

The Gouy-Stodola Theorem and the derivation of exergy revised

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ABSTRACT

The Gouy-Stodola Theorem is the theoretical basis for allocating irreversibility and for identifying the maximum possible efficiency for any kind of energy conversion system. The well-known theorem is re-obtained in this paper, relaxing the hypothesis about a constant value for temperature and pressure of the reference environment. The equations that have been derived taking into account the variation of reference temperature and pressure show that two additional terms appear in both reversible and irreversible maximum useful work output, besides the well-known terms. These additional terms take into account the potential useful work (exergy) destruction related to the variation of the ambient condition during the considered time interval. In this way the Gouy-Stodola Theorem still holds, but the allocation of exergy destruction is generally different from that calculated in the usual hypothesis of constant temperature and pressure of the reference environment. The Gouy-Stodola Theorem is also used in various textbooks for defining the flow and the non-exergy of a control volume. The same approach is applied in this paper, highlighting the differences and the difficulties related to the variation of the reference pressure and temperature in the reference environment.

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1. Introduction

The Gouy-Stodola Theorem is the theoretical basis for allocating irreversibility and for identifying the maximum possible efficiency for any kind of energy conversion system [1,2]. In this paper, the well-known theorem is re-obtained, relaxing the hypothesis about a constant value for temperature and pressure (T° , P°) of the reference environment. Even if this may seem a quite obvious generalization of the Gouy-Stodola Theorem, very few paper in literature discuss the issue, in particular, a paper published in 2004 by Camdali and Tunc [3] introduce a generalized exergy balance which holds also for time dependent reference temperature and pressure (T° , P°), but a multiple reference temperature is introduced in the exergy definition and the paper focus on the application to high temperature processes, like those inside a jet engine. The effects of different options for constant values of (T° , P°) are analyzed for instance by Brodyanskii and Kalinin [4] and Rosen and Dincer [5], but without introducing the possible variations along time of the same parameters in the derivation of the flow and non-flow

availability, whilst Bonetti and Kokogiannakis [6] recognize the potential impact of reference temperature variations during time, but then they conclude that, for their approach, the fluctuating value of the external temperature brings perplexing results about exergy storage and finally adopt constant reference values. More recently the issue of exergy analysis with variable temperature and pressure (T° , P°) of the reference environment has been rebooted by Reini and others [7,8], with special attention for the application to energy systems operating close to the actual temperature of the environment, like thermal storage and solar thermal systems, where the effect of time-dependent ambient reference conditions is expected to be more relevant.

In the present paper, the approach presented in Ref. [7,8] is summarized and developed in view of the reformulation of the Gouy-Stodola Theorem; the results show that two additional terms appear in the expression for the reversible output work, besides the well-known terms. These additional terms take into account the reduction (or the increment) in the reversible useful work output, related to the variation of the ambient conditions, during the considered time interval.

Finally, the revised version of the Gouy-Stodola Theorem is applied (as is done in various textbooks) to the definition of the flow-exergy of a material stream, crossing the boundaries of a generic control volume, and the formulation of flow-exergy,

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Nomenclature		\dot{S}_{gen}	entropy generation rate, W/K
A	non-flow availability, J	t	time, s
B12	flow availability during time interval 1 → 2, J	T	temperature, K
\dot{B}_i	flow availability rate, W	\bar{T}°	integral average reference temperature, K
cP	specific heat at constant pressure, J/(kg K)	T*	additional reference temperature, K
Ξ	non-flow exergy, J	V	volume, m ³
E	energy, J	<i>Subscripts and superscripts</i>	
\dot{E}_{Q_i}	exergy rate of heat, W	0	property at equilibrium with reference ambient conditions
E_w	exergy of useful work, J	0	property of the reference ambient
Exi	flow exergy of the material stream \dot{m}_i , J	12	from instant t1 to instant t2
η_{ex}	exergy efficiency,	a	air surrounding the system
h, h'	specific, total specific enthalpy, J/kg	av	average
\dot{m}	mass flows rate, kg/s	e	exit
M	mass, kg	ex	exergy
P	pressure, N/m ²	i	inlet, generic index
\dot{Q}_i	heat transfer rate, W	in-out	inlet flows minus outlet flows
s	specific entropy, J/(kg*k)	rev	reversible
S	entropy, J/K		

consistent with the hypothesis of variable temperature and pressure (T° , P°) of the reference environment, is obtained.

Notice that the actual option of producing electric power (exergy) from the daily variations of the ambient temperature, without any additional energy input, has been recently proved by an experiment developed at MIT [9], based on a thermo-electric technology. In exergy terms, this experiment proves that the non-flow exergy of a system has to be regarded as affected by the time variations of temperature of the reference environment and that the oscillation of the non-flow exergy can be (partially) converted into a real work output, without any exergy input from the outside the system.

2. The Gouy-Stodola Theorem with variable ambient conditions

The well-known Gouy-Stodola Theorem can be obtained by combining energy and entropy balance of the control volume

shown in Fig. 1 [2]. The hypothesis of constant values for temperature and pressure (T° , P°) of the reference environment is introduced by the conventional approach and, with the additional hypothesis of avoiding mixing of heterogeneous flows, a differential equation is obtained, showing that the useful work produced by the control volume for the outside is equal to five terms that, following Bejan [2], can be identified as:

- the variations of the non-flow availability accumulated inside the volume,
- the exergy of heat entering the volume,
- the flow availability of mass entering the volume,
- minus the flow availability of mass exiting the volume,
- minus the exergy destruction rate ($T^\circ \dot{S}_{gen}$) inside the volume itself.

If the hypothesis of constant ambient conditions is relaxed and

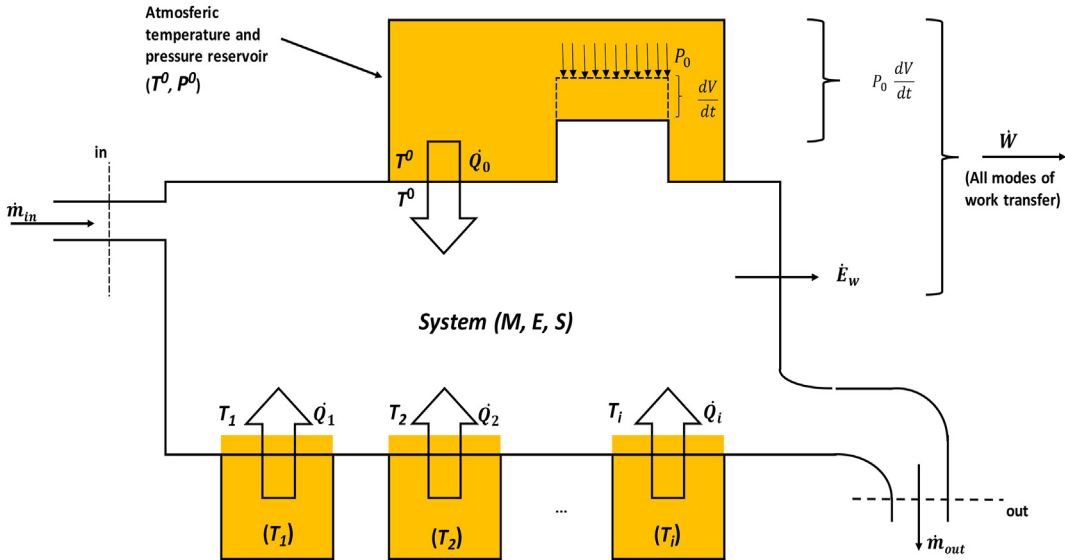


Fig. 1. A generic Control Volume exchanging heat, mass and work with the environment, from Ref. [2].

T° and P° are regarded as time-dependent variables, the differential relation has to be integrated in the considered time interval (from generic instant 1 to instant 2), therefore the useful work produced by the control volume for the outside, in that time interval, can be expressed as:

$$E_{W12} = \int_1^2 \left(-\frac{dE}{dt} + T^\circ \frac{dS}{dt} - P^\circ \frac{dV}{dt} \right) dt + \sum_i \int_1^2 \dot{Q}_i \left(1 - \frac{T^\circ}{T_i} \right) dt + \int_1^2 [\dot{m}_i (h'_i - T^\circ s_i) - \dot{m}_e (h'_e - T^\circ s_e)] dt - \int_1^2 T^\circ \dot{S}_{gen} dt \quad (1)$$

By applying integration by parts and rearranging terms, the following formulation can be obtained [8]:

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$$E_{W12} = -\Delta_{12}(E - T^\circ S + P^\circ V) - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt + \sum_i \int_1^2 \dot{Q}_i \left(1 - \frac{T^\circ}{T_i} \right) dt + \int_1^2 \dot{m}_i (h'_i - T^\circ s_i) dt - \int_1^2 \dot{m}_e (h'_e - T^\circ s_e) dt - \int_1^2 T^\circ \dot{S}_{gen} dt \quad (2)$$

It is worth noting that the last term in (2) is the only one where the entropy generation appears and in fact, it accounts for the reduction in the useful work produced by the control volume for the outside, because of the irreversibility inside the control volume itself. By considering a reversible (ideal) process inside the control volume, while all thermodynamic variables as well as all heat and mass flows (except the heat \dot{Q}_0 , exchanged with the reference environment) are kept unchanged, the maximum useful reversible work that could be produced by the system, in the time interval from instant 1 to 2, can be expressed as:

$$E_{(W12)rev} = -\Delta_{12}(E - T^\circ S + P^\circ V) - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt + \sum_i \int_1^2 \dot{Q}_i \left(1 - \frac{T^\circ}{T_i} \right) dt + \int_1^2 \dot{m}_i (h'_i - T^\circ s_i) dt - \int_1^2 \dot{m}_e (h'_e - T^\circ s_e) dt \quad (3)$$

Therefore, equation (2) can be re-written as:

$$E_{W12} = E_{(W12)rev} - \int_1^2 T^\circ \dot{S}_{gen} dt \quad (4)$$

The last term in (4) is the *lost work* [1] and it can be regarded as the difference between the maximum reversible useful work that could be produced by the system and the actual work produced, during the same time interval from instant 1 to 2.

Equation (4) expresses the famous Gouy-Stodola Theorem in its well-known form, except for having all term integrated in time during the process (1 → 2), and it reads (adapted from Refs. [1], in *italic* the non-conventional part of the definition that is necessary to take into account the variations of T° and P° during the considered time interval): “The useful work produced by a control volume for the outside is equal to the maximum useful work, that could be produced in case of reversible processes inside the control volume itself, minus a term that is *in each time instant* proportional to the entropy production because of irreversibility, through a coefficient that is the temperature at which the system is free to exchange *in that time instant* an arbitrary amount of heat.”

It is worth noting that equation (4) is perfectly consistent with the usual formulation of the Gouy-Stodola Theorem [1], whilst the formulation of the maximum reversible useful work contains some additional terms, which will be discussed in the following.

It is worth noting also that, if the entropy generation rate \dot{S}_{gen} were a constant (i.e. if a steady-state entropy production could be considered inside the control volume), the lost work would be anyway a function of time, because of the time variation of T° . In this case, by introducing the integral average value of the ambient temperature (\bar{T}°) during the process (1 → 2), the lost work becomes:

$$\dot{S}_{gen} = const \rightarrow \int_1^2 T^\circ \dot{S}_{gen} dt = \Delta t_{12} \frac{\int_1^2 T^\circ dt}{\Delta t_{12}} \dot{S}_{gen} = \Delta t_{12} \bar{T}^\circ \dot{S}_{gen} \quad (5)$$

The well-known exergy destruction term $\bar{T}^\circ \dot{S}_{gen}$ appears into equation (4). Notice that \bar{T}° cannot generally be approximated by the average temperature of the site where the process occurs, but the actual time interval when the process takes place and the actual values assumed by $T^\circ(t)$ must be taken into account.

2.1. Flow and non-flow availability with variable ambient conditions

The first term at the right hand side in equation (2) can be easily identified as the variation in the *non-flow availability* (A) of the control volume during the process, as it is usual in the exergy analysis at constant ambient reference conditions [2], so that the following equation (6) can be written:

$$A \equiv E - T^\circ S + P^\circ V \rightarrow -\Delta_{12}(E - T^\circ S + P^\circ V) = A_1 - A_2 \quad (6)$$

Notice that all variables in equation (6) generally depend on time: energy (E), entropy (S) and volume (V) because of the proceeding of the energy conversion process inside the control volume, and (T° , P°) because of the ambient condition variations during the same time interval, therefore, the non-flow availability would depend on time even if the thermodynamic state variables of the control volume were constant, because of the effect of the ambient condition variations.

Equation (2) contains also a term related to each heat transfer to (or from) the control volume, where the well-known Carnot coefficient appears; it can be easily identified as the *exergy rate* (\dot{E}_{Q_i}) of the heat, therefore, the *exergy* ($E_{Q_{12i}}$) of the heat transfer to (or from) the control volume during the process (1 → 2) can be consistently calculated as:

$$\dot{E}_{Q_i} \equiv \dot{Q}_i \left(1 - \frac{T^\circ}{T_i} \right) \rightarrow E_{Q_{12i}} = \int_1^2 \dot{Q}_i \left(1 - \frac{T^\circ}{T_i} \right) dt = \int_1^2 \dot{E}_{Q_i} dt \quad (7)$$

In the hypotheses of steady-state conditions for the i -th heat flow ($\dot{Q}_i = \text{const}$; $T_i = \text{const}$) and by introducing the integral average value of the ambient temperature (\bar{T}°) during the process (1→2) as in the previous paragraph, the exergy and the average exergy rate of a heat flow can be expressed as in equations (8) and (9), respectively:

$$E_{Q12i} = \dot{Q}_i \int_1^2 \left(1 - \frac{T^\circ}{T_i}\right) dt = \Delta t_{12} \dot{Q}_i \left[1 - \frac{1}{T_i} \frac{\int_1^2 T^\circ dt}{\Delta t_{12}}\right] \\ = \Delta t_{12} \dot{Q}_i \left(1 - \frac{\bar{T}^\circ}{T_i}\right) \quad (8)$$

$$\dot{E}_{Q_i-av} = \dot{Q}_i \left(1 - \frac{\bar{T}^\circ}{T_i}\right) \quad (9)$$

A similar approach can be applied also to the terms in Equation (2) related to the mass exchange.

For the generic material stream \dot{m}_i , the *flow-availability rate* (\dot{B}_i) and the *flow-availability* (B_{12i}) are defined, respectively:

$$\dot{B}_i \equiv \dot{m}_i (h'_i - T^\circ s_i) \rightarrow B_{12i} = \int_1^2 \dot{m}_i (h'_i - T^\circ s_i) dt = \int_1^2 \dot{B}_i dt \quad (10)$$

By introducing the hypotheses of steady-state conditions also for the i -th material flows ($\dot{m}_i = \text{const}$; $T^\circ = \text{const}$; $s_i = \text{const}$), the flow-availability and the average flow-availability rate become, respectively:

$$B_{12i} = \dot{m}_i \int_1^2 (h'_i - T^\circ s_i) dt = \Delta t_{12} \dot{m}_i \left[h'_i - \frac{\int_1^2 T^\circ dt}{\Delta t_{12}} s_i \right] = \Delta t_{12} \dot{m}_i (h'_i - \bar{T}^\circ s_i) \quad (11)$$

$$\dot{B}_{i-av} \equiv \dot{m}_i (h'_i - \bar{T}^\circ s_i) \quad (12)$$

Taking previous definition into account, the maximum useful reversible work in equation (3) reads:

$$E_{(W12)rev} = A_1 - A_2 - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt + \sum_i \int_1^2 \dot{E}_{Q_i} dt + \int_1^2 \dot{B}_i dt \\ - \int_1^2 \dot{B}_e dt \quad (13)$$

The two integral terms related to dT°/dt and to dP°/dt in Equation (13) are additional terms, with respect to the reversible work obtained if (T° , P°) were constant. Notice that these two terms can be either positive or negative. For instance, let's consider a constant value for the entropy S in the first of the two: the whole term is positive if the ambient temperature decreases during the process, whilst the opposite happens if it increases. In other words, these two terms account for the destruction, or the generation, of the potential useful work that could be obtained by the control volume, because of ambient condition variations. It is worth noting that, if these two terms were not taken into account, it would imply an underestimation (or overestimation) of the exergy destruction in the Gouy-Stodola Theorem (Equation (4)) even if the exergy of the heat exchanged and the flow-availability of each material flow were

properly evaluated. For this reason, the first term of the two is named the *Thermal Availability Gap*, while the second is named the *Mechanical Availability Gap* and the two together are the *Thermo-Mechanical Availability Gap* – TMAG.

To fix ideas, let's consider the following ideal experiment: A thermal storage is charged by means of a reversible heat pump, receiving the heat from the environment. The storage is then kept in perfect thermal isolation for a certain time interval, and finally it is discharged by means of a thermal cycle, operating the inverse transformations of the heat pump. Both the charge and discharge processes are reversible and instantaneous. Neglecting the variations of the ambient temperature with time, the conclusion must be inferred that the whole process cannot produce any net useful work for the outside, because exactly the same work is consumed during the charge phase and obtained during the discharge one. But let's consider now that the ambient temperature were sensibly *lower* during the discharge phase: the useful work produced during this phase would be greater than that consumed during the previous charging phase, with some net useful work produced for the outside. This fact is clearly unexplainable for conventional exergy analysis, with constant T° , unless that the heat pump and the cycle were considered not in contact with the environment, but with two other different heat reservoirs or sinks.

On the contrary, it is clear that the heat pump and the cycle are in contact with the environment, but, by applying Equation (2), it can be inferred that, during the keeping of the thermal storage in perfect isolation, additional non-flow availability is created inside its control volume because of the reduction of the ambient temperature T° during this time interval. In fact, during the keeping of the thermal storage in perfect isolation, it is neither receiving additional flow availability, or exergy of heat, from the outside, nor useful work is exchanged. Nevertheless the non-flow availability (A_2) has to be greater when the ambient temperature T° is lower, with respect to A_1 , when it was higher, so that a term is required in the maximum useful reversible work - equation (13) - to take this greater availability into account and to put it in relation with the trend of the reference ambient temperature during time. The previously defined *Thermal Availability Gap*, expresses exactly this quantity, consistently with all previous definitions of flow and non-flow availability.

Notice finally that, if also the control volume can be regarded to be in stationary conditions (i.e. its thermodynamic state (E , S , V) remains unchanged) besides all heat and mass flows, the Thermo-Mechanical Availability Gap becomes equal to $A_2 - A_1$, so that the following Equation (14) is obtained:

$$\dot{E}_W = \sum_i \dot{Q}_i \left(1 - \frac{\bar{T}^\circ}{T_i}\right) + \sum_i \dot{m}_i (h'_i - \bar{T}^\circ s_i) + \bar{T}^\circ \dot{S}_{gen} \quad (14)$$

This is quite similar to the well-known availability balance [2] obtained with constant temperature and pressure, except for the usage of the integral average value of the ambient temperature (\bar{T}°) in replacement of the constant arbitrary value T° .

3. Flow and non-flow exergy with variable ambient conditions

The Gouy-Stodola theorem – Equations (3) and (4) – is used not only for calculating the reversible work and then obtaining the exergy destruction (or *irreversibility*) in the whole process, but also for calculating the flow exergy of each material stream crossing the boundaries of the control volume and the non-flow exergy of the control volume itself.

According to a lot of textbooks and papers (see, for instance

Ref. [10]) the exergy of a thermodynamic system is defined as:

“the maximum theoretical useful work (shaft work or electrical work) obtainable as the system is brought into complete thermodynamic equilibrium with the thermodynamic environment while the system interacts with this environment only”.

To apply this definition also when the environment conditions (T° , P°) are time-dependent functions, it has to be slightly modified, by stating that the system is brought *at any time instant* into complete thermodynamic equilibrium with the thermodynamic environment, at $T^\circ(t)$, $P^\circ(t)$.

3.1. Non-flow exergy

Consistently with previous exergy definition, the maximum theoretical useful work obtainable from the control volume alone can be calculated from Equation (13), by fixing equal to zero all mass and heat exchanges (except the heat \dot{Q}_0 , exchanged with the reference environment), and assuming states 1 and 2 as follows:

$$E_{(W12)rev} = A_1 - A_2 - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt \quad (15)$$

State 1: is the current state of the system at the generic instant t .

State 2: is the complete thermodynamic equilibrium with the environment, at $T^\circ(t)$, $P^\circ(t)$.

It is evident from Equation (15) that, in case of time-dependent reference environment conditions, the instant at which the complete thermodynamic equilibrium with the environment is reached generally affects the maximum theoretical useful work obtainable, so that an additional hypothesis has to be introduced in the revised definition of the non-flow exergy.

In this paper, it is assumed that the state of complete thermodynamic equilibrium with the environment has to be calculated at *the same time instant* at which the current state of the system is considered. This means that an instantaneous reversible process is considered to bring the system *at any time instant* into complete thermodynamic equilibrium with the environment, at $T^\circ(t)$, $P^\circ(t)$. Taking into account that in the exergy definition we are dealing in any case with an ideal reversible process, to consider an ideal reversible *and instantaneous* process has not to be regarded as a drawback. In this case, the Thermo-Mechanical Availability Gap is equal to zero because, during an instantaneous process, (T° , P°) have to be regarded as constants, therefore their variability cannot affect the exergy evaluation. Therefore, the *non-flow exergy* ($\Xi_{(t)} \equiv E_{(W12)rev}$) of the system can be obtained as:

$$\begin{aligned} \Xi_{(t)} = A_{(t)} - A_{0(t)} = & (E_{(t)} - T^\circ_{(t)} S_{(t)} + P^\circ_{(t)} V_{(t)}) \\ & - (E_{0(t)} - T^\circ_{(t)} S_{0(t)} + P^\circ_{(t)} V_{0(t)}) \end{aligned} \quad (16)$$

Agreeing with an alternative option, having the advantage of avoiding a time-dependent value of A_0 , an additional reference temperature, T^* , may be introduced, at which the equilibrium with the reference environment is regarded to be reached, even if the real ambient reference temperature $T^\circ(t)$ has a different value, depending on the time instant. The same has to be done for P° . This approach is presented by Gogus, Camdali, and Kavsaoglu in Ref. [11]. In spite of the cited advantage in the numerical calculation of the non-flow exergy Ξ , this approach can be regarded to introduce some inconsistencies between the expression of the reversible work in the Gouy-Stodola theorem and the exergy definition. In fact, a situation may happen where the non-flow exergy of a control volume is zero, but some reversible work could be obtained from it, in principle, consistently with Equation (3) and with the definition of exergy, or where the non-flow exergy of a control volume is

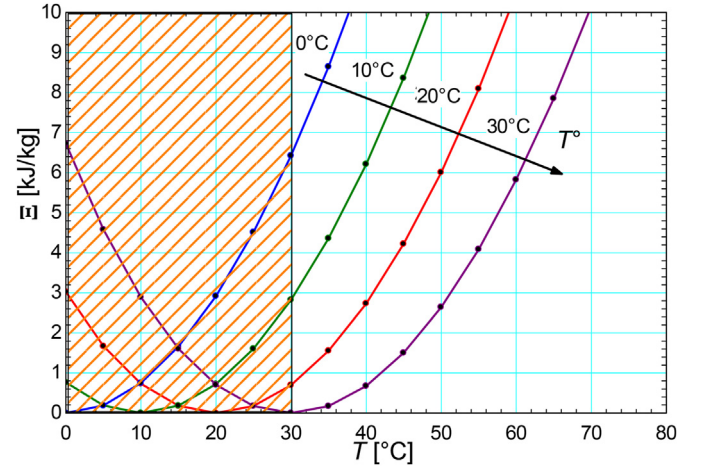


Fig. 2. Exergy of a thermal storage vs. its temperature introducing T° as a constant parameter.

greater than zero, but no reversible work could be obtained from it following the prescription of exergy definition.

To fix ideas, let's consider a thermal storage made up with an incompressible fluid, at a constant temperature T , neglecting the effect of ambient pressure variation. By introducing the model of incompressible fluid into equation (16), the following equation (17) is obtained:

$$\Xi_{(t)} = c_p \left[T - T^\circ_{(t)} \left(1 - \ln \frac{T^\circ_{(t)}}{T} \right) \right] \quad (17)$$

Equation (17) holds for both hot and cold storages and shows that the non-flow exergy of a thermal storage at a temperature level $T \neq T^\circ$ is always positive. In Fig. 2 the exergy of a thermal storage is shown vs. its temperature level T , introducing the ambient temperature T° as a parameter. In Fig. 2 water is considered as the incompressible fluid and T° is varying in the range 0–30 °C.

Let's consider also an ideal, instantaneous charging process (1→2) of the hot storage at a temperature level T , at which it is described by the state variables (E , S) according to the incompressible fluid model, then let's consider a keeping of the storage in isolation during a time interval (2→3) and finally an ideal, instantaneous process (3→4) of completely discharging the hot storage, reaching the thermal equilibrium with the environment (the effect of ambient pressure variation is neglected, see Fig. 3).

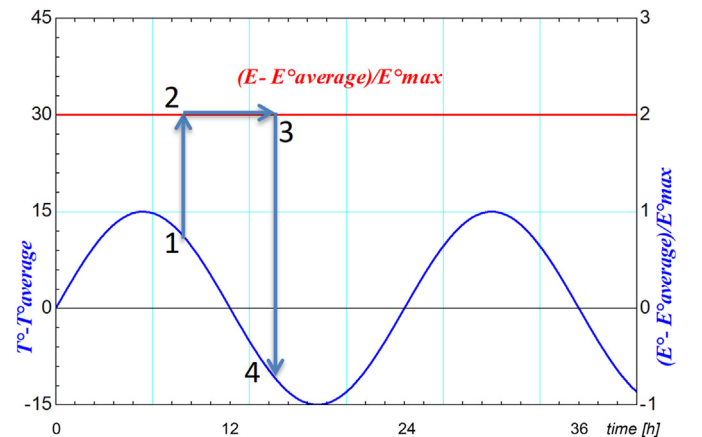


Fig. 3. An ideal charge/discharge process of a thermal storage.

During the charging phase, an ideal Carnot machine, operating like a heat pump, extracts heat from the environment to heat the storage: the higher the temperature T° , the lower the reversible work required to charge the storage at the defined temperature level. Therefore, it would be possible, in principle, to charge the storage when the temperature T° were high (for instance, $T^\circ_{(1)} = 30^\circ\text{C}$) and discharge it when the temperature T° were lower (for instance, $T^\circ_{(3)} = 10^\circ\text{C}$). This ideal process is shown in Fig. 4 for a maximum temperature of the storage equal to 50°C . The percentage of useful work, obtained during the discharging phase because of the reduction of temperature T° , is shown vs. the maximum temperature of the storage itself on the right hand side scale of the same Fig. 4. Notice that, for the considered storage temperature (50°C) this value is equal to 75%, i.e. 25% of the reversible work obtained during the discharge phase has been supplied to the storage during the previous charge phase. The gain is even higher for lower values of the storage temperature.

Obviously, real world processes cannot happen instantaneously. Therefore, the useful work (or the exergy) required during the charging phase has to be calculated by Eq. (18), and similarly for the useful work produced during the discharging phase:

$$E_{W12} = -\Delta_{12}(E - T^\circ S + P^\circ V) - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt - \int_1^2 T^\circ \dot{S}_{gen} dt \quad (18)$$

A more realistic example is shown in Refs. [7], where a simple sensible heat storage is charged by a solar thermal field during the day, then its energy is exploited during the night for operating a small Organic Rankine Cycle (ORC). A single day operation is considered, with 12 sunny hours and 12 dark hours. In that paper the conclusions state that: "... if the storage alone is considered, the calculations show that neglecting the term related to $dT^\circ(t)/dt$ [...] implies an underestimation of the exergy destruction due to entropy generation inside the control volume. [...] During the discharge phase, there are no high temperature processes and electric power is produced exploiting the non-flow exergy previously accumulated inside the storage. In this phase, neglecting the term related to $dT^\circ(t)/dt$ [...] prevents of highlighting that an important amount of potential useful work is not utilized, but it is destroyed by entropy generation, [...] and for the operation

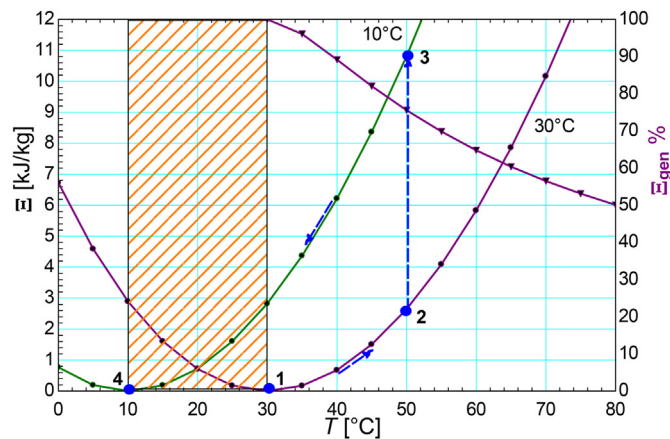


Fig. 4. Exergy of a thermal storage and its % generated by variable T° vs. its temperature level T .

strategy chosen for the whole system. Also the exergy efficiency of the discharge phase, when the ORC is producing the useful power, is affected by $T^\circ = f(t)$; it results equal to 31% taking into account the reference ambient temperature variations, whilst it is over-estimated up to 5% points if a constant value is assumed".

3.2. Flow exergy

A procedure similar to that presented in the previous paragraph can be used to define the flow exergy of a material stream. Let's consider a particular process of the system in Fig. 1, where the thermodynamic state (E, S, V) of the control volume remains unchanged and, in addition, all mass and heat exchanges are fixed equal to zero, except the heat exchange with the environment and two material streams, defined as follows:

- \dot{m}_i is a generic entering flow, (its current state being defined by enthalpy h'_i and entropy s_i) the flow exergy of which is the object of the calculation,
- $\dot{m}_e = \dot{m}_i$ is the same flow, leaving the system into complete thermodynamic equilibrium with the environment at $T^\circ(t)$, $P^\circ(t)$, having, therefore, total enthalpy h'_{0i} and entropy s_{0i} , notice that they both are time-dependent.

The reversible useful work reads:

$$E_{(W12)rev} = A_1 - A_2 - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt + \int_1^2 \dot{m}_i (h'_i - T^\circ s_i) dt - \int_1^2 \dot{m}_i (h'_{0i} - T^\circ s_{0i}) dt \quad (19)$$

Because of the hypothesis introduced about the thermodynamic state (E, S, V) of the control volume, it can be easily demonstrated that the Thermo-Mechanical Availability Gap becomes equal to $A_2 - A_1$, so that the first four terms on the right side of Equation (19) are equal to zero, as a whole. By introducing once again the hypothesis of evaluating the complete thermodynamic equilibrium with the environment at $T^\circ(t)$, $P^\circ(t)$ at the same time instant at which the current state of the system is considered, the two left integral terms can be grouped into a unique integral, obtaining the flow exergy ($EX_{12i} \equiv E_{(W12)rev}$) of the material stream \dot{m}_i :

$$EX_{12i} = \int_1^2 \dot{m}_i [(h'_i - h'_{0i}) - T^\circ (s_i - s_{0i})] dt = \int_1^2 (\dot{B}_i - \dot{B}_{0i}) dt \equiv \int_1^2 \dot{E}x_i dt \quad (20)$$

where, consistently with previous definitions, $\dot{E}x_i \equiv (\dot{B}_i - \dot{B}_{0i})$ is the flow exergy rate of the same material stream. Notice that all thermodynamic variables in Equation (20) generally time-depend, even if it is not explicitly underlined in the same equation. In this case too, an additional reference temperature, T^* , may be introduced, at which the equilibrium with the reference environment is regarded to be reached, in order of avoiding to deal with a time-dependent thermodynamic condition of the flow leaving the system into complete thermodynamic equilibrium with the environment at $T^\circ(t)$ and $P^\circ(t)$. Analogously to the case of non-flow exergy definition, in this alternative option, some inconsistencies would be introduced into the expression of the reversible work in the Gouy-Stodola theorem and into the exergy definition. In particular, the

cold sink, for instance the air surrounding the system at temperature $T_a(t)$, would be apparently able to supply an *unlimited* amount of exergy to the system itself, except at the moment in which $T_a(t) = T^*$ [12].

3.3. Exergy balance with variable ambient conditions

The expressions obtained for the flow and the non-flow exergy can be introduced into the formulation of the reversible work (Equation (13)). In particular, previous definitions directly imply that:

$$A_1 - A_2 = \Xi_1 - \Xi_2 + A_{01} - A_{02} \quad (21)$$

$$\sum_{in-out} \int_1^2 \dot{m}_i (h'_i - T^\circ s_i) dt = \sum_{in-out} \int_1^2 \dot{E}x_i dt + \sum_{in-out} \int_1^2 \dot{m}_i (h'_{0i} - T^\circ s_{0i}) dt \quad (22)$$

Therefore, Equation (13) can be re-written as the following Equation (23):

$$E_{(W12)rev} = \Xi_1 - \Xi_2 + A_{01} - A_{02} - \int_1^2 \frac{dT^\circ}{dt} S dt + \int_1^2 \frac{dP^\circ}{dt} V dt + \sum_i \int_1^2 \dot{E}Q_i dt + \sum_{in-out} \int_1^2 \dot{E}x_i dt + \sum_{in-out} \int_1^2 \dot{m}_i (h'_{0i} - T^\circ s_{0i}) dt \quad (23)$$

To simplify this relation, let's consider the following ideal condition of the same system under examination (Fig. 1):

- The control volume is in complete thermodynamic equilibrium with the environment at $T^\circ(t)$, $P^\circ(t)$ at any time instant,
- All input/output material streams are exchanged reversibly, but also their thermodynamic states are in complete thermodynamic equilibrium with the environment at $T^\circ(t)$, $P^\circ(t)$ at any time instant.

In such a condition, the reversible work produced for the outside during the time interval from instant 1–2 has to be necessarily equal to zero, because there is no thermal or pressure gradient neither inside the system, nor between the system and the environment. Therefore, the following Equation (24) can be inferred from Equation (13):

$$0 = A_{01} - A_{02} - \int_1^2 \frac{dT^\circ}{dt} S_0 dt + \int_1^2 \frac{dP^\circ}{dt} V_0 dt + \sum_{in-out} \int_1^2 \dot{m}_i (h'_{0i} - T^\circ s_{0i}) dt \quad (24)$$

By introducing Equations (23) and (24) into the Gouy-Stodola Theorem – Equation (4) – the *Exergy Balance* of the system during the time interval from instant 1 to 2 is obtained:

$$E_{W12} = \Xi_1 - \Xi_2 - \int_1^2 \frac{dT^\circ}{dt} (S - S_0) dt + \int_1^2 \frac{dP^\circ}{dt} (V - V_0) dt + \sum_i \int_1^2 \dot{E}Q_i dt + \sum_{in-out} \int_1^2 \dot{E}x_i dt - \int_1^2 T^\circ \dot{S}_{gen} dt \quad (25)$$

The two integral terms related to dT°/dt and to dP°/dt in Equation (25) are defined as the *Thermal Exergy Gap*, and the *Mechanical Exergy Gap*, respectively, and the two together are the *Thermo-Mechanical Exergy Gap* – TMEG, consistently with the previous definitions.

It is worth noting that the Thermo-Mechanical Exergy Gap may produce a positive, or negative, variation in non-flow exergy of the system even if it is perfectly isolated and the reason is exactly the same reason why the Thermo-Mechanical Availability Gap may produce a positive, or negative, variation in non-flow availability of the system, as explained at the end of chapter 2.1. Therefore, if the assumption that the reference temperature (and pressure) can change during time is introduced in the analysis, the consequence is that the non-flow exergy and the non-flow availability of an isolated system may change even without entropy generation, or destruction, inside its control volume. This fact is real and is confirmed not only by the conceptual experiment described in Chapter 3.1, but also by the experiment developed at MIT [9], where the oscillation of the ambient temperature (and therefore of the non-flow exergy of a system) are partially converted into a real work output, without any exergy input from the outside the system. This real strategy of energy harvesting cannot be explained if we don't accept that exergy is first created inside the control volume and then it is partially converted into some useful work output. On the other hand, we have to recognize that actual changes in reference temperature and pressure are possible only if there is a driving force, pushing the environment through continuously different states. The driving force can be internal to the environment, so that some kind of exergy reservoir has to be continuously consumed, or external to the couple made up by the system and the environment. In this case no environmental resources have to be consumed, as is the case of the reference environment on the surface of the Earth, if reference temperature variation driven by the Sun are taken into account. In the perspective of the macro-system made up by the considered system, the Earth and the Sun, the reference temperature and pressure may be regarded as constant by making reference to the conditions of the interplanetary space, so that the 1:1 link between entropy generation, or destruction, and exergy destruction, or generation, respectively, appears explicitly again.

If a negative value of the Thermo-Mechanical Exergy Gap were neglected, it can be demonstrated that the exergy efficiency of the system would be underestimated. The opposite would happen in case of neglecting a positive value of the Thermo-Mechanical Exergy Gap. Let's show this result in the particular case of the discharging of a thermal storage, producing the work E_{W12} for the outside through a heat engine, operating between the storage and the environment temperatures.

In this case, there is no exergy exchange related to heat or material flows and the exergy efficiency during the time interval has to

be defined as:

$$\eta_{ex12} \equiv \frac{E_{W12}}{\dot{E}_{(W12)rev}} = \frac{E_{W12}}{\dot{E}_1 - \dot{E}_2 - \int_1^2 \frac{dT^\circ}{dt} (S - S_0) dt + \int_1^2 \frac{dP^\circ}{dt} (V - V_0) dt} \quad (26)$$

It is worth noting that previous Equation (26) has to contain the Thermo-Mechanical Exergy Gap, otherwise the exergy efficiency could not become equal to one in case of fully reversible processes inside the control volume. If a positive value of the Thermo-Mechanical Exergy Gap were neglected, the result would be an underestimation of the denominator in Equation (26) and then, an overestimation of the exergy efficiency as a whole.

Notice finally that, if the control volume and all heat and mass flows can be regarded to be in stationary conditions, the Thermo-Mechanical Exergy Gap becomes equal to $\dot{E}_1 - \dot{E}_2$, so that two expressions for the Exergy Balance and for the exergy efficiency are obtained (Equation (27), (28)) which are quite similar to the well-known ones obtained with constant T° and P° , except for the usage of the integral average value of the ambient temperature (\bar{T}°) in replacement of the constant arbitrary value T° :

$$\dot{E}_W = \sum_i \dot{Q}_i \left(1 - \frac{\bar{T}^\circ}{T_i}\right) + \sum_i \dot{m}_i [(h'_i - h'_{0i}) - \bar{T}^\circ (s_i - s_{0i})] + \bar{T}^\circ \dot{S}_{gen} \quad (27)$$

$$\eta_{ex} \equiv \frac{\dot{E}_W}{\dot{E}_{(W)rev}} = \frac{\dot{E}_W}{\sum_i \dot{Q}_i \left(1 - \frac{\bar{T}^\circ}{T_i}\right) + \sum_i \dot{m}_i [(h'_i - h'_{0i}) - \bar{T}^\circ (s_i - s_{0i})]} \quad (28)$$

An application of the Exergy Balance with varying reference environment temperature to an energy system (an Air Handling Unit) in stationary conditions, has been recently proposed by G. Streckienė et al. [13], without, however, providing a theoretical justification for the value adopted for T° .

4. Conclusions

In this paper a not-conventional approach to the Gouy-Stodola Theorem is presented, where the usual hypothesis of constant ambient conditions is relaxed and T° and P° are regarded as time-dependent variables. The main conclusions obtained can be summarized in the following.

The Gouy-Stodola Theorem still holds and it reads: "The useful work produced by a control volume for the outside is equal to the maximum work, that could be produced in case of reversible processes inside the control volume itself, minus a term that is in each time instant proportional to the entropy production because of irreversibility, through a coefficient that is the temperature at which the system is free to exchange in that time instant an arbitrary amount of heat."

The formulation of the reversible work appearing in the Gouy-Stodola Theorem contains two additional terms, with respect to the formulation obtained in the hypothesis of constant ambient conditions. They can be either positive or negative and they account for the destruction, or the generation, of the potential useful work that could be obtained by the control volume, because of ambient condition variations. For this reason, they are named the *Thermo-Mechanical Availability Gap* – TMAG.

The exergy of each heat exchanged and the flow and non-flow availability can be defined also if T° and P° are regarded to be time-dependent. Also in this case the exergy balance of a generic control volume can be derived by the Gouy-Stodola Theorem; in the time-dependent formulation of the exergy balance the *Thermo-Mechanical Exergy Gap* – TMEG – appears, accounting for exergy destruction (or production) inside the control volume, not because of irreversibility, but because of the variation of the environmental conditions during the operation of the system. Therefore, neglecting the Thermo-Mechanical Exergy Gap results in an overestimation (or underestimation) of the exergy destruction because of irreversibility inside the control volume, during the considered time interval. At the same time, the exergy efficiency of the system would be underestimated (or overestimated, respectively). On the other hand, if the driving force pushing the environment through continuously different states were introduced into the analysis, a macro-system could be, in principle, defined where the 1:1 link between entropy generation, or destruction, and exergy destruction, or generation, respectively, would appear explicitly again.

If the control volume and all heat and mass flows can be regarded to be in stationary conditions, expressions quite similar to the well-known ones at constant T° and P° are obtained for the reversible work, for the flow and the non-flow availability as well as for all terms inside the Exergy Balance and the exergy efficiency, except for the usage of the integral average value of the ambient temperature (\bar{T}°) during the time interval, in replacement of the constant arbitrary value T° . This means that the time location and extension of the considered process do affect the value of the average ambient temperature that has to be used for a proper evaluation of the exergy balance.

CRediT authorship contribution statement

Mauro Reini: Conceptualization, Methodology, Validation, Formal analysis, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision. **Melchiorre Casisi:** Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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