cycle we find it in its precise initial condition. No change remains in the work reservoir as the work originally deposited there by process 3(a) has been retrieved and transformed into heat by process 3(b). Based on these considerations we can specify the changes experienced by these bodies as follows: The final condition of the hot reservoir equals its initial condition minus an amount of heat Q_h; the final condition of the cold reservoir equals its initial condition plus an amount of heat Q_h.

The fact that the initial and final conditions of the reservoirs for the processes depicted in Figures 2 and 3(c) are the same, allows us to conclude that these processes are equivalent and if so, that the same entropy change applies for both of them. That this is so can be shown by comparing the result for the process of Figure 2 given by

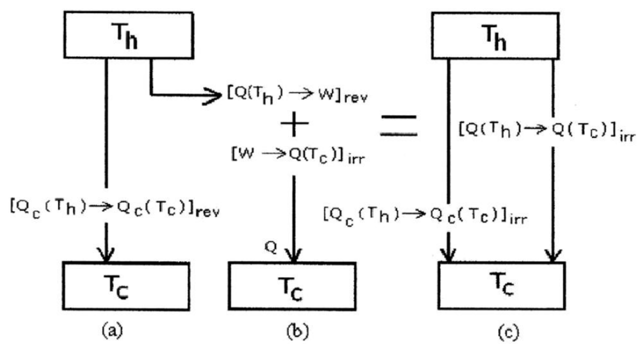

Figure 3 : Out of the amount of heat Q_h released by the hot reservoir of temperature T_h, the reversible engine shown in (a) manages to transfer the smaller amount Q_c to the cold reservoir of temperature T_c, and to transform the difference $Q = Q_h - Q_c$ into the equivalent amount of work W. This amount of work will be now, as shown in (b), frictionally degraded into the equivalent amount of heat Q, and as such it will end up in the cold reservoir. The final result of the concatenation of processes (a) and (b) is shown in (c). The fact that at the end of one cycle the ideal gas acting as variable body in process (a) returns to its initial condition, combined with the fact that the work generated at (a) is dissipated as heat in (b), allows us to realize that in (c) the only bodies changing are the heat reservoirs. The net effect of process (c) is identical to that of the irreversible transfer shown in Figure 2.

equation 6, with that obtained for process 3(c) through the addition of the entropy changes of processes 3(a) and 3(b), as follows

$$\begin{aligned}\Delta S[\text{process } 3(c)] &= \Delta S[\text{process } 3(a)] + \Delta S[\text{process } 3(b)] \\ &= \Delta S[Q_c(T_h) \rightarrow Q_c(T_c)]_{rev} + \Delta S[Q(T_h) \rightarrow W]_{rev} \\ &\quad + \Delta S[W \rightarrow Q(T_c)]_{irr} \\ &= 0 + 0 + \frac{W}{T_c} = \frac{W}{T_c}\end{aligned} \tag{7}$$

The entropy change assigned in equation 7 to transformation $[W \rightarrow Q(T_c)]_{irr}$ comes from the thermodynamic result that associates an entropy increase of magnitude $\delta W/T$ to the irreversible degradation of an amount of work δW into heat at temperature T[3,4]. It should also be noted that in Figure 3(c) the combination of transformations $[Q(T_h) \rightarrow W]_{rev}$ and $[W \rightarrow Q(T_c)]_{irr}$ has been substituted by the expression $[Q(T_h) \rightarrow Q(T_c)]_{irr}$. According to this, the entropy change for this last transformation can be written as follows

$$\begin{aligned}\Delta S[Q(T_h) \rightarrow Q(T_c)]_{irr} &= \Delta S[Q(T_h) \rightarrow W]_{rev} \\ &+ \Delta S[W \rightarrow Q(T_c)]_{irr} = 0 + W/T_c = W/T_c\end{aligned} \tag{8}$$

Therefore

$$\Delta S[\text{process3(c)}] = \Delta S[Q(T_h) \rightarrow Q(T_c)]_{irr} = W/T_c \tag{9}$$

The irreversible label attached to both of the transformations appearing in 3(c) comes from the fact the reversion of either, or both, Q and Q_c, back to the hot reservoir, demands the expenditure of an amount of work that we don't have. If performed, these reversions will leave a permanent change in that body called to supply the missing work. With these precisions aside, we can now recognize that equation 9 is a statement of the fact that the entropy change for process 3(c) finds *sole quantification* in terms of the entropy change of transformation $[Q(T_h) \rightarrow Q(T_c)]_{irr}$. But if this so, then the other transformation there involved $[Q_c(T_h) \rightarrow Q_c(T_c)]_{irr}$, takes place at constant entropy, i.e.

$$\Delta S[Q_c(T_h) \rightarrow Q_c(T_h)]_{irr} = 0 \tag{10}$$

The realization that the process to which equation 10 makes reference is reversible attending to its entropy change, and irreversible attending to the impossibility of transferring Q_c back to the hot reservoir without changes in other bodies remaining, attest to the lack of equivalence between the constant-entropy criterion of reversibility and that embodied by the possibility of restoring the initial condition of the universe. The only possibility open for the constant-entropy criterion to remain valid in regard to what equation 10 expresses i.e. the only possibility for us to trade 'irr' for 'rev' in equation 10 demands of Q_c the ability to flow of itself, unassisted, from the cold to the hot reservoir. In other words the validity of the constant-entropy reversibility criterion demands the non-validity of the second law understood as: Heat cannot, of itself, pass from a colder to a hotter body.

The fact that the unassisted transfer of Q_c from the cold to the hot reservoir is denied by experience confirms the irreversibility of $[Q_c(T_h) \rightarrow Q_c(T_c)]_{irr}$, and negates the association between reversibility and a zero entropy change.

DISCUSSION

Beyond the equivalence of processes 2 and 3(c) made manifest by the identity of their entropy changes, an essential difference remains: The fact that while in process 2 the entropy change is made up of the entropy contributions coming from each and every unit of heat irreversibly flowing from the hot to the cold reservoir; in process 3(c) the entropy change can be traced to the irreversible transfer of the amount of heat Q through the combination of a work-producing/work-degrading process, with the irreversible transfer of the remaining amount of heat Q_c, taking place at constant entropy. This constant entropy irreversible process not only contradicts the supposed equivalence between the constant-entropy reversibility criterion and that based on the possibility of recuperating the original universe, it also negates the equivalence between the said constant-entropy reversibility criterion and the principle: Heat cannot, of itself, pass from a colder to a hotter body.

The previous considerations have brought to light the essential characteristics of a thermodynamic impasse demanding a solution, an impasse which, in this author's opinion, might very well indicate a subtle yet fundamental inconsistency in the edifice of the second law

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