

Lost Work, Extra Work and Entropy production for a system with complexity: the stepwise ideal gas Carnot cycle

Franco di Liberto
Dipartimento di Scienze Fisiche Università di Napoli "Federico II"
INFN- Sezione di Napoli, Cnism-CNR-INFN, Unità di Napoli
diliberto@na.infn.it

Abstract

This paper is an extension of a previous paper [F. di Liberto-Phi. Mag. **87**,569 (2007)] devoted to Lost work and entropy production; here we introduce also the Extra work (i.e. $W_{Extra} = W_{in} - W_{Rev}$) in an irreversible process and apply both the concepts to the analysis of a system with complexity: the stepwise ideal gas Carnot cycle. A stepwise Carnot cycle is performed by means of N small weights, (here called dw 's), which are first added and then removed from the piston of the vessel containing the gas. The work performed by the gas can be found as increase of the potential energy of the dw 's. We identify each single dw and thus evaluate its raising i.e. its increase in potential energy. In such a way we find how the energy output of the cycle is distributed among the dw 's. The size of the dw 's affects the Entropy production and therefore the Lost and Extra work. The raising distribution depends on the removing process we choose. Since these processes are $N!$, there are $N!$ distributions of the raisings of the dw 's

1-Introduction

As pointed out in a previous paper [1], entropy production and its relation to the available energy are fascinating subjects which in last years have attracted many physics researches [5-11].

It is well known [1-10] that for some elementary irreversible process, as the irreversible isothermal expansion of a gas in contact with a heat source T , the work done by the gas W_{out} is related to the reversible isothermal work W_{Rev} (i.e. the work performed by the gas in the corresponding reversible process) by the relation

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

where ΔS_U is the total entropy change of the universe (system + environment). The degraded energy $T \Delta S_U$ is usually called 'the Lost work' W_{Lost}

$$W_{Lost} = W_{Rev} - W_{out} \quad (2)$$

The latter can be interpreted as the missing work: i.e. the additional work that could have been done in the related reversible process (here the reversible isothermal expansion); it is also called 'energy unavailable to do work'.

On another hand in the irreversible isothermal compression $T \Delta S_U$ is called W_{Extra} i.e. the excess of work performed **on** the system in the irreversible process with respect to the reversible one.

$$W_{Extra} = W_{in} - W_{Rev} \quad (3)$$

Due to the energy balance, the same relation holds for the amounts of heat given to the source T , i.e. we have

$$Q_{out} = Q_{Rev} + T \Delta S_U \quad (4)$$

Therefore $T \Delta S_U$ is also called the 'Excess of heat' (Q_{Extra}), i.e. the additional heat that has been given to the source [8,9].

The total variation of Entropy, ΔS_U , is usually called 'Entropy production'; we shall call the latter π_U .

The second Law claims that $\pi_U \geq 0$ and the entropy is an extensive quantity which in the transfers between systems can only increase or stay unchanged.

2-Entropy production, Lost Work and Extra Work in isothermal irreversible processes.

Let us first consider the isothermal irreversible expansion ($A \rightarrow B$) of an ideal gas in contact with a heat source T where $V_B = V_A + \Delta V$ e $P_B = P_A - \Delta P$ with $\Delta P > 0$, $\Delta V > 0$. In such simple process some heat $Q_{in} \equiv W_{out} = P_B \Delta V = (P_A - \Delta P) \Delta V$ ¹ goes from the heat source T to the ideal gas. There is an increase of

entropy of the ideal gas, $\Delta S_{gas} = \int_A^B \frac{\delta Q_{Rev}}{T} = \frac{Q_{Rev}}{T}$ and a decrease of the entropy of the heat source ($-\frac{Q_{in}}{T}$),

where

¹ The quantities Q_{in} , Q_{out} , Q_{Rev} are positive

$$Q_{\text{Rev}} = \int_A^B \delta Q_{\text{Rev}} = W_{\text{Rev}} = \int_A^B P dV = RT \ln \frac{V_B}{V_A} = RT \ln \left(1 + \frac{\Delta V}{V_A} \right) = RT \left[\frac{\Delta V}{V_A} - \frac{1}{2} \left(\frac{\Delta V}{V_A} \right)^2 + \dots \right]$$

therefore the entropy production is $\pi_U \equiv \Delta S_U = \frac{Q_{\text{Rev}}}{T} - \frac{Q_{\text{in}}}{T} > 0$ (5)

Since $Q_{\text{Rev}} > Q_{\text{in}}$ we find in the ideal gas an amount of entropy greater than that taken from the heat source T .

If, for example $\Delta V = 3V_A$ we have $\pi_U = R \ln 4 - \frac{3}{4}R = 0,636R$

On another hand for the isothermal irreversible compression of the ideal gas ($B \rightarrow A$) some heat Q_{out} goes from

the gas to the source T . We have a decrease of the gas entropy $\Delta S_{\text{gas}} = \int_B^A \frac{\delta Q_{\text{Rev}}}{T} = -\frac{Q_{\text{Rev}}}{T}$ and an increase of

the source entropy, $\left(\frac{Q_{\text{out}}}{T} \right)$ where $Q_{\text{out}} = W_{\text{in}} = P_A (V_B - V_A) = P_A \Delta V$

Therefore in the compression the entropy production, is

$$\pi_U \equiv \Delta S_U = \frac{Q_{\text{out}}}{T} - \frac{Q_{\text{Rev}}}{T} > 0 \quad (\text{since } Q_{\text{out}} > Q_{\text{Rev}}) \quad (6)$$

Which, for $\Delta V = 3V_A$ gives $\pi_U = \frac{P_A \Delta V}{T} - R \ln \left(1 + \frac{\Delta V}{V_A} \right) = 3R - R \ln 4 = 1,614R$

In order to find how the previous entropy productions affects the dissipation of energy, we have to remark that the irreversibility of a generic process ($A \rightarrow B$) is due, in general, to internal and external irreversibility, therefore, as shown in [1,2,5] the related entropy production π_U can be expressed as a sum of two terms: the internal entropy production, $\pi_{\text{int}} \geq 0$ and the external entropy production, $\pi_{\text{ext}} \geq 0$ i. e.

$$\pi_U = \pi_{\text{int}} + \pi_{\text{ext}} \quad (7)$$

This result is not trivial since $\pi_{\text{int}} \neq \Delta S_{\text{sys}}$; there are in fact many processes for which $\Delta S_{\text{sys}} < 0$, and $\pi_{\text{int}} \geq 0$. The system entropy production π_{int} is defined [1,2,5] by the relation

$$\Delta S_{\text{sys}} = S_{\text{in}} - S_{\text{out}} + \pi_{\text{int}} \quad (8)$$

where S_{in} e S_{out} are respectively the quantity of entropy which comes into and comes out of the system in the

irreversible process; $\Delta S_{\text{sys}} = \int_A^B \frac{\delta Q_{\text{Rev}}}{T_{\text{sys}}}$ is the entropy variation of the system from A to B and does not

depend on the particular process. Similarly the external Entropy production, π_{ext} is given by the relation

$$\Delta S_{\text{ext}} = S_{\text{in}}^{\text{ext}} - S_{\text{out}}^{\text{ext}} + \pi_{\text{ext}} \quad (9)$$

or by relation (7). It is easy to verify that for both previous irreversible isothermal processes $\pi_{\text{ext}} = 0$ and

therefore that for both the expansion and the compression $\pi_{\text{int}} = \pi_U$.

In Appendix we give the relations for the Lost Work and Extra Work for isothermal processes with internal and external irreversibility ($\pi_{\text{ext}} \neq 0$) From relations (A4) and (A6) it follows that the Lost Work for an isothermal expansion at temperature $T = T_0$ and without external irreversibility ($\pi_{\text{ext}} = 0$) is

$$W_{\text{Lost}} = W_{\text{Rev}} - W_{\text{out}} = T_0 \pi_{\text{int}} \quad (10)$$

and that the Extra Work for an isothermal compression at $T = T_B$ (with $\pi_{\text{ext}} = 0$) is

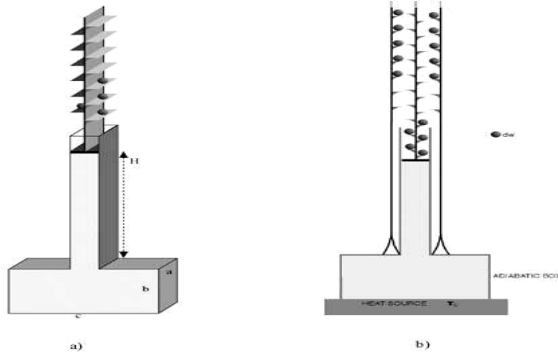
$$W_{\text{Extra}} = W_{\text{in}} - W_{\text{Rev}} = T_B \pi_{\text{int}} \quad (11)$$

In the next section by means of relations (10) and (11) we study the Lost Work and the Extra Work for the Stepwise Carnot Cycle.

3-The step-wise ideal gas Carnot cycle and dissipated energy

In order to perform an ideal gas stepwise cycle we need a heat source, a heat sink, a vessel with a free piston and a large number (N) of small “driving weights” to increase or decrease slowly, step by step, the external pressure P . If the steps are infinitesimally small the cycle is “reversible”.

In order to evaluate the work performed by the ideal gas during the cycle, the displacements of the small driving weights (dw) must be done carefully. We let them move on and off the piston only horizontally. To this end we assume that the handle of the piston is endowed with so many shelves that we can move each dw horizontally (and without friction) from (or to) the corresponding fixed shelf which belongs to the dw 's Reservoir. (The dw 's Reservoir is a vertical sequence of horizontal shelves on which the dw 's are initially located). Such an ideal device is shown schematically in Fig.1.



**Figure 1 a) The adiabatic vessel with some dw 's on the piston.
b) Cross section view of the vessel showing two supports for the dw 's (the dw 's Reservoir)**

Therefore at the end of the cycle the overall raising, on the dw 's Reservoir, of the k -th dw from its initial height ($h_{k,0}$) to the final one ($h_{k,f}$) is

$$h_k = h_{kf} - h_{k0} \quad (12)$$

Since a friction-less process is assumed, the vertical motion of the dw 's is only due to the gas and the total work (W) performed by the ideal gas can be found as increase of potential energy of the dw 's on the Reservoir, i.e.

$$W = \sum_{i=1}^Z P_i \Delta V_i = mg \sum_{k=1}^N h_k \quad (13)$$

where P_i is the external pressure at step i (after the addition or removal of the i -th dw) $\Delta V_i = V_i - V_{i-1}$, is the volume variation from step $(i-1)$ to step i and mg is the weight of the generic dw . Relation (13) has been proved elsewhere [3]. In the next section the raisings of the single dw on the reservoir are evaluated.

3.1- The raisings of the dw 's for a step-wise Carnot cycle

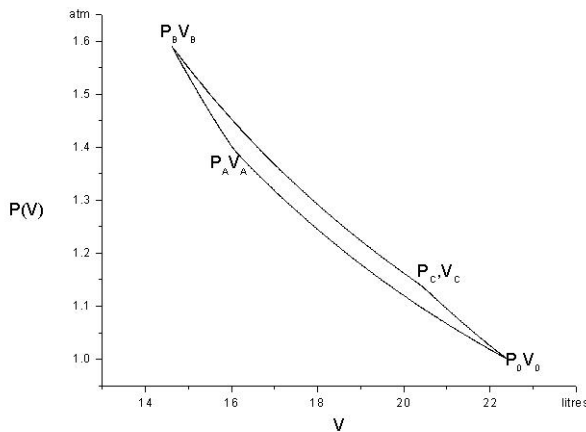


Figure 2 The step-wise Carnot cycle with very small steps.

We have considered here $N=610$ dw 's and therefore $2N=1220$ steps. The mass of each dw is $m=0.1$ Kg. The surface of the piston is $S=100$ cm², so that at each step in the compression the pressure increase is $\Delta P=P_0/1033$, i.e.

$$P_i = P_0 + i\Delta P \quad \text{for } i \in [1, N] \quad (14a)$$

And for each step in the expansion the pressure decreases by ΔP i.e.

$$P_{N+l} = P_0 + (N-l)\Delta P \quad \text{for } l \in [1, N] \quad (14b)$$

Notice moreover that $V_{2N} = V_0$ and $V_N = V_B$ i.e. the volume at step $2N$ is the initial volume and the volume at step N is the smallest volume in the cycle.

A cycle as the Carnot or Stirling cycles, in which there are no isobaric steps, can be performed through $Z=2N$ steps. In each of the first N steps one dw is added on the piston (and removed from the Reservoir at its initial height h_0); in each of the following N steps one dw is removed from the piston (and brought back to the Reservoir at its final height, say h_f). The k -th dw is the dw which has been added on the piston at the k -th step in the compression.

The cycle we consider is reported in Figure 2. The chosen values of P and V are easily available in ordinary conditions. In the first N steps the dw 's are added on the piston to perform first an isothermal compression ($O \rightarrow A$) and then an adiabatic compression ($A \rightarrow B$). In the remaining N steps the dw 's are removed from the piston in order to return to the initial state ($B \rightarrow C \rightarrow O$). The working fluid is the ideal gas and the free piston is mass less. The vertical vessel's walls are heat insulating and the vessel's diathermal floor is made adiabatic when needed. The values in Fig. 2 are $P_0=1$ at, $V_0=22.4$ l, $T_0=273.15$ K, $\gamma=1.4$, $P_A=1.3969$ at, $V_A=16.034$ l, $P_C=1.1385$ at, $V_C=20.416$ l, $T_C=283.47$ K.

Keeping in mind how we perform the Carnot cycle, let us take a closer look at the last dw . It is clear that its raising in the Reservoir is negative: when it leaves the Reservoir and is added on the piston, it (together with the piston and the previous dw 's) moves downward; afterwards, at step $N+1$, during the expansion, it is removed and it goes to rest on the fixed shelf of the Reservoir in front of it. It will stay on the piston for one step only! i.e.

$$h_N = (V_N - V_{N-1})/S .$$

Similarly the last but one dw moves downward for two steps and moves upward for one step. It performs two "negative" steps and one "positive" step

$$h_{N-1} = \frac{1}{S} (V_{N+1} - V_{N-2}) = \frac{1}{S} (V_{2N-(N-1)} - V_{(N-1)-1}) \quad (15)$$

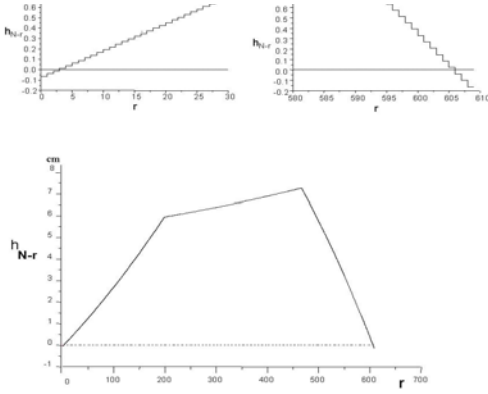


Fig. 3. Overall raising on the reservoir of each dw . In the zoom of the extremity of the graph, one can see that the last dw 's and the first ones have negative raising

By means of relations (15) one can calculate [4] the overall raising of each of the N dw 's on the Reservoir i.e. the h_k 's. The overall raisings are reported in Fig.3, where h_N is given for $r=0$, h_{N-1} for $r=1$ and so on .. h_1 for $r=609$. The inserts in the upper part of Fig. 3 show that the last dw 's and the first ones have negative raisings; it is clear that the negative raisings disappear only for the « reversible cycle » i.e. in the limit $N \rightarrow \infty$ (and therefore $\Delta P \rightarrow 0$, $m \rightarrow 0$).

Therefore for the k -th dw

$$h_k = \frac{1}{S} (V_{2N-k} - V_{k-1})$$

And $h_1 = \frac{1}{S} (V_{2N-1} - V_0)$: the first dw moves downward for N steps and moves upward for $N-1$ steps.

3.2 Lost work and extra work step by step and the total dissipated energy

One may observe that in the cycle there has been an Entropy production: in fact in each isothermal step of the compression ($O \rightarrow A$) at temperature T_0 , from relation (6) we have

$$\pi_{i-int} = \frac{P_{i+1}\Delta V_i}{T_0} - R \ln\left(1 + \frac{\Delta V_i}{V_{i+1}}\right) \simeq \frac{P_{i+1}\Delta V_i}{T_0} - R \left[\frac{\Delta V_i}{V_{i+1}} - \frac{1}{2} \left(\frac{\Delta V_i}{V_{i+1}} \right)^2 \right] \simeq \frac{R}{2} \left(\frac{\Delta V_i}{V_{i+1}} \right)^2 \quad (16a)$$

therefore $W_{i-Extra} = W_{i-irrev} - W_{i-Rev} = T_0 \pi_{i-int}$

$$\text{and in each isothermal step in the expansion } \pi_{i-int} = \frac{R}{2} \left(\frac{\Delta V}{V} \right)^2 = \frac{R}{2} \left(\frac{\Delta P}{P} \right)^2 \quad (16b)$$

and $W_{i-Lost} = W_{i-Rev} - W_{i-irrev} = T_B \pi_{i-int}$ where T_B is the temperature of the hot heat source.

To evaluate the entropy production in the adiabatic steps we must recall that for such steps it has been shown [4]

$$\text{that } \frac{\Delta V_i}{V_i} = -\frac{1}{\gamma} \frac{\Delta P_i}{P_{i+1}} \quad \text{where } \gamma = \frac{C_P}{C_V} \quad V_{i+1} - V_i = \Delta V_i \quad \text{and} \quad P_{i+1} - P_i = \Delta P_i$$

Therefore the entropy production is

$$\pi_{i-int} = \Delta S_U = \int_i^{i+1} \frac{\delta Q}{T} = C_V \ln \frac{T_{i+1}}{T_i} + R \ln \frac{V_{i+1}}{V_i} \quad \text{which at first order gives}$$

$$\pi_{i-int} = C_V \frac{T_{i+1} - T_i}{T_i} + R \frac{V_{i+1} - V_i}{V_i} \quad \text{and since } C_V (T_{i+1} - T_i) = -P_{i+1} (V_{i+1} - V_i)$$

$$\pi_{i-int} = -\frac{P_{i+1} (V_{i+1} - V_i)}{T_i} + R \frac{V_{i+1} - V_i}{V_i} = -\frac{R P_{i+1} \Delta V_i}{P_i V_i} + \frac{R \Delta V_i}{V_i} = R \frac{\Delta V_i}{V_i} \left(1 - \frac{P_{i+1}}{P_i} \right) = R \gamma \left(\frac{\Delta V_i}{V_i} \right)^2 = \frac{R}{\gamma} \left(\frac{\Delta P_i}{P_{i+1}} \right)^2 \quad (17)$$

Finally we can conclude that the Dissipated energy i.e. w_D , is

$$W_D = \sum_{i=1}^{2N} T_i \pi_{i-int} = W_{Extra} + W_{Lost} \quad \text{where}$$

$$W_{Extra} = \sum_{i=1}^N T_i \pi_{i-int} = \sum_{i=1}^{n_1} T_0 \pi_{i-int} + \sum_{i=n_1+1}^{n_1+n_2} T_i \pi_{i-int} \quad (18)$$

And

$$W_{Lost} = \sum_{i=N+1}^{2N} T_i \pi_{i-int} = \sum_{i=1}^{N+n_3} T_B \pi_{i-int} + \sum_{i=N+n_3+1}^{2N} T_i \pi_{i-int} \quad (19)$$

Where n_1, n_3 are the numbers of isothermal steps and n_2, n_4 are the numbers of adiabatic steps.

3.3 Complexity in the raisings pattern

The raising h_i depends on the removing process we choose (the number of such processes is $N!$). In the previous sections we have chosen the Simplest Process (SP) (the removing process that starts with the last dw and ends with the first dw). Let us see how the raisings of the single dw 's change for a Complex Process (CP), in which we start from the $(N-L)$ -th dw , ($L < N$), go progressively to the last one, and then from the $(N-L-1)$ -th dw , go to the first. If the first removed dw is the $(N-L)$ -th with $1 < L < N$ the history of each dw will change. For the $(N-L)$ -th dw (which has been on the piston for the last $L+1$ steps of the compression) we clearly have

$$h_{N-L} = \sum_{i=N-L}^N \Delta H_i = H_N - H_{N-L-1} = \frac{1}{S} (V_N - V_{N-L-1})$$

which is negative and remains still negative in the $N \rightarrow \infty$ limit i. e. also for "Reversible cycles" [4].

For the $(N-(L-1))$ -th dw , which has been on the piston for the last L steps of the compression and the first step of the expansion (i.e. the step in which the $(N-L)$ -th dw has been removed) we clearly have

$$h_{N-(L-1)} = \sum_{i=N-(L-1)}^{N+1} \Delta H_i = H_{N+1} - H_{N-L} = \frac{1}{S} (V_{N+1} - V_{N-L})$$

Therefore if we denote with h_{N-r}^L the raisings in such CP for $r \leq L$ we have

$$\begin{aligned} h_{N-r}^L &= \sum_{i=N-r}^N \Delta H_i + \sum_{i=N+1}^{N+L-r} \Delta H_i = H_{N+L-r} - H_{N-r-1} = \\ &= \frac{1}{S} (V_{N+L-r} - V_{N-r-1}). \end{aligned} \quad (20)$$

This last relation allows to evaluate the raisings of the dw 's directly from the P - V diagram of the Carnot-cycle. We have only to look at the ΔV relative to a pressure variation $(\Delta P)^* = (2r+1-L)\Delta P$.

From the PV diagram we see that for $(\Delta P)^* > 0$ we have $\Delta V < 0$ and hence $h_{N-r}^L < 0$ and for $(\Delta P)^* < 0$ we have $\Delta V > 0$ and hence $h_{N-r}^L > 0$.

For $r > L$ the way in which the previous L dw 's have been removed has no influence, therefore for $r > L$ the raisings are the same as in the SP i. e.

$$h_{N-r}^L = h_{N-r} = H_{N-r} - H_{N-r-1} = \frac{1}{S} (V_{N-r} - V_{N-r-1})$$

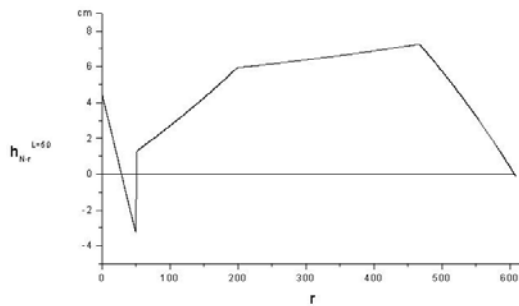


Figure 4 Overall raising for each dw for the removing process which starts from the $(N-L)$ -th dw i.e. the 560- dw

Obviously we expect that

$$W \equiv \sum_1^Z P_i \Delta V_i = g \sum_{k=1}^N m_k h_k = g \sum_{k=1}^N m_k h_k^L \quad (21)$$

since for each of the $N!$ possible processes the work performed by the gas in the cycle is the same.

In Figure 4 we report the raisings of the dw 's for a Complex Process with $L=50$. Notice that the raisings of the last 50 dw 's are here completely different from those in the SP.

The previous removing process is only one of the many Complex Process that one can perform.

The removing process are $N!$. For each process we have a different distribution for the raisings h_k .

4 Summary

In this paper we have introduced the Extra Work which together with the Lost Work gives the Dissipated energy in the irreversible processes. The analysis is confined mainly to irreversible isothermal process even if the known results [2,4] are used for the adiabatic processes.

The new and previous results are used to evaluate the Dissipated energy for a stepwise ideal gas Carnot Cycle , a system with complexity. The complexity arises from the fact that there are $N!$ different distribution for the raisings h_k .i.e the work output of the Carnot cycle can be distributed in $N!$ ways among the N dw 's.

Acknowledgements: I greatly indebted to M. Zannetti and G. Monroy for the useful comments.

Appendix :Lost Work and Extra Work for isothermal processes with external irreversibility

Here we evaluate the Lost Work for the expansion and the Extra work for the compression when there is external irreversibility.

In sec.2.2 and in sec.3 of paper[1] an we have shown that if the irreversible isothermal expansion is performed by means of a (shorter) contact with an heat source at $T_{ext} > T$ we have $\pi_{ext} \neq 0$ i.e.

$$\pi_{ext} = \frac{Q_{in}}{T} - \frac{Q_{in}}{T_{ext}} \quad (A1)$$

and for the Endo-reversible process, i.e. the process in which the gas performs the reversible isothermal expansion $A \rightarrow B$

$$\pi_{ext}^{Endo} = \frac{Q_{Rev}}{T} - \frac{Q_{Rev}}{T_{ext}} \quad (A2)$$

Similarly if the irreversible isothermal compression is performed by means of a (shorter) contact with an heat source at $T_{ext} < T$ we have $\pi_{ext} \neq 0$ i.e.

$$\pi_{ext} = \frac{Q_{out}}{T_{ext}} - \frac{Q_{out}}{T} \quad \text{and} \quad \pi_{ext}^{Endo} = \frac{Q_{Rev}}{T_{ext}} - \frac{Q_{Rev}}{T} \quad (A3)$$

To evaluate the Lost Work for the expansion with $T_{ext} > T$ we calculate the work available in the related Reversible process and subtract from it W_{out} , the effective work done in the irreversible process. This difference gives the Lost Work.

The 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 $W_{Rev}(gas) = Q_{Rev}$; 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 $Q_{Rev} \frac{T_{ext}}{T}$

performs the Work $W_{Rev}(engine) = Q_{Rev} \frac{T_{ext}}{T} (1 - \frac{T}{T_{ext}})$, therefore the total reversible work is

$$W_{RevTotal} = W_{Rev}(gas) + W_{Rev}(engine) = Q_{Rev} + Q_{Rev} \frac{T_{ext}}{T} (1 - \frac{T}{T_{ext}})$$

The Work performed by the gas in the irreversible expansion is $W_{out} = Q_{in}$, therefore

$$W_{Lost} = W_{RevTotal} - W_{out} = Q_{Rev} - Q_{in} + Q_{Rev} \frac{T_{ext}}{T} - Q_{Rev} = T\pi_{in} + T_{ext}\pi_{ext}^{Endo} \quad (A4)$$

On the other hand for the compression with an heat source at $T_{ext} = T$

$$W_{Extra} = W_{in} - W_{Rev} = Q_{out} - Q_{Rev} = T\pi_{int} \quad (A5)$$

but if one uses a heat source at $T_{ext} < T$, from the Reversible work necessary to perform the isothermal compression at temperature T we have to subtract the work of the reversible engine which subtracts Q_{out} from

heat source T (the gas) and gives to the source T_{ext} the heat $Q^{Min} = \frac{T_{ext}}{T} Q_{out}$, i.e.

$$W_{Rev}^{ext} = Q_{out} - Q^{Min} = T_{ext} \left(\frac{Q_{out}}{T_{ext}} - \frac{Q_{out}}{T} \right) = T_{ext}\pi_{ext}$$

therefore the Extra work is

$$W_{Extra} = W_{in} - (W_{Rev} - W_{Rev}^{ext}) = Q_{out} - Q_{Rev} + Q_{out} - T_{ext} \frac{Q_{out}}{T} = T\pi_{int} + T_{ext}\pi_{ext} \quad (A6)$$

References

- [1] F. di Liberto-*Phi. Mag.* **87**,569 (2007)
- [2] F. di Liberto- *Giornale di Fisica* **49**,1-14,(2008)
- [3] F. di Liberto, , *Physica A* **314** 331-344 (2002)
- [4] F. di Liberto, <http://babbage.sissa.it/abs/physics/0006073>
- [5] G. Job and R. Ruffler “Physical Chemistry” Job Foundation (Hamburg 2007)
- [6] P.V. Conevey . *Nature* **333**, 409 (1988)
- [7] H.S. Leff, *Am. J. Phys.* **46** 218 (1978);
- [8] V.T. Marcella, , *Am . J. Phys.* **60** 888-895 (1992).
- [9] R.E. Reynolds, *Am. J. Phys.* **62** 92 (1994)
- [10] H.U. Fuchs, *The dynamics of heat* (Springer, New York 1996).
- [11] L.G. Chen, C. Wu and F.R. Sun,, *J. Non- Equil. Thermodyn.* **25** 327 (1999) and References therein.