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Entropy production and lost work for some irreversible processes

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In this paper we analyse in depth the Lost Work in an irreversible process (i.e. $W_{Lost} = W_{Rev} - W_{Irrev}$). This quantity is also called 'degraded energy' or 'Energy unavailable to do work'. Usually in textbooks one can find the relation $W_{Lost} \equiv T \Delta S_U$, which, for many processes, is not suitable to evaluate the Lost Work. Here we find for W_{Lost} a more general relation in terms of internal and external Entropy production, π_{int} and π_{ext} , quantities which enable also to write down in a simple way the Clausius inequality. 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 Fuchs (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 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

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

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

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

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

$$Q = Q_{\text{Rev}} - T \Delta S_U$$

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 ‡ .

The total variation of Entropy, ΔS_U , is usually called 'Entropy production'. The second Law claims that

$$\Delta S_U \geq 0$$

The relation between Entropy production and W_{Lost} (or Q_{Lost}) is the main subject of this paper. In Sec.3 we will find a relation more general than relation (1). To introduce the subject let us remind the steps that lead to the relation (1).[9]

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_{ext} and performs some work W , the entropy production of the Universe, i. e. the variation of Entropy of the system+variation of Entropy of the external source, is

$$\Delta S_U \equiv \Delta S_{\text{sys}} + \Delta S_{\text{ext}} = \Delta S_{\text{sys}} - \frac{Q}{T_{\text{ext}}} \quad (2)$$

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

$$T_{\text{ext}} \Delta S_U = T_{\text{ext}} \Delta S_{\text{sys}} - \Delta U_{\text{sys}} - W \quad (3)$$

If the process is reversible then $\Delta S_U = 0$ and $W \equiv W_{\text{Rev}} = T_{\text{ext}} \Delta S_{\text{sys}} - \Delta U_{\text{sys}}$,

$$\text{Therefore } T_{\text{ext}} \Delta S_U = W_{\text{Rev}} - W = W_{\text{Lost}} \quad (4)$$

which defines the Lost Work and proves relation (1). There are however some irreversible processes for which relation (4) is not suitable to evaluate the Lost Work, for example the irreversible adiabatic processes, [11] in which there is some W_{Lost} , some Entropy production ΔS_U , but no external source T_{ext} .

In general for an irreversible process, $\Delta S_U > 0$, from relation (3), it follows

$$W < W_{\text{Rev}} \quad (5)$$

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

‡ 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

In Sec. 3 we evaluate W_{Lost} for some simple irreversible processes, refine relation (4) 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 external source, their entropy productions has been called respectively internal and external, i.e. $\Delta S_U = \pi_{int} + \pi_{ext}$

In Sec.2 the entropy balance and the entropy productions for irreversible processes are analyzed by means of the substance-like approach. 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 Entropy production for elementary processes. First we analyse the *reversible* isothermal expansion (A \rightarrow B) of one mole of monatomic ideal gas at temperature T which receives the heat Q from a source at temperature T . For the ideal gas we have

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

where $S_{out} = 0$ and the Entropy which comes into the system is $S_{in} = \frac{Q_{Rev}}{T} = R \ln \frac{V_B}{V_A}$, since

$$Q_{Rev} = \int_A^B \delta Q_{Rev} = \int_A^B P dV = RT \ln \frac{V_B}{V_A}. \text{ The heat which flows from the heat source into the gas is } Q_{Rev}, \text{ which}$$

is also the work performed by the system in the reversible isothermal expansion. The increase in Entropy for

the gas is $\Delta S_{gas} = \int_A^B \frac{\delta Q}{T} = R \ln \frac{V_B}{V_A}$; $R=8.314 \text{ J/mol. K}^\circ$ is the universal constant for the gases.

For the heat Source it holds

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

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

For the Universe $\Delta S_U = \Delta S_{gas} + \Delta S^{ext} = 0$. 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 .

D) Thermal contact with a source at temperature $T_{ext} = T$

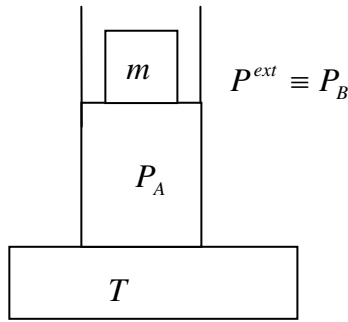


Figure 1. Ideal gas in thermal contact with the heat source T

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 of area Σ . 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

$$\text{expansion the gas has performed the work } W = P^{ext} \Sigma \frac{(V_B - V_A)}{\Sigma} = \frac{3}{4} RT \quad (8)$$

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

$$Q = W \quad (9)$$

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

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

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

$$\text{and } S_{in} = \frac{Q}{T} = \frac{3}{4} R, \quad \text{so we can see that } \Delta S_{gas} \neq S_{in} - S_{out}.$$

To restore the balance one must add to the right-hand side a quantity π_{int} , the Entropy production due to the internal irreversibility

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

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

On the same footing, to take in account the external irreversibility, we introduce the quantity π_{ext} which is defined by the general relation

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

$$\text{Whith the constraint that } \Delta S_U = \Delta S_{gas} + \Delta S^{ext} = \pi_{in} + \pi_{ext} \quad (12)$$

In this irreversible process, since $\Delta S^{ext} = \frac{-Q}{T}$, $S_{in}^{ext} = 0$ and $S_{out}^{ext} = \frac{Q}{T}$ it is easy to verify that $\pi_{ext} = 0$

There is no external irreversibility, there is no external Entropy production. It is well known indeed that the isothermal exchanges of heat between heat reservoirs are reversible.

In the following , as consequence of definitions (11) and (12) we define π_U , the entropy production due to the internal and external entropy productions :

$$\Delta S_U = \Delta S_{syst} + \Delta S^{ext} = \pi_U = \pi_{int} + \pi_{ext} \quad (13)$$

The entropic balance (10) is reported in Fig. 2, where the circle is the system (i.e. the ideal gas)

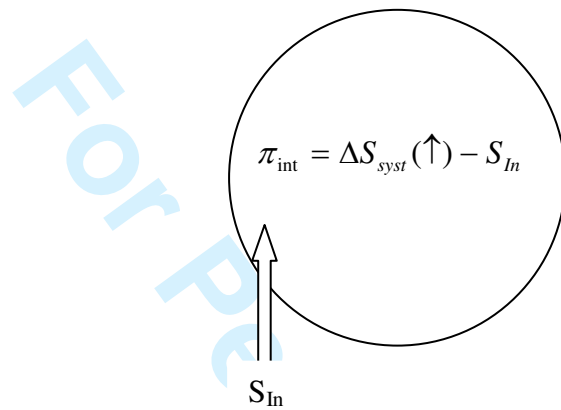


Figure 2. The entropic balance for the ideal gas.

The entropic balance for the heat source (11) is reported in Fig. 3, where the square is the heat source T

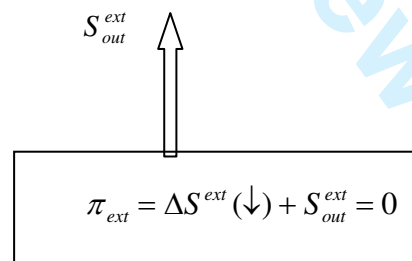


Figure 3. The entropic balance for the heat source T

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

In this case we want to make the previous irreversible expansion of the gas ,from the state (P_A, V_A, T) to the state (P_B, V_B, T) by means of the heat Q coming from the heat source $T_{ext} > T$. 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. It is clear that in such new process there is some external irreversibility, some external Entropy

production π_{ext} , because the heat Q flows from a hotter (T_{ext}) to a colder source (T). For such irreversible flow of the heat Q it is well known that the change in entropy is $\Delta S = \frac{Q}{T} - \frac{Q}{T_{ext}}$. This quantity will be our

external entropy production i.e. $\pi_{ext} = \frac{Q}{T} - \frac{Q}{T_{ext}}$; therefore

$$\pi_U = \Delta S_{syst} + \Delta S^{ext} = \frac{Q_{Rev}}{T} - \frac{Q}{T_{ext}} = \pi_{int} + \pi_{ext} = \pi_{int} + \frac{Q}{T} - \frac{Q}{T_{ext}} \quad (14)$$

which gives for the internal entropy production the result

$$\pi_{int} = \frac{Q_{Rev}}{T} - \frac{Q}{T} \quad (15)$$

More examples of Entropy productions in irreversible processes are given in ref [11].

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

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

The second law of the thermodynamics claims that the global Entropy production is greater or equal zero i.e. $\Delta S_U \geq 0$, but from these examples we see that also $\pi_{int} \geq 0$ and $\pi_{ext} \geq 0$, 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[§] [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:

$$0 = \oint dS_{syst} = \oint \frac{\delta Q}{T_{syst}} + \pi_{int} \Rightarrow \oint \frac{\delta Q}{T_{syst}} \leq 0 \quad (16)$$

where $\delta Q > 0$, i.e. it is positive, when it comes into the system and T_{syst} 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 external source, when it makes a whatsoever cycle, from relation (11), it follows

[§] 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 π is negative (if any) are more efficient than the corresponding reversible processes. Here we will find always $\pi \geq 0$.

$$0 = \oint dS^{ext} = \oint \frac{\delta Q}{T_{ext}} + \pi^{ext} \Rightarrow \oint \frac{\delta Q}{T_{ext}} \leq 0^{**} \quad (17)$$

3-Lost Work : examples and general expression

In this section we evaluate the Lost Work for 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 us to check whether relation (5) is suitable to give the Lost Work in terms of the Entropy production. As already pointed out, for adiabatic processes [11] we need a more general relation than (4). 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

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

On the other hand relation (4) 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 brings the heat Q_{Rev} to the ideal gas at temperature T and takes from the

heat source T_{ext} the heat Q^{Max} which is related to Q_{Rev} by the relation $\frac{Q^{Max}}{T_{ext}} = \frac{Q_{Rev}}{T}$: it therefore does the

work $W_{Rev}(engine) = Q^{Max} - Q_{Rev}$. The total reversible work is

$$W_{RevTot} = W_{Rev}(gas) + W_{Rev}(engine) = Q^{Max} \quad (18)$$

On the other hand the work performed by the gas in the irreversible expansion is $W = Q = \frac{3}{4} RT$, therefore

$$W_{Lost} = W_{RevTot} - W = Q^{Max} - Q \quad (19a)$$

The same result is given by the relation (4)

$$W_{Lost} = T_{ext}\pi_U = T_{ext} \left(\frac{Q_{Rev}}{T} - \frac{|Q_{irrev}|}{T_{ext}} \right) = Q^{Max} - Q. \quad (!9b)$$

Relation (4) is therefore suitable to evaluate the Lost Work in this process. On the other hand we are aware of the fact that the Lost Work is due to internal and external irreversibility and we expect that

** A similar remark is due to Marcella[9]

$$1) W_{Lost} (int) = Q_{Rev} - Q = RT \ln 4 - \frac{3}{4} RT \quad (20)$$

$$2) W_{Lost} (ext) = Q^{Max} - Q_{Rev} \quad (21)$$

But relation (4) does not give this deep insight.

Therefore we want to write down a more intuitive and general expression of the Lost Work in terms of the internal and external Entropy production, which can be suitable also for irreversible adiabatic processes[11].

Let us outline the way to find it. We simply replicate, for each subsystem, the argument reminded in the introduction. 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

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

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

If the process is Endo-reversible ($\pi_{int} = 0$), we have

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

Which defines W_{Rev}^{Endo} , therefore

$$T_{sys} \pi_{int} = W_{Rev}^{Endo} - W = Q_{Rev} - Q \quad (23)$$

i.e. $T_{sys} \pi_{int} = W_{Lost} (int)$ is the lost work due to the internal irreversibility, i.e. the lost work with respect to the Endo-reversible process, the process in which the gas performs the reversible isothermal expansion $A \rightarrow B$

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

$$\pi_{ext}^{Endo} = \frac{Q_{Rev}}{T} + \Delta S_{ext} = \frac{Q_{Rev}}{T} - \frac{Q_{Rev}}{T_{ext}}$$

And by the definition of Q^{Max}

$$T_{ext} \pi_{ext}^{Endo} = Q^{Max} - Q_{Rev} \quad (24)$$

As expected! Relations (23) and (24) are obtained by simply replication, for each subsystem, of the argument outlined in the introduction.

Therefore, in general

$$W_{Lost} = T_{sys} \pi_{int} + T_{ext} \pi_{ext}^{Endo} \quad (25a)$$

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

$$W_{Lost} = \int_A^B T_{sys} \delta \pi_{int} + T_{ext} \pi_{ext}^{Endo} \quad (25b)$$

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

$$W_{Lost} = \int_A^B T_{sys} \delta\pi_{int} + \int_C^D T_{ext} \delta\pi_{ext}^{Endo} \quad (25c)$$

In ref [11] applications of relations (25) are given for other irreversible processes : isobaric, adiabatic etc.

4- Conclusion

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 a general 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.

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APPENDIX A

Here we prove relations (25b) and (25c)

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 δQ comes in the system and some work δW leaves it, therefore from relation (10) and the First Law

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

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

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

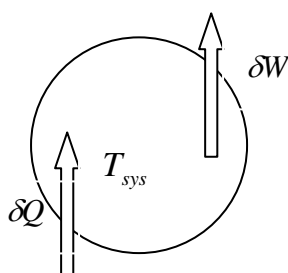


Fig. 4 Some heat comes in the system and some work leaves the system in the infinitesimal step.

If the infinitesimal process is Endo-Reversible ($\delta\pi_{int}^{q.s.} = 0$) it holds $0 = T_{sys} dS_{syst} - dU_{sys} - \delta W_{Rev}^{Endo}$

Therefore

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

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

Therefore

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

Remark that for the adiabatic process, many Endo-reversible paths are possible[11]

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

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

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

Or for T_{ext} ranging between T_C and T_D

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

In conclusion for both temperatures variable

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

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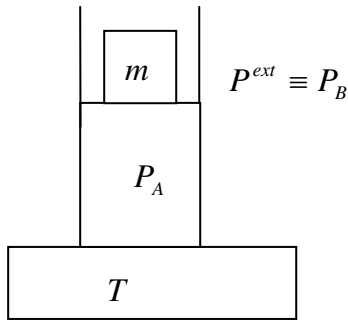


Figure 1. Ideal gas in thermal contact with the heat source T

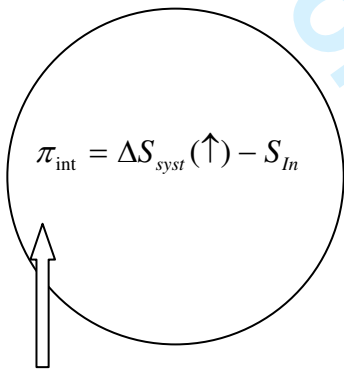


Figure 2. The entropic balance for the ideal gas

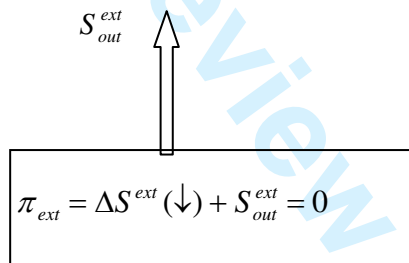


Figure 3. The entropic balance for the heat source T

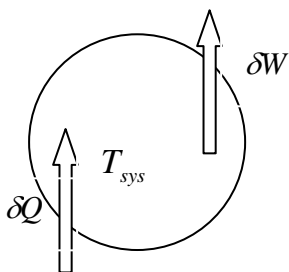


Fig. 4 Some heat comes in the system and some work leaves the system in the infinitesimal step.