

# Entropy production and lost work for irreversible processes

FRANCO di LIBERTO

Dipartimento di Scienze Fisiche  
 Università di Napoli “Federico II”  
 Complesso universitario Monte S. Angelo  
 Via Cintia - 80126 Napoli (Italy)  
[diliberto@na.infn.it](mailto:diliberto@na.infn.it)  
 tel. + 39 081 676486 - fax + 39 081 676346

In this paper we analyse in depth the Lost Work in an irreversible process (i.e.  $W_{IRREV} = W_{REV} - W_{Lost}$ ). This quantity is also called ‘degraded energy’ or ‘Energy unavailable to do work’. Usually in textbooks one can find the relation  $W_{Lost} \equiv T\Delta S_U$ . Here we show that  $W_{Lost}$  can be expressed in terms of internal and external Entropy production,  $\pi_{int}$  and  $\pi_{ext}$ , quantities which enable to write down in a simple way the

Clausius inequality. We will show that  $W_{Lost} \equiv \int_A^B T_{sys} \delta\pi_{int} + T_{ext} \int_A^B \delta\pi_{ext}^{Endo}$ , where  $T_{sys}$  is the temperature of the system during the corresponding quasi-static process and  $T_{ext}$  is the temperature of the external heat source during the related Endo-reversible process.  $\delta\pi_{ext}^{Endo}$  is the infinitesimal entropy production in each infinitesimal step of such Endo-reversible process. Examples are given for elementary processes.

**Keywords:** irreversibility, entropy production, adiabatic process

## 1. Introduction

Entropy production, a fascinating subject, has attracted many physics researches even in cosmological physics [1], moreover in the past ten years there has been renewed interest in thermodynamics of heat engines; many papers address issues of maximum power, maximum efficiency and minimum Entropy production both from practical and theoretical point of view [2-6].

One of the main points in this field is the analysis of Available Energy and of the Lost Work. Here we give a general relation between Lost Work and Entropy production merging together the pioneering papers of Sommerfeld (1964), Prigogine (1967), Leff (1975) and Marcella (1992), which contain many examples of such relation, and the substance-like approach to the Entropy of the Karlsruhe Physics Course due mainly to Job (1972), Falk, Hermann and Schmid (1983) and Fucks (1987).

It is well known [7-13] that for some elementary irreversible process, like the irreversible isothermal expansion of an ideal gas in contact with an heat source  $T$ , the work performed by the gas in such process

$W_{irrev}$  is related to the reversible work  $W_{Rev}$  (i.e. the work performed by the gas in the corresponding reversible process) by means of the relation

$$W_{irrev} = W_{Rev} - T \Delta S_U \quad (1)$$

where  $\Delta S_U$  is the total entropy change of the universe (system + environment). The degraded energy  $T\Delta S_U$  is usually called  $W_{Lost}$  ‘the Lost work’, i. e.:

$$W_{Lost} = W_{Rev} - W_{irrev}$$

the work that could have been performed in the related reversible process (here the reversible expansion); it is also called ‘energy unavailable to do work’.

By the energy balance, the same relation holds for the amount of heats extracted from the source  $T$

$$Q_{irrev} = Q_{Rev} - T \Delta S_U$$

Therefore  $T\Delta S_U$  is also called the ‘Lost heat  $Q_{Lost}$ ’, i.e. the additional heat that could have been drawn from the source in the related reversible process <sup>‡</sup>[9].

The total variation of Entropy,  $\Delta S_U$ , is usually called ‘Entropy production’. To be precise let us call it here  $\pi_U$ . The second Law claims that

$$\pi_U \geq 0$$

The relation between Entropy production and  $W_{Lost}$  (or  $Q_{Lost}$ ) is the main subject of this paper. Let us outline the steps that lead to the relation (1).

For a process (A→B) in which the system (for example, the ideal gas) absorbs a given amount of heat  $Q$  from the heat source at temperature  $T_s$  and performs some work  $W$ , the entropy production of the Universe, i. e. the total variation of Entropy of system+environment, is

$$\pi_U = \Delta S_{sys} - \frac{Q}{T_s} \quad (2)$$

From the energy balance  $\Delta U_{sys} = Q - W$  it follows

$$T_s \pi_U = T_s \Delta S_{sys} - \Delta U_{sys} - W \quad (3)$$

---

<sup>‡</sup> For an irreversible compression  $T\Delta S_U$  is sometime called  $W_{Extra}$  or  $Q_{Extra}$  [10] i.e. the excess of work performed on the system in the irreversible process with respect to the reversible one (or the excess of heat given to the source in the irreversible process). In a forthcoming paper we will show that  $W_{Extra}$  is related to the environment temperature and to the entropy productions

If the process is reversible then  $\pi_U = 0$  and  $W \equiv W_{Rev} = T_s \Delta S_{sys} - \Delta U_{sys}$ , which shows that the *Reversible Work* in a given process depends only on the endpoints and on the heat sources of the environment [9].

In general for an irreversible process,  $\pi_U > 0$ , i.e. from relation (3), it follows

$$W_{irrev} < W_{Rev} \quad (4)$$

i.e. the Reversible Work is the maximum amount of work that can be performed in the given process, and

$$W_{Lost} = W_{Rev} - W_{irrev} = T_s \pi_U \quad (5)$$

which defines the Lost Work and proves relation (1).

There are however some irreversible processes for which relation (5) is not suitable to evaluate the Lost Work, for example the irreversible adiabatic processes, in which there is some  $W_{Lost}$ , some Entropy production  $\pi_U$ , but no external source  $T_s$ .

In Sec. 3 we evaluate  $W_{Lost}$  for some simple irreversible processes, refine relation (5) taking account of internal and external irreversibility and give a general procedure to evaluate the Lost Work. Such procedure follows from the analysis of Sec.2 where it has been shown that often the total Entropy production is due to the entropy production of the sub-systems. When the subsystems are the system and the environment their entropy productions has been called respectively internal and external, i.e.  $\pi_U = \pi_{int} + \pi_{ext}$

In Sec.2 we analyse by means of the substance-like approach the entropy balance and the entropy productions for some elementary irreversible processes.

In the following the heat quantities  $Q$ 's are positive unless explicitly stated and the system is almost always the ideal gas.

## 2. Entropy production for irreversible processes

In this Section are given some examples of Energy conservation and Entropy production for elementary processes.

First we analyse the *irreversible isothermal expansion* (A-->B) of one mole of monatomic ideal gas which receives the heat  $Q_{irrev}$  from a source at temperature  $T$ .

To be clear let us first analyse with the substance-like approach the Energy balance for this process. For the system (the ideal gas), we have  $\Delta U_{syst} = E_{in} - E_{out}$ , where  $E_{in}$  is the energy which enters into the system ( i.e.  $Q_{irrev}$ ), and  $E_{out}$  is the energy which flows out of the system (i.e.  $W_{irrev}$ , the work performed by the gas);  $\Delta U_{syst}$  is the gain of Internal Energy of the system. For the heat source the gain is  $\Delta U_{Heat-source} = -Q_{irrev}$

Therefore for the Universe (*system+environment*)  $\Delta U_U = \Delta U_{Heat-source} + \Delta U_{system} = W_{irrev}$ . Of course for the isolated system *ideal-gas+heat source+air-around* we have  $\Delta U_{Total} = 0$ , since the Energy is conserved. All this is for the Energy balance.

For the Entropy things are different: the Entropy is conserved only for reversible processes, for example in the *reversible* isothermal expansion  $A \rightarrow B$ , for the ideal gas we have

$$\Delta S_{syst} = S_{in} - S_{out} \quad (6)$$

where  $S_{out} = 0$  since no entropy goes out of the system, the Entropy which comes into the system is

$$S_{in} = \frac{|Q_{Rev}|}{T} = R \ln \frac{V_B}{V_A}, \text{ since } Q_{Rev} = \int_A^B \delta Q_{Rev} = \int_A^B P dV = RT \ln \frac{V_B}{V_A}. Q_{Rev} \text{ is the work performed by the system}$$

in the reversible isothermal expansion and is also the heat which flows from the heat source into the system.

The intrinsic increase in Entropy<sup>§</sup> for the system is  $\Delta S_{sys} = \int_A^B \frac{\delta Q}{T} = R \ln \frac{V_B}{V_A}$ ;  $R=8.314 \text{ J/mol. K}^\circ$  is the

universal constant for the gases.

For the Heat Source (which is the external world) we have

$$\Delta S^{ext} = S_{in}^{ext} - S_{out}^{ext} \quad (7)$$

where  $\Delta S^{ext} = \frac{-|Q_{Rev}|}{T}$ ,  $S_{in}^{ext} = 0$  and  $S_{out}^{ext} = \frac{|Q_{Rev}|}{T}$ .

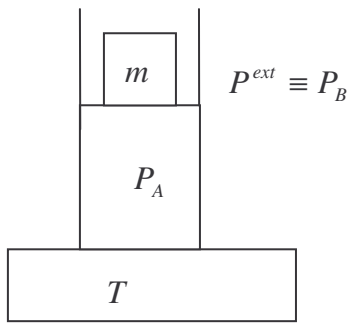
For the Universe, *ideal gas+heat-source*,  $\Delta S_U = \Delta S_{syst} + \Delta S^{ext} = 0 = S_{in}^U - S_{out}^U$  where  $S_{in}^U = S_{out}^U = 0$  since there is no Entropy flowing through the composite system, i.e. the composite system is thermally isolated, it behaves like an isolated system. Of course for the total system *ideal-gas+heat source+air-around*, which is totally isolated we have  $\Delta S_{Total} = 0$ . In this example (a reversible process) the Entropy is conserved.

Let us turn to the irreversibility and take a look at the *irreversible* isothermal expansion at temperature  $T$  of one mole of monatomic ideal gas from the state A to the state B (let, for example,  $P_A = 4P_B$ ). This can be done by means of thermal contact with a source at temperature  $T$  or at temperature greater than  $T$ .

---

<sup>§</sup>  $\Delta S_{sys}$  is usually called (internal) "Entropy creation" [15]

I) Thermal contact with a source at temperature  $T$



The ideal gas, in contact with the source  $T$ , is at pressure  $P_A = 4P_B = 4P^{ext}$  by means of some mass  $m$  on the mass-less piston. Let  $V_A$  be its volume. The mass is removed from the piston and the ideal gas performs an isothermal irreversible expansion and reaches the volume  $V_B$  at pressure  $P_B = P^{ext}$ . In the expansion the gas has performed the work

$$W_{irrev} = P_B (V_B - V_A) = \frac{3}{4}RT \quad (8)$$

By means of the Energy Balance we can see that the heat which lives the source and goes into the system is

$$Q_{irrev} = W_{irrev} \quad (9)$$

The intrinsic increase of the Entropy in the ideal gas is the same as for the reversible process i.e.

$$\Delta S_{sys} = \int_A^B \frac{\delta Q_{Rev}}{T} = R \ln \frac{V_B}{V_A} = R \ln 4$$

We can verify that now relation (6) is not fulfilled, in fact  $S_{out} = 0$ , since no Entropy goes out from the system

$$S_{in} = \frac{|Q_{irrev}|}{T} = \frac{3}{4}R, \text{ so } \Delta S_{syst} \neq S_{in} - S_{out}.$$

To restore the balance we must add to the right-hand side a quantity  $\pi_{int}$ , the Entropy production\*\* due to the internal irreversibility

$$\Delta S_{syst} = S_{in} - S_{out} + \pi_{int} \quad (10)$$

We see that  $\pi_{int}$  is  $\pi_{int} = R \ln 4 - \frac{3}{4}R$ .

On the contrary for the heat source the relation (6) is fulfilled

$$\Delta S^{ext} = S_{in}^{ext} - S_{out}^{ext}$$

in fact  $\Delta S^{ext} = \frac{-|Q_{irrev}|}{T}$ ,  $S_{in}^{ext} = 0$  and  $S_{out}^{ext} = \frac{|Q_{irrev}|}{T}$ .

There is no external irreversibility, there is no external Entropy production, in the general relation

$$\Delta S^{ext} = S_{in}^{ext} - S_{out}^{ext} + \pi_{ext} \quad (11)$$

\*\* This definition of Entropy production is different from the ‘‘Entropy creation’’, they coincide only for adiabatic processes.

here we have  $\pi_{ext} = 0$ . It is well known indeed that the isothermal exchanges of heat between heat reservoirs are *reversible*.

For the Universe (ideal gas+heat source ) we have

$$\Delta S_U = \Delta S_{syst} + \Delta S^{ext} = S_{in}^U - S_{out}^U + \pi_U = \pi_U \quad (12)$$

because  $S_{in}^U = S_{out}^U = 0$

and here

$$\pi_U = \pi_{int} + \pi_{ext} = \pi_{int} \quad (13)$$

since  $\pi_{ext} = 0$ .

The only source of Entropy is the internal irreversibility.

The entropic balance (10) is reported in Fig. 1, where the circle is the system (i.e. the ideal gas)

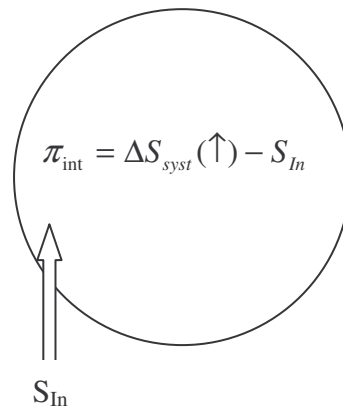


Figure 1. The entropic balance for the ideal gas.

The entropic balance for the heat source (11) is reported in Fig. 2, where the square is the heat source T

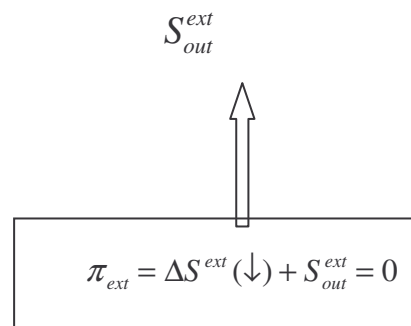


Figure 2. The entropic balance for the heat source T

II) Thermal contact with an heat source at  $T_{ext} > T$  for instance  $T_{ext} = \frac{4}{3}T$ .

The gas ,which is in the state  $(P_A, V_A, T)$  is brought in thermal contact with the heat source  $T_{ext}$  and the mass on the piston is removed. The thermal contact with the source is now shorter than before in order to not increase the temperature of the gas. Now  $Q_{irrev}$ ,  $W_{irrev}$ ,  $W_{Rev}$ ,  $\pi_{int}$  and  $\Delta S_{syst}$  are the same as before, but

$\Delta S^{ext} = -\frac{|Q_{irrev}|}{T_{ext}}$ , therefore

$$\pi_U = \Delta S_{syst} + \Delta S^{ext} = R \ln \frac{V_B}{V_A} - \frac{|Q_{irrev}|}{T_{ext}} = \pi_{int} + \pi_{ext} = R \ln 4 - \frac{|Q_{irrev}|}{T} + \pi_{ext} \quad (14)$$

which implies that  $\pi_{ext}$  is different from zero, it is

$$\pi^{ext} = \frac{|Q_{irrev}|}{T} - \frac{|Q_{irrev}|}{T_{ext}} = \frac{|Q_{irrev}|}{T} \left(1 - \frac{T}{T_{ext}}\right) = \frac{|Q_{irrev}|}{T} \eta \quad (15)$$

where  $\eta$  is the performance of a reversible engine working between  $T_{ext}$  and  $T \leq T_{ext}$

This result is general whenever we have some heat which flows from a hotter to a colder source. Here

$$\pi^{ext} = \frac{3}{4}R \cdot \frac{1}{4} = \frac{3}{16}R$$

Let us give three more examples of Entropy productions in irreversible processes

III) For the irreversible process in which the heat  $|Q|$  flows from the source  $T_1$  to the colder source

$T_2$  we can easily verify that  $\pi_U = \Delta S_U = \frac{|Q|}{T_2} - \frac{|Q|}{T_1}$  and that

$$\pi_U = \frac{|Q|}{T_2} \left(1 - \frac{T_1}{T_2}\right) = \frac{|Q|}{T_2} \eta \quad (16)$$

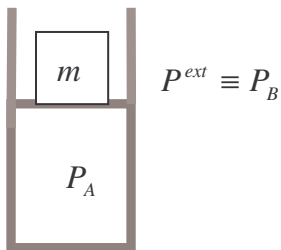
Where  $\eta$  is the performance of a reversible engine working between the heat sources  $T_2 \leq T_1$

As pointed out by S.K. Das [11] it is interesting to consider the case of two heat sources with finite capacity  $C$ . In the irreversible process the heat can flow until the temperature

$$T_0 = \frac{1}{2}(T_2 + T_1)$$

is reached. The total heat which flows is  $Q = C(T_1 - T_0)$ . In the related reversible process however the final temperature is  $T_0 = \sqrt{T_1 T_2}$ ; in Appendix B we find the Entropy production and the Lost Work for this process.

## IV) Irreversible adiabatic expansion



The vessel is thermally isolated. The ideal gas, is maintained at pressure  $P_A = 4P_B = 4P^{ext}$  by means of some mass  $m$  on the mass-less piston. Let  $V_A$  be its volume and  $T_A = \frac{P_A V_A}{R}$  the initial temperature. The mass is removed from the piston and the ideal gas performs an adiabatic irreversible expansion and reaches the volume  $V_B$  at pressure  $P_B = P^{ext}$ . Since no heat has gone into the system, the work performed by the gas in the expansion is  $W_{irrev} = -\Delta U_{sys} = -C_V (T_B - T_A)$

Moreover  $S_{in} = S_{out} = 0$ , therefore

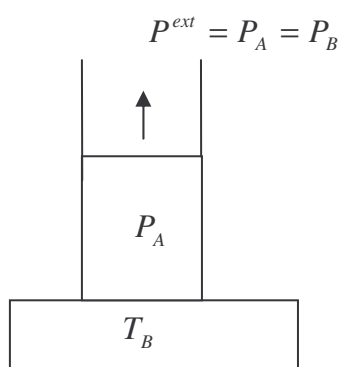
$$\pi_U = \pi_{in} = \Delta S_{sys} \quad (17)$$

where there is no external irreversibility.

To evaluate the intrinsic increase of the Entropy in the ideal gas (the internal “creation of entropy”), we must follow one of the many reversible paths from A to B. Here we take the reversible isotherm (A→C) + the reversible isochoric (C→B). Since by First Law  $\delta Q = PdV + C_V dT$ , it follows

$$\Delta S_{sys} = \int_A^B \frac{\delta Q_{Rev}}{T} = \int_A^C \frac{PdV}{T} + \int_C^B \frac{C_V dT}{T} = R \ln \frac{V_B}{V_A} + C_V \ln \frac{T_C}{T_B}$$

V) Finally let us consider the irreversible isobaric expansion at pressure  $P_A$  of one mole of monatomic ideal gas from the state A to the state B for which, for example,  $T_B = 2T_A$ .



The ideal gas, initially at temperature  $T_A$  is brought in thermal contact with the source  $T_B = 2T_A$ , then an irreversible isobaric expansion at pressure  $P_A = P_B = P^{ext}$  takes place and the ideal gas reaches the final state B. Let  $V_A$  be the initial volume and  $V_B$  the final volume. In the expansion the gas has performed the work ( $=E_{out}$ )

$$W_{irrev} = P_A (V_B - V_A) = R(T_B - T_A) \quad (18)$$

and has extracted from the source  $T_B$  the heat ( $=E_{in}$ )  $|Q_{irre}| = C_p (T_B - T_A)$ .

From the energy balance we understand that there has been an increase of internal energy  $\Delta U_{A-B} = E_{in} - E_{out} = C_V (T_B - T_A)$



where  $C_p$  and  $C_v$  are the molar specific heats respectively at constant pressure and at constant volume.

For this process

$$\pi_U = \Delta S_{\text{sys}} + \Delta S^{\text{ext}} = C_p \ln \frac{T_B}{T_A} - \frac{|Q_{\text{irrev}}|}{T_B} \quad (19)$$

As in the previous cases we want to find  $\pi_{\text{int}}$  and  $\pi_{\text{ext}}$  i.e. the Entropy production due to the internal irreversibility and that due to the external irreversibility.

The path we follow is to analyse the related externally reversible process (Eso-reversible process); for this we evaluate the Entropy production, which is therefore due only to the internal irreversibility. This will be  $\pi_{\text{int}}$ . From this we can have  $\pi_{\text{ext}}$  (the Entropy production due to the external irreversibility) by subtracting  $\pi_{\text{int}}$  from  $\pi_U$  i.e.

$$\pi_{\text{ext}} = \pi_U - \pi_{\text{int}} \quad (20)$$

Remark that this procedure allows to evaluate  $\pi_{\text{int}}$  and  $\pi_{\text{ext}}$  also for the previous process (II), in fact to perform the Eso-reversible process in which the gas at temperature  $T$  receives the heat  $Q_{\text{irrev}}$ , we need an auxiliary heat source at  $T$ , from which the gas takes  $Q_{\text{irrev}}$ , and an auxiliary reversible heat engine which takes the heat  $Q^{\text{Eso}}$  from  $T_{\text{ext}}$  and gives to the source at  $T$  the heat  $Q_{\text{irrev}}$ . In such Eso-reversible process

$$\pi_U^{\text{Eso}} = \pi_{\text{int}} = \frac{Q_{\text{Rev}}}{T} - \frac{Q_{\text{irrev}}}{T} \text{ and } Q^{\text{Eso}} = \frac{T_{\text{ext}}}{T} Q_{\text{irrev}}; \text{ from relation (20) we could have } \pi_{\text{ext}} = \frac{Q_{\text{irrev}}}{T} - \frac{Q_{\text{irrev}}}{T_{\text{ext}}},$$

which is relation (15).

Here, for the isobaric, to perform the Eso-reversible process we need a sequence of heat sources ranging from  $T_A$  to  $T_B$ , from which the gas takes, at each infinitesimal step, the heat  $\delta Q$  to perform the irreversible isobaric expansion, and an auxiliary reversible heat engine which takes from the source  $T_B$  the heat

$$\delta Q^{\text{Eso}} = \frac{T_B}{T} \delta Q \text{ and give to the source } T \text{ of the sequence, the heat } \delta Q = C_p dT. \text{ Such an engine at each step}$$

$$\text{performs the work } \delta W_{\text{Rev}} = \delta Q^{\text{Eso}} \left(1 - \frac{T}{T_B}\right). \text{ Obviously } Q^{\text{Eso}} = \int_A^B \delta Q^{\text{Eso}} = C_p T_B \int_A^B \frac{dT}{T} = T_B C_p \ln \frac{T_B}{T_A}$$

In this Externally reversible process (Eso-reversible) the Entropy production due to the Internal irreversibility  $\delta\pi_{\text{int}}$  at each step is due to the infinitesimal variation of Entropy of the gas (i.e.  $dS_{\text{sys}}^{\text{Eso}} = C_p \frac{dT}{T}$ ) and to the infinitesimal variation of Entropy of that heat source of the sequence which is active in the step (i.e.

$$dS_{\text{ext}}^{\text{Eso}} = -C_p \frac{dT}{T}) \text{ hence}$$

$$\delta\pi_{\text{int}} = dS_{\text{sys}}^{\text{Eso}} + dS_{\text{ext}}^{\text{Eso}} = C_p \frac{dT}{T} - C_p \frac{dT}{T} = 0$$

We find therefore that  $\pi_{\text{int}} = 0$ , there is no internal Entropy production in this Eso-reversible process; therefore

$$\pi_{\text{ext}} = \pi_U = C_P \ln \frac{T_B}{T_A} - \frac{|Q_{\text{irrev}}|}{T_B} \quad (21)$$

The total entropy production is only due to the external irreversibility, therefore the Eso-reversible process is also Totally-reversible. If we call  $Q^{\text{Max}}$  the Maximum quantity of heat that the external source gives in the totally-reversible process, here we have that  $Q^{\text{Eso}} = Q^{\text{Max}}$ . Of course  $Q_{\text{irrev}} \leq Q^{\text{Eso}} \leq Q^{\text{Max}}$  and  $Q_{\text{irrev}} \leq Q_{\text{Endo}} \leq Q^{\text{Max}}$ ; we understand that the processes for which  $Q_{\text{Endo}} = Q^{\text{Max}}$  are the Endo-reversible processes, which are also Totally -reversible, i.e. the Endo-reversible processes for which  $\pi_{\text{ext}} = 0$ .

To conclude this Section we remark that the global Entropy change is related the local Entropy productions by means of the following relation:

$$\pi_U \equiv \Delta S_U = \Delta S_{\text{sys}} + \Delta S^{\text{ext}} = \pi_{\text{int}} + \pi_{\text{ext}}$$

The second law of the thermodynamics claims that the global Entropy production is greater or equal zero  $\Delta S_U \geq 0$ , i.e.  $\pi_U \geq 0$  but from all these examples we see that also  $\pi_{\text{int}} \geq 0$  and  $\pi_{\text{ext}} \geq 0$ , this suggests that in each subsystem the Entropy cannot be destroyed. On the other hand, from the substance-like approach of Karlsruhe, i.e. from the local Entropy balance, (that we can write for each subsystem) this condition is completely natural<sup>††</sup> [7],[12]. The proof that for each subsystem  $\pi \geq 0$  has been given in Sommerfeld (1964) [7].

Moreover as a consequence of this formulation of the Second law of the Thermodynamics we have the following formulation of Clausius inequality: if the system makes a whatsoever cycle, relation (10) implies:

$$0 = \oint dS_{\text{sys}} = \oint \frac{\delta Q}{T_{\text{sys}}} + \pi_{\text{int}} \Rightarrow \quad \oint \frac{\delta Q}{T_{\text{sys}}} \leq 0 \quad (22)$$

where  $\delta Q > 0$ , i.e. it is positive, when it comes into the system and  $T_{\text{sys}}$  is the system's temperature in each step of the cycle. This formulation of the Clausius inequality seems more simple and elegant than the traditional one.

Similarly for the environment, when it makes a whatsoever cycle, from relation (11), we have

---

<sup>††</sup> This local formulation of the second law was also given by Prigogine [7]. In a recent paper [14] it has been pointed out that those irreversible processes for which some local entropy production  $\pi$  is negative (if any) are more efficient than the corresponding reversible processes. Here we will find always  $\pi \geq 0$ .

$$0 = \oint dS^{ext} = \oint \frac{\delta Q}{T_{ext}} + \pi^{ext} \Rightarrow \oint \frac{\delta Q}{T_{ext}} \leq 0^{\ddagger\ddagger} \quad (23)$$

### 3-Lost Work : examples and general expression

In this section we evaluate the Lost Work for each of the processes of the Sec.2. For each process we can easily evaluate the work available in the related totally- Reversible process, from this we subtract the effective work performed in the irreversible process and this difference gives the Lost Work. This enables to check how suitable relation (5) is to give the Lost Work in terms of the Entropy production. As already pointed out, for adiabatic processes we need a relation more general than relation (5). In this section such general link between Entropy production and Lost Work is finally given.

I) For the irreversible isotherm expansion at temperature  $T$ , as has been already shown, the Lost Work is given by

$$W_{Lost} = W_{Rev} - W_{irrev} = RT \ln 4 - \frac{3}{4} RT$$

or

$$Q_{Lost} = Q_{Rev} - Q_{irrev} = RT \ln 4 - \frac{3}{4} RT$$

On the other hand relation (5) gives the same result.

$$W_{Lost} = T\pi_U = T\pi_{int} = T(R \ln 4 - \frac{3}{4} R)$$

II) For the irreversible isotherm expansion at temperature  $T$ , by means of a source at  $T_{ext} \geq T$ , the Total Reversible Work is the Reversible work of the gas + the work of an auxiliary reversible engine working between  $T_{ext}$  and  $T$ . For the gas  $W_{Rev}(gas) = Q_{Rev} = RT \ln 4$

The auxiliary reversible engine, which brings the heat  $Q_{Rev}$  to the system (the ideal gas at temperature

$T$ ) and takes from the heat source  $T_{ext}$  the heat  $Q_{Rev} \frac{T_{ext}}{T}$  does the Work

$$W_{Rev}(engine) = Q_{Rev} \frac{T_{ext}}{T} \left(1 - \frac{T}{T_{ext}}\right)$$

Therefore the total reversible work is

$$W_{RevTotal} = W_{Rev}(gas) + W_{Rev}(engine) = Q_{Rev} + Q_{Rev} \frac{T_{ext}}{T} \left(1 - \frac{T}{T_{ext}}\right) = Q_{Rev} \frac{T_{ext}}{T} = Q^{Max} \quad (24)$$

---

<sup>‡‡</sup> A similar remark is due to Marcella[9]

On the other hand the Work performed by the gas in the irreversible expansion is  $W_{irrev} = Q_{irrev} = \frac{3}{4}RT$ , therefore

$$W_{Lost} = W_{RevTotal} - W_{irrev} = Q^{Max} - Q_{irrev} \quad (25a)$$

The same result we have from the relation (5)

$$W_{Lost} = T_{ext} \pi_U = T_{ext} \left( \frac{Q_{Rev}}{T} - \frac{|Q_{irrev}|}{T_{ext}} \right) = Q^{Max} - Q_{irrev} . \quad (25b)$$

We can also compute the Lost Work due respectively to the internal and external irreversibility

$$W_{Lost} = T_{ext} \pi_U = T_{ext} (\pi_{int} + \pi_{ext}) = T_{ext} \left( \frac{Q_{Rev}}{T} - \frac{|Q_{irrev}|}{T} \right) + T_{ext} \left( \frac{|Q_{irrev}|}{T} - \frac{|Q_{irrev}|}{T_{ext}} \right) \quad (26)$$

Let us call  $Q^{Upper}$  the quantity  $Q_{irrev} \frac{T_{ext}}{T}$  i.e.  $Q^{Upper} = Q_{irrev} \frac{T_{ext}}{T}$ . The second term, the Lost Work due to the External irreversibility is the work of a reversible engine which takes from  $T_{ext}$  the heat  $Q^{Upper}$  and gives to the system the heat  $Q_{irrev}$

$$W_{Lost}(ext) = T_{ext} \pi_{ext} = Q^{Upper} \left( 1 - \frac{T}{T_{ext}} \right) = Q^{Upper} \eta = Q^{Upper} - Q_{irrev} \quad (27)$$

The first term, i.e. the lost Work due to the internal irreversibility, is

$$W_{Lost}(int) = T_{ext} \pi_{int} = Q^{Max} - Q^{Upper} \quad (28)$$

It says that the internal irreversibility is a constraint which forbids the extraction of *the maximum available heat, i.e.  $Q^{Max}$*

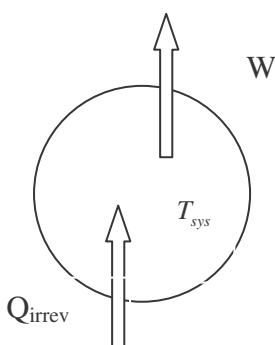
On the other hand, from the physical point of view we understand that

$$1) W_{Lost}(int) = Q_{Rev} - Q_{irrev} = RT \ln 4 - \frac{3}{4}RT$$

$$2) W_{Lost}(ext) = Q^{Max} - Q_{Rev}$$

Therefore there are also physical reasons to write down a more intuitive and general expression of the Lost Work in terms of the internal and external Entropy production.

Let us outline the way to find it. Looking at the System at temperature  $T_{sys}$ , in the process some heat  $Q$  comes in and some work  $W$  comes out, therefore from relation (10) and the First Law



$$\Delta S_{sys} = \frac{Q}{T_{sys}} + \pi_{int}$$

$$T_{sys} \pi_{int} = \Delta S_{sys} - Q = \Delta S_{sys} - \Delta U_{sys} - W$$

If the process is Endo-reversible we have

$$0 = \Delta S_{sys} - \Delta U_{sys} - W_{Rev}^{Endo}$$

Therefore

$$T_{sys} \pi_{int} = W_{Rev}^{Endo} - W = Q_{Rev} - Q_{irrev} \quad (29)$$

i.e.  $T_{sys} \pi_{int} = W_{Lost}(int)$  it is the lost work due to the internal irreversibility, i.e. the lost work with respect to the Endo-reversible process.

It remains to evaluate the external Lost Work with respect to the Endo-reversible process. In the Endo-reversible process, from relation (11)

$$\begin{aligned} \pi_{ext}^{Endo} &= \frac{Q_{Rev}}{T} + \Delta S_{ext} = \frac{Q_{Rev}}{T} - \frac{Q_{Rev}}{T_{ext}} \\ T_{ext} \pi_{ext}^{Endo} &= T_{ext} \frac{Q_{Rev}}{T} - Q_{Rev} = Q^{Max} - Q_{Rev} = T_{ext} \frac{Q_{Rev}}{T} \left(1 - \frac{T}{T_{ext}}\right) \end{aligned} \quad (30)$$

As expected! Relations (29) and (30) are more intuitive than the relations (27) and (28)

Therefore, in general

$$W_{Lost} = T_{sys} \pi_{int} + T_{ext} \pi_{ext}^{Endo} \quad (31a)$$

or if the system has variable temperature (See Appendix A)

$$W_{Lost} = \int_A^B T_{sys} \delta \pi_{int} + T_{ext} \pi_{ext}^{Endo} \quad (31b)$$

Or for both temperatures variable, and for  $T_{ext}$  ranging between  $T_C$  and  $T_D$  (See Appendix A)

$$W_{Lost} = \int_A^B T_{sys} \delta \pi_{int} + \int_C^D T_{ext} \delta \pi_{ext}^{Endo} \quad (31c)$$

**III)** For the irreversible process in which the heat  $|Q|$  flows spontaneously from the source  $T_1$  to the colder source  $T_2$  there is no irreversible work ( $W_{irrev} = 0$ ). The only reversible work is the work made by the auxiliary reversible engine, which carries to  $T_2$  the heat  $Q$ , and takes from the heat source  $T_1$  the heat

$Q^{Max} = Q \frac{T_1}{T_2}$  therefore we have

$$W_{RevTotal} = W_{Rev}(engine) = Q \frac{T_1}{T_2} \left(1 - \frac{T_2}{T_1}\right) = Q \frac{T_1}{T_2} - Q = Q^{Max} - Q$$

Therefore

$$W_{Lost} = W_{RevTotal}$$

On the other hand, we have the same result from the relation (5)

$$W_{Lost} = T_1 \pi_U = T_1 \frac{Q}{T_2} \left(1 - \frac{T_2}{T_1}\right) = Q^{Max} - Q \quad (32)$$

Remark that *unfortunately* in the text-books, for such process we find

$$W_{Lost} = T_2 \pi_U = T_2 \frac{Q}{T_2} \left(1 - \frac{T_2}{T_1}\right) = Q \left(1 - \frac{T_2}{T_1}\right) . \quad (33)$$

that is the reversible work of an engine which takes  $Q$  from  $T_1$  and brings to  $T_2$  the heat

$$Q_{down} = Q \frac{T_2}{T_1}$$

Also using relation (31 a) for this process we have (let the system be the heat source  $T_1$ )

$$W_{Lost} = T_{ext} \pi_{ext}^{Endo} = T_1 \left(\frac{Q}{T_2} - \frac{Q}{T_1}\right) = Q^{Max} - Q .$$

The analysis of the Lost Work when  $T_1$  and  $T_2$  have finite heat capacity  $C$  is reported in Appendix B

IV) For the Irreversible adiabatic expansion ( $A \rightarrow B$ ) of the ideal gas, there is no external irreversibility, no  $Q_{irrev}$  and no external heat source. The irreversible Work, can be easily computed by means of the Energy balance  $W_{irrev} = -\Delta U_{sys} = -C_V (T_B - T_A) = C_V (T_A - T_B)$ . Moreover remember that

$$\pi_U = \pi_{int} = \Delta S_{sys} = \int_A^B \frac{\delta Q_{Rev}}{T} = \int_A^C \frac{PdV}{T} + \int_C^B \frac{C_V dT}{T} = R \ln \frac{V_B}{V_A} + C_V \ln \frac{T_C}{T_B}$$

and observe that, since there is no thermal interaction with external world, we **cannot** compute  $W_{Lost}$  by means of relation (5), and that the related reversible process from A to B can be made in many different way, For each one of this, here we evaluate the Reversible Work and then the Lost Work.

- a) We can go from A to B by means of the reversible isotherm ( $A \rightarrow C$ ) + the reversible isochoric ( $C \rightarrow B$ ); since there is no work in the isochoric

$$W_{Rev}(a) = \int_A^B PdV = \int_A^C PdV = RT \ln \frac{V_C}{V_A}$$

The Lost Work is therefore, since  $V_B = V_C$

$$W_{Lost}(a) = W_{RevTotal} - W_{irrev} = RT \ln \frac{V_B}{V_A} + C_V (T_B - T_A) \quad (34)$$

Since from the Energy balance (the First Law)  $\delta Q = PdV + C_V dT$ , in the infinitesimal step( See AppendixA)

$$\delta\pi_{\text{int}} = dS = \frac{\delta Q}{T_{\text{sys}}} = \frac{PdV}{T_{\text{sys}}} + C_V \frac{dT}{T_{\text{sys}}} \quad (35)$$

From (31b) we have

$$W_{\text{Lost}} = \int_A^B T_{\text{sys}} \delta\pi_{\text{int}} = RT \ln \frac{V_B}{V_A} + C_V (T_B - T_A) \quad (36)$$

b) We can go from A to B by means of the reversible adiabatic (A→D) + the reversible isochoric (D→B)

The reversible work is the work made in reversible adiabatic (A→D) in which  $PV^\gamma = \text{Const.}$ ,  $\gamma = \frac{C_P}{C_V}$

i.e.

$$W_{\text{Rev}}(b) = \int_A^D PdV = \text{Const.} \int_A^D V^{-\gamma} dV = C_V (T_A - T_D)$$

Therefore

$$W_{\text{Lost}}(b) = W_{\text{Rev}}(b) - W_{\text{irrev}} = C_V (T_A - T_D) + C_V (T_B - T_A) = C_V (T_B - T_D)$$

To find this by means of relation (31b) we use relation (35)

$$\delta\pi_{\text{int}}(b) = dS_{\text{sys}}(b)$$

And since  $dS_{\text{sys}}(b) = 0$  in the adiabatic A→D and  $dS_{\text{sys}}(b) = \frac{C_V dT}{T}$  in isochoric we have from (31b)

$$W_{\text{Lost}}(b) = \int_A^B T_{\text{sys}} \delta\pi_{\text{int}}(b) = \int_D^B C_V dT = C_V (T_B - T_D)$$

c) We can go from A to B by means of the reversible isobaric (A→E) and the reversible isochoric (E→B). The total reversible work is the work made in the reversible isobaric (A→E). In the isobaric

$P(V) = P_A$ , therefore

$$W_{\text{Rev}}(c) = \int_A^E PdV = P_A \int_A^E dV = P_A (V_E - V_A)$$

Therefore

$$W_{\text{Lost}}(c) = W_{\text{Rev}}(c) - W_{\text{irrev}} = P_A (V_E - V_A) + C_V (T_B - T_A)$$

To find this by means of relation (31b), recall again that

$$\delta\pi_{\text{int}}(c) = dS_{\text{sys}}(c)$$

And since  $dS_{\text{sys}}(c) = C_P \frac{dT}{T}$  in the isobaric A→E and  $dS_{\text{sys}}(c) = \frac{C_V dT}{T}$  in isochoric E→B

from (31b) we have

$$\begin{aligned} W_{\text{Lost}}(c) &= \int_A^B T_{\text{sys}} \delta\pi_{\text{int}}(c) = \int_A^E C_P dT + \int_E^B C_V dT = C_P (T_E - T_A) + C_V (T_B - T_E) = \\ &= R(T_E - T_A) + C_V (T_B - T_A) \end{aligned}$$

The paths a), b) and c) are only three of the possible reversible paths from A to B

V) For the irreversible isobaric expansion at pressure  $P_A$  of one mole of monatomic ideal gas from the state A to the state B for which, for example,  $T_B = 2T_A$ , the irreversible work is

$$W_{irrev} = P_A (V_B - V_A) = R(T_B - T_A) \text{ and } \pi_{ext} = \pi_U = C_P \ln \frac{T_B}{T_A} - \frac{|Q_{irrev}|}{T_B}.$$

The total Reversible work is the reversible work made by the gas (which is identical to the irreversible work) and the work made by the auxiliary reversible engine working between  $T_B$  and the variable temperature  $T$  of the sequence of sources which we use to make the reversible isobaric expansion.

$$W_{RevTotal} = W_{Rev}(gas) + W_{Rev}(engine) = P_B (V_B - V_A) + \int_A^B \delta Q^{Eso} \left(1 - \frac{T}{T_B}\right)$$

where  $\delta Q^{Eso} = \frac{T_B}{T} C_P dT = \delta Q^{Max}$

Therefore

$$W_{Lost} = W_{RevTotal} - W_{irrev} = C_P T_B \ln \frac{T_B}{T_A} - C_P (T_B - T_A)$$

On the other hand by relation (5)

$$W_{Lost} = T_B \pi_U = T_B \pi_{ext} = C_P T_B \ln \frac{T_B}{T_A} - C_P (T_B - T_A)$$

It easy to verify that we can compute  $W_{Lost}$  with relation (31 b)

$$W_{Lost} = \int_A^B T_{sys} \delta \pi_{int} + T_{ext} \pi_{ext}^{Endo} = T_B \int_A^B \delta \pi_{ext}^{Endo}$$

In fact from relation (11) at each infinitesimal step of the Endo-reversible process. Since  $\delta Q \equiv C_P dT$  and  $T_{sys}$  ranges between  $T_A$  and  $T_B$

$$\delta \pi_{ext}^{Endo} = \frac{\delta Q}{T_{sys}} - \frac{\delta Q}{T_{ext}} = \frac{C_P dT}{T} - \frac{C_P dT}{T_B} = \frac{C_P dT}{T} \left(1 - \frac{T}{T_B}\right)$$

It follows

$$W_{Lost} = T_B \int_A^B \delta \pi_{ext}^{Endo} = \int_A^B T_B \frac{C_P dT}{T} \left(1 - \frac{T}{T_B}\right) = T_B C_P \ln \frac{T_B}{T_A} - C_P (T_B - T_A)$$



## 4- Conclusion

By means of the substance-like approach we have shown that the *entropy production*  $\pi$  and *entropy creation*  $\Delta S$ , are different concepts. They coincide only for adiabatic processes or when the whole Universe (system+environment) is investigated. The Second Law is a constraint on the total entropy creation, i.e. there are many processes in which one subsystem has negative entropy creation  $\Delta S$ , instead the entropy production, for each subsystem, is always  $\pi \geq 0$ . We have shown that the relation  $\pi_U = \pi_{int} + \pi_{ext}$  is suitable to give in a short way the Clausius inequality and mainly to give an expression of the Lost Work in terms of the entropy production. We believe that the relation  $\pi_U = \pi_{int} + \pi_{ext}$  will be also useful to make an analysis of the Extra Work ( $W_{Extra}$ ) i.e. the excess of work that is performed on the system in some irreversible process. The excess will be evaluated with respect to work performed in the reversible one. That analysis is in progress.

**Acknowledgments** : This work is mainly due to useful discussion with Marco Zannetti, Caterina Gizzi-Fissore, Michele D'Anna, Corrado Agnes and with my friend Franco Siringo to whose memory this paper is especially dedicated.

## APPENDIX A

Here we prove relations (31b) and (31c)

When  $T_{sys}$  and  $T_{ext}$  are variable, we must consider infinitesimal steps, i.e. the related quasi-static process.

Looking at the System at temperature  $T_{sys}$ , in the infinitesimal process some heat  $\delta Q$  comes in the system and some work  $\delta W$  leaves it, therefore from relation (10) and the First Law

$$dS_{sys} = \frac{\delta Q}{T_{sys}} + \delta\pi_{int}^{q.s.}$$

Where  $\delta\pi_{int}^{q.s.}$  is the infinitesimal entropy production in the related quasi-static irreversible process.

$$T_{sys} \delta\pi_{int}^{q.s.} = T_{sys} dS_{sys} - \delta Q = T_{sys} dS_{sys} - dU_{sys} - \delta W$$

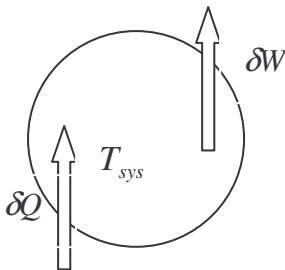


Fig. 4 Some heat comes in the system and some work leaves the system in the infinitesimal step.

If the infinitesimal process is Endo-Reversible ( $\delta\pi_{int}^{q.s.} = 0$ ) we have

$$0 = T_{sys} dS_{sys} - dU_{sys} - \delta W_{Rev}^{Endo}$$

Therefore

$$T_{\text{sys}} \delta\pi_{\text{int}}^{q.s.} = \delta W_{\text{Rev}}^{\text{Endo}} - \delta W = \delta Q_{\text{Rev}} - \delta Q_{\text{irrev}} \quad (\text{A1})$$

i.e.  $T_{\text{sys}} \delta\pi_{\text{int}}^{q.s.} = \delta W_{\text{Lost}}(\text{int})$  is the infinitesimal Lost work due to the Internal irreversibility, i. e. the infinitesimal Lost work with respect to the Endo-reversible process.

Therefore

$$W_{\text{Lost}}(\text{int}) = \int_A^B T_{\text{sys}} \delta\pi_{\text{int}}^{q.s.} = \int_A^B \delta W_{\text{Rev}}^{\text{Endo}} - \int_A^B \delta W$$

Remark that for the adiabatic process, many Endo-reversible paths are possible; therefore for each Endo-reversible path connecting A and B, we evaluate the Lost Work for the related quasi-static process. Moreover in that case  $\delta\pi_{\text{int}}^{q.s.} = dS_{\text{sys}}$

Finally we evaluate for each infinitesimal step the External Lost Work with respect to the Endo-reversible process. In each step the Endo-reversible process

$$\begin{aligned} \delta\pi_{\text{ext}}^{\text{Endo}} &= \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}} - dS_{\text{ext}} = \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}} - \frac{\delta Q_{\text{Rev}}}{T_{\text{ext}}} \\ T_{\text{ext}} \delta\pi_{\text{ext}}^{\text{Endo}} &= T_{\text{ext}} \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}} - \delta Q_{\text{Rev}} = \delta Q^{\text{Max}} - \delta Q_{\text{Rev}} = T_{\text{ext}} \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}} \left(1 - \frac{T_{\text{sys}}}{T_{\text{ext}}}\right) = T_{\text{ext}} \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}} \eta \end{aligned} \quad (\text{A2})$$

Where  $\eta$  is the performance of the heat engine that works between  $T_{\text{ext}}$  and  $T_{\text{sys}}$ . Therefore

$$W_{\text{Lost}}(\text{ext}) = T_{\text{ext}} \pi_{\text{ext}}^{\text{Endo}} \quad (\text{A3a})$$

Or for  $T_{\text{ext}}$  ranging between  $T_C$  and  $T_D$

$$W_{\text{Lost}}(\text{ext}) = \int_C^D T_{\text{ext}} \delta\pi_{\text{ext}}^{\text{Endo}} \quad (\text{A3b})$$

In conclusion for both temperatures variable

$$W_{\text{Lost}} = \int_A^B T_{\text{sys}} \delta\pi_{\text{int}}^{q.s.} + \int_C^D T_{\text{ext}} \delta\pi_{\text{ext}}^{\text{Endo}} \quad (\text{A4})$$

## APPENDIX B

*Lost Work and Entropy production in the thermal contact of two heat sources with finite heat capacity*

Let  $T_1$  and  $T_2$  be two heat sources with finite heat capacity  $C$ , for example two identical objects, respectively at temperature  $T_1$  and  $T_2$ .

In order to transfer in a reversible way some heat from  $T_1$  to  $T_2$ , we need an auxiliary reversible engine which can work until both bodies reach the same temperature  $T_0$ .

In such a process  $T_1$  has given to the engine the total heat  $Q_1 = C(T_1 - T_0)$ , and  $T_2$  has received from the engine the heat  $Q_2 = C(T_0 - T_2)$ , therefore the Reversible work performed by the engine is

$$W_{\text{Rev}} = Q_1 - Q_2 = C(T_1 + T_2 - 2T_0) \quad (\text{B1})$$

Since no work has been performed in the corresponding irreversible process, we have  $W_{\text{Lost}} = W_{\text{Rev}}$ .

In order to find  $T_0$  we must remind that at in each infinitesimal step during the reversible process the following relation is satisfied

$$\frac{|\delta Q_1|}{X} = \frac{|\delta Q_2|}{Y} \quad (\text{B2})$$

Where  $X$  is the decreasing temperature of the source  $T_1$ , which at the end takes the value  $T_0$ , and  $Y$  is the increasing temperature of  $T_2$ . Moreover since  $|\delta Q_1| = C|dX|$  and  $|\delta Q_2| = CdY$ , from relation (B2)  $T_0$  is such that

$$\int_{T_1}^{T_2} \frac{C|dX|}{X} = \int_{T_2}^{T_0} \frac{CdY}{Y} \quad (\text{B3})$$

And since  $|dX| = -dX$  by integration we have

$$-C \ln \frac{T_0}{T_1} = C \ln \frac{T_0}{T_2} \quad (\text{B4})$$

From which it follows that  $T_0 = \sqrt{T_1 T_2}$ .

The entropy production in this reversible process is, of course, zero. In the corresponding irreversible process, in which, at each step, some heat  $|\delta Q|$  goes from  $T_1$  to  $T_2$ , we have

$$\delta \pi_U = \frac{|\delta Q|}{Y} - \frac{|\delta Q|}{X} \quad (\text{B5})$$

In order to evaluate the total Entropy production, let us introduce an auxiliary source  $T_0$  which, at each step, receives the amount of heat  $|\delta Q|$  from the source at temperature  $X$  and gives it to the source at temperature  $Y$ ; relation (B5) becomes

$$\delta \pi_U = \left( \frac{|\delta Q|}{Y} - \frac{|\delta Q|}{T_0} \right) + \left( \frac{|\delta Q|}{T_0} - \frac{|\delta Q|}{X} \right) = \delta \pi_2 + \delta \pi_1 \quad (\text{B6})$$

Where

$$\delta \pi_2 = \frac{|\delta Q|}{Y} \left( 1 - \frac{Y}{T_0} \right) = \frac{|\delta Q|}{Y} \eta(Y) \quad \text{and} \quad \delta \pi_1 = \frac{|\delta Q|}{T_0} \left( 1 - \frac{T_0}{X} \right) = \frac{|\delta Q|}{T_0} \eta(X)$$

Here  $\eta(Y)$  is the performance of a reversible engine that works between  $T_0$  and  $Y$  and  $\eta(X)$  the performance of the engine that works between  $X$  and  $T_0$ , therefore at each infinitesimal step

$$\delta W_{Lost} = Y\delta\pi_2 + T_0\delta\pi_1 \quad (B7)$$

$W_{Lost}$  can be computed by means of (B7) and (31c), but we can find it also from the total Entropy production,  $\pi_U$ . From relation (B5), using the relation  $|\delta Q| = -CdX = CdY$  and relation (B4) (which defines  $T_0$ ), we have

$$\begin{aligned} \pi_U &= \int_{T_2}^{T_0} \frac{|\delta Q|}{Y} \left(1 - \frac{Y}{T_0}\right) + \int_{T_1}^{T_0} \frac{|\delta Q|}{T_0} \left(1 - \frac{T_0}{X}\right) = \\ &= \int_{T_2}^{T_0} \frac{CdY}{Y} - \frac{C}{T_0}(T_0 - T_2) - \frac{C}{T_0}(T_0 - T_1) + \int_{T_1}^{T_0} \frac{CdX}{X} = \\ &= \frac{C}{T_0}(T_1 + T_2 - 2T_0) \end{aligned} \quad (B8)$$

On the right hand side we have the total Reversible Work, i.e. the Lost Work in this process, therefore

$$T_0 \pi_U = W_{Lost} \quad (B9)$$

Relation (B9) and also Relations (31) confirm the Marcella (1992) assertion that the degradation of energy is always, in some way, proportional to the Entropy production; in our case the proportionality constant is  $T_0$ .

## References

- [1] W.H. Zurek, Entropy Evaporated by a Black Hole, *Phys.Rev. Lett* **49** 1683 (1982);  
P. Kanti, Evaporating black holes and extra-dimensions, *Int. J. Mod. Phys.* **A19** 4899 (2004).
- [2] F. Angulo-Brown, An ecological optimization criterion for finite-time heat engines, *J. Appl. Phys.* **69** 7465 (1991).
- [3] Z. Yan and L. Chen, The fundamental optimal relation and the bounds of power output efficiency for an irreversible Carnot engine, *J. Phys . A: Math. and Gen* **28**, 6167 (1995).
- [4] A. Bejan, Entropy generation minimization: the new thermodynamics of finite size devices and finite-time processes, *J. Appl. Phys.* **79** 1191 (1996) and References therein.
- [5] L.G. Chen, C. Wu and F.R. Sun, Finite time thermodynamics or entropy generation minimization of energy systems, *J. Non- Equil. Thermodyn.* **25** 327 (1999) and References therein.
- [6] A.M. Tsirlin and V. Kazakov, Maximal work problem in finite-time Thermodynamics, *Phys. Rev.* **E 62** 307 (2000);  
E. Allahverdyan and T. M Nieuwenhuizen, Optimizing the Classical Heat Engine, *Phys. Rev. Letters* **85** 232 (2000);
- F. di Liberto, Complexity in step-wise ideal gas Carnot cycle, *Physica A* **314** 331-344 (2002).
- [7] H.L. Callendar, The Caloric Theory of Heat and Carnot's Principle, *Proc. Phys. Soc.* **23** 153 (1911);

- A. Sommerfeld, Thermodynamics and Statistical Mechanics, in *Lectures in Theoretical Physics* –Vol. V - Chp.II, Sec.21, pp. 152-155 (Academic Press, 1964);
- I. Prigogine, *Thermodynamics of irreversible Processes* (Interscience Publishers, New York, 1967).
- G. Job, *Neudarstellung der Warmlehre, die Entropie als Wärme* (Berlin, 1972).
- G. Falk, F. Hermann and G.B. Schmid, Energy Forms or Energy Careers, *Am. J. Phys.* **51** 1074 (1983).
- [8] H.S. Leff and L. Jones Gerald, Irreversibility, entropy production and thermal efficiency, *Am. J. Phys.* **43** 973 (1975);
- H.S. Leff, Heat engine and the performance of the external work, *Am. J. Phys.* **46** 218 (1978);
- H.S. Leff, Thermal efficiency at maximum work output: new results for old heat engines, *Am. J. Phys* **55** 602 (1987);
- P.T. Landsberg and H.S. Leff, Thermodynamic cycles with nearly universal maximum-work efficiencies, *J. Phys. A: Math. and Gen* **22** 4019 (1989).
- [9] V.T. Marcella, Entropy production and the second law of thermodynamics: an introduction to second law analysis, *Am. J. Phys.* **60** 888-895 (1992).
- [10] R.E. Reynolds, Comment on ‘Entropy production and the second law of thermodynamics: an introduction to second law analysis’, *Am. J. Phys.* **62** 92 (1994).
- [11] S.K. Das Comment on ‘Entropy production and the second law of thermodynamics: an introduction to second law analysis’, *Am. J. Phys.* **62** 1151-1152 (1994).
- [12] M. Vicentini Missoni, *Dal calore all’Entropia* (La Nuova Italia Scientifica, Roma, 1992);
- H.U. Fuchs, *The dynamics of heat* (Springer, New York 1996).
- F. Hermann, The Karlsruhe Physics Course, *Eur. J. Phys.* **21** 49 (2000) ;
- C. Agnes, M. D’Anna, F. Hermann and P. Pianezz, L’Entropia Giocosa, *Atti XLI Congresso AIF*, **34** (2002).
- M. D’Anna, U. Kocher, P. Lubini, S. Sciorini”L’equazione di bilancio dell’energia e dell’entropia” *La fisica nella Scuola* **Vol.XXXVIII** (2005,)290
- [13] O. Kafri., Y.B. Band and R.D. Levine, Is work output optimized in a reversible operation?, *Chem. Phys. Lett.* **77** 441 (1981).
- [14] J.I. Beldria, Positive and negative entropy production in an ideal-gas expansion, *Europhys. Lett.* **70** 446 (2005).
- [15] G. Gallavotti “Nonequilibrium thermodynamics ?” *cond-mat/0301172*  
 G. Gallavotti, E.G.D. Cohen “Note on nonequilibrium stationary states and entropy” *cond-mat/0312306*  
 G. Gallavotti “ Entropy production in nonequilibrium thermodynamics: a review “*cond-mat/0312657*