Bases for second law analyses of solar-powered systems, Part 2: the external temperature

Michel PONS

CNRS-LIMSI, Orsay, France, michel.pons@limsi.fr

ABSTRACT: In any textbook on Thermodynamics the second law, especially the exergy analysis, is exposed with heat sources at constant temperatures. However, ambient temperature essentially fluctuates. Should exergy be defined with respect to a fluctuating external temperature or with respect to a fixed value? With the help of very simple case studies, the present study clearly answers. Moreover, it presents a guide for fixing that constant value and a thermodynamic meaning is given to the exergy of heat fluxes received by ambient air.

Keywords: exergy, process analysis, theoretical thermodynamics.

NOMENCLATURE

- $b$: Specific exergy [Jkg$^{-1}$]
- $c_p$: Specific heat [Jkg$^{-1}$K$^{-1}$]
- $h$: Specific enthalpy [Jkg$^{-1}$]
- $T$: Temperature [K]
- $t$: Time [s]
- $s$: Specific entropy [Jkg$^{-1}$K$^{-1}$]
- $w$: Specific work [Jkg$^{-1}$]

Indexes

- $0$: Reference
- $C$: Carnot
- $e$: External air
- $f$: Final
- $i$: Initial
- $t$: Time dependent

Greek letters

- $\eta$: Cycle efficiency

1. INTRODUCTION

Solar energy is becoming more and more attractive, first because the oil prizes are increasing continuously, second because global warming is a major concern. Solar-powered systems for producing electricity, heat or cold are thus being developed all around the world. Like for other developing technologies, those systems deserve optimization. For this purpose second law analysis, based on either entropy- or exergy-balances, is a very powerful tool for analyzing the irreversibilities of a considered system [1]. It helps, 1/ to explain the difference between the maximal possible efficiency (typically the Carnot efficiency) and the actual one; 2/ to identify the components or sub-processes mainly responsible for the efficiency losses; 3/ to propose solutions.

As solar energy makes second law analyses much more complex than those exposed in textbooks, it offers a real challenge to thermodynamicists. Indeed, the two main energy sources (sources in the thermodynamic meaning: source or sink), i.e. the solar radiation and the ambient air, are highly fluctuating. The question of solar radiation, its radiative character, direct plus diffuse, is addressed in the first part of this work. This second part focuses on the fluctuations of external temperature and
their thermodynamic consequences with respect to second law analyses, especially exergy analyses.

As said in the first part, serious analyses of solar systems require rigorous integration of energy-, entropy-, and exergy-fluxes over a reasonable period, at least one day, better several days if not a whole season. For instance, all the start-up and shut-down procedures must be integrated. Over such long periods, the temperature of ambient air (called here external temperature) surely fluctuates, with magnitudes as high as tens of Kelvin. However, the ambient air is the neutral heat source with respect to which exergy is defined. Those fluctuations thus raise two questions somehow correlated.

The first question is: how must exergy be defined when the external temperature fluctuates? May the reference temperature involved in the definition of exergy fluctuate with the external temperature, or must it be fixed? Here is a concrete example. In part one of this work the exergy flux \( B \) corresponding to the solar flux \( I \) with entropy content \( J \) is defined as \( e_B = -IT J \), where \( T_e \) is a reference temperature equal to the external temperature; this exergy flux is then integrated over each day. In this formula should \( T_e \) be the actual (i.e. time dependent) external temperature \( T_e(t) \), or should it be a constant temperature?

In the latter case, a second question raises: which value should \( T_e \) take?

Those questions are especially crucial when thinking of solar-powered air-conditioning, an emerging technology [2-6]. Indeed, these processes may combine nocturnal ventilation when possible, direct evaporation and full air-conditioning. In such cases, external air sometimes contributes to the process (for instance when nocturnal ventilation is operated) and sometimes is what the process works against (when air-conditioning is operated). Can such qualitative differences be translated in terms of exergy analysis, or must the external air always be considered as dead state with zero exergy?

In textbooks, the second law is introduced in its principle via either entropy or exergy [1,7-10]. Moreover and probably for sake of simplicity all the heat sources, including the ambient air, are assumed to be at constant temperature. To the author’s knowledge, none of them addresses the question of fluctuating ambient temperature, a fact that cannot be denied. In journal literature the question is very rarely mentioned. When it is, the answer is presented as optional just as if either choice (constant reference temperature or fluctuating) were valid.

The analysis presented herein is very simple but it clearly demonstrates that the answer is unique, even if some of its consequences are somehow disturbing in the field of exergy analyses. The analysis is then further continued with the idea of giving the fluctuations of external temperature a thermodynamic meaning in terms of irreversibility while keeping the main idea lying under the original definition of exergy.

2. ENTHALPY, ENTROPY AND EXERGY

We present our analysis for cases where only thermal energy, more precisely sensible heat is involved. Moreover and without any lack of generality, we assume that specific heat is constant. Indeed, any inconsistency that would occur in this very simple framework will also exist in more general cases. The analysis can easily be extended to cases involving mechanical energy, expansion work, chemical reactions, etc.

Whatever the framework, it is well-known that enthalpy and entropy are state functions defined except for an additive constant. Let us represent this additive constant by the reference temperature \( T_0 \) where enthalpy and entropy vanish. In our framework enthalpy and entropy write:

\[
h = c_p(T - T_0); \quad s = c_p \ln(T/T_0) \quad (1)
\]
At this point, $T_0$ is an arbitrarily fixed temperature. From those two state functions, let us define the function $b$ according to:

$$b = h - T_e s = c_p [(T - T_0) - T_e \ln(T / T_0)]$$ \hspace{1cm} (2)

where $T_e$ is the external temperature.

Generally, thermodynamics are more interested in changes of functions (enthalpy, entropy, or Gibbs energy for instance) during a transformation from an initial state to a final one than in the absolute values of those functions. In our framework, i.e. for a temperature change from initial $T_i$ to final $T_f$, the changes of $h$, $s$, and $b$ are:

$$\Delta h = c_p (T_f - T_i); \quad \Delta s = c_p \ln(T_f / T_i)$$

$$\Delta b = \Delta h - T_e \Delta s$$

$$\Delta b = c_p [(T_f - T_i) - T_e \ln(T_f / T_i)]$$ \hspace{1cm} (3)

It can be seen that the temperature $T_0$ is not involved in the eqs. (3), its choice may indeed be arbitrary. On the contrary, $T_e$, which is the factor multiplying entropy in the definition of $b$, see eq. (2), still plays a role in $\Delta b$.

Let us now consider that the system at temperature $T$ undergoes an infinitely small temperature change $\delta T$. The corresponding changes in enthalpy and entropy are:

$$\delta h = c_p \delta T; \quad \delta s = c_p \frac{\delta T}{T}$$ \hspace{1cm} (4)

Let us also consider a reversible cycle operated between the system and the ambient air at $T_e$ during this transformation. This cycle can be an engine cycle ($\delta T < 0$) or a heat pump cycle ($\delta T > 0$). The amount of mechanical work produced (positive or negative) by this cycle during the temperature change $\delta T$ is:

$$\delta w = (-\delta h) \eta_C = (-c_p \delta T) \left(1 - \frac{T_e}{T}\right)$$

$$\delta w = -\delta h - T_e \delta s = -\delta b$$ \hspace{1cm} (5)

Any change in $-b$ is, as expected, the amount of mechanical work that can potentially be produced by reversible cycles operated between the system under consideration and the external air. This is the definition of exergy (availability).

Note that $T_e$ occurs in eq. (5) only as cold source the temperature of the Carnot cycle. Basing the definition of exergy on changes would not require the final state to be at $T_e$ nor that $T_0=T_e$ in eq. (2). Only in a second step and if the function $b$ of eq. (2) should in addition be the total amount of mechanical work potentially produced by reversible cycles operated between the system and the external air during the whole transformation leading the system from its present state to equilibrium with external air, then one must fix $T_0=T_e$ in eq. (2). Note that the same result is obtained when $T_0= T_e$ in eq. (3) (final state is equilibrium with ambient air) and applying the sign change of eq. (5). As a result, note that function $b$ vanish when $T$ equals $T_e$ only when this additional constraint on the meaning of $b$ is applied.

### 3. FIRST CASE STUDY

Let us consider one kilogram of purely liquid water, initially at 100°C (373.15K) and cooled down to ambient temperature $T_e$.

Let us first consider independently two values of $T_e$: 40 and 20°C (313.15 and 293.15K).

Table I presents the enthalpy and exergy changes for each of these two cases. In case 2 the system releases 33% more heat than in case 1. Meanwhile, the exergy change is increased by 81%. This larger increase has two causes: first, the amount of heat supplied to the Carnot cycle is

| Table I: Enthalpy and exergy changes [in kJ] of one kilogram liquid water cooled from 100°C down to $T_e$. |
| --- | --- | --- | --- |
| Case | $T_e$ | $-\Delta h$ | $-\Delta b$ |
| 1 | 40°C | 251.1 | 21.37 |
| 2 | 20°C | 334.8 | 38.77 |
increased (+33%); second, the efficiency of the Carnot engine is enhanced because the temperature of its cold source is lowered. Figure 1 schematically presents the conjunction of these two effects.

In order to introduce a change in external temperature, let us consider now that while water is cooled down from 100°C to external temperature $T_e$, $T_e$ decreases from 40°C to 20°C. Now $T_e$ is time dependent, $T_e(t)$. Figure 2 presents schematically this very simple case of varying external temperature, case 3. The question is: how should exergy $b$ be defined? Should the $T_e$ of eq. (2) be fixed, or should it follow the changes of external temperature? Let us study the second choice, and define $b$ as

$$b_t = c_p [(T - T_e) - T_e \ln(T/T_e)] \quad (6)$$

where $T_e$ is time dependent, $T_e(t)$. In the initial state of case 3 ($T=100°C$, $T_e=40°C$), this function $b_t$ takes the value of $-\Delta b$ in case 1 Table I: 21.37kJ. In the final state ($T=20°C$), it obviously vanishes: equilibrium with external air is dead state.

Figure 1: Schematic representation of Carnot cycles operated between a system being cooled and external air, for two values of $T_e$: 40°C (solid lines) and 20°C (dashed lines).

Figure 2: Schematic representation of a case where external temperature changes (from 40°C to 20°C) during the considered transformation.

Now, what is the amount of work $w_3$ produced by the Carnot engine operated between the system being cooled and external air, as shown in Figure 2?

Assuming that $20 \leq T_e(t) \leq 40°C$; $w_3$ is strictly larger than the work produced in case 1 (21.37kJ) for two reasons: 1/ the system undergoes a larger temperature change, 2/ the Carnot engine has better efficiency because its cold source is at lower temperature. It is also strictly less than that produced in case 2 (38.77kJ), although the system undergoes the same temperature change, because the cold source temperature of the Carnot cycles is larger than in case 2. Actually, for evaluating that amount of work $w_3$ one must specify the correlation between the respective evolutions of $T(t)$ and $T_e(t)$.

A simple case is that where a time scale exists (whatever) on which both functions are linear, just as shown in Figure 2. Some algebra leads then to the expression of $w_3$:

$$w_3 = c_p [T(0) - T_e(0)] \left[1 - \frac{T_f}{T(0)-T_f} \frac{\ln(T(0))}{T_f} \right]$$

where $T(0)$ and $T_e(0)$ are the initial system and external temperatures and $T_f$ is their
common final value. In our case, one obtains $w_3=28.49 \text{kJ}$, a value which fulfils the two inequalities mentioned above:

$$21.37 < 28.49 < 38.77 \text{[kJ]}.$$ 

Completely different values of $w_3$ will be obtained for other functions $T_e(t)$, for instance presenting a minimum or a maximum as shown in Figure 3-a and 3-b. Obviously, such cases can be observed in actual meteorological data. Figure 3-c presents two unrealistic cases (piecewise linear evolutions) however mentioned because they lead to values of $w_3$ approaching either values of $\Delta b$ given in Table I, case 1 for the solid line, case 2 for the dashed line.

This very simple case study leads to the following intermediate result: when the external temperature changes, there is no correlation between the amount of work $w_3$ produced by the Carnot cycles (operated between the system and ambient air) and the changes of the function $b_t$ defined by eq. (6). Indeed, the work $w_3$ depends on the whole evolution of $T_e$ occurring during the system transformation and not only on its initial and final values. Moreover, it can easily be seen that the function $b_t$ is not a state function: even if the system itself is in steady state (constant temperature), a simple change of external temperature makes $b_t$ change.

Going back to eq. (2), it can easily be shown that the same intermediate result still holds if just one of the two temperatures $T_0$ and $T_e$ is time dependent. A robust definition of exergy requires $T_0$ and $T_e$ to be constant, not necessarily equal.

**4. SECOND CASE STUDY**

Let us consider now a reversible engine cycle operated between a heat source at 100°C and ambient air at $T_e(t)$, and that $T_e$ changes between 20 and 40°C. Let us consider a heat input of one kilojoule at 100°C. If the cycle operates when $T_e=20\text{°C}$ it produces 214.4J mechanical energy, and 160.9J if $T_e=40\text{°C}$.

The time constant for processing that kilojoule of heat can easily be much shorter than the fluctuation period of $T_e$, for instance $T_e=40\text{°C}$ at midday and $T_e=20\text{°C}$ at midnight. Such fluctuations can be observed in nature. Let us in addition assume that the heat flux is delivered exactly when $T_e$ is maximal.

If the heat flux is immediately supplied to the Carnot engine and processed, it produces 160.8J mechanical energy. This could be the exergy content of that kilojoule.

However, one can think of another reversible process: in a first step that heat is stored in an ideal storage (without any loss nor temperature change) until the external temperature reaches its minimal value; then the heat is released and processed, thus producing then 214.4J mechanical energy.
This also could be the exergy content of that kilojoule. What is then the exergy corresponding to that kilojoule delivered at $100^\circ$C? The question cannot receive any firm answer when exergy is defined with respect to a time-dependent external temperature.

This second case study leads to the same conclusion as the first one: exergy must be defined with respect to constant reference temperatures $T_0$ and $T_e$.

Moreover the second case introduces the notion of heat storage. When, like in textbooks, the heat source temperatures are constant, the question of heat storage between the system and its sources makes no sense. However, many real processes do involve heat storage. And when such storages exist, they multiply to infinity the number of reversible cycles that can be operated between the system and ambient air at fluctuating temperature.

5. TOWARD A SOLUTION

5.1 Definition of exergy

For second-law analyses to be reliable, exergy must be defined in a robust way, even when the external temperature fluctuates, a natural feature. The two very simple case studies presented above demonstrate strong lacks of robustness if exergy is defined with respect to a time-dependent external temperature. To the author’s knowledge, such a study was never published.

Thermodynamic consistency requires exergy to be defined with constant $T_e$ and $T_0$ in eq. (2), i.e.

$$b = c_p \left( (T - T_0) - T_e \ln \left( T/T_0 \right) \right).$$  \hspace{1cm} (7)

and more generally: $b = h - T_{e0}s$.

Indeed, defining exergy as a linear combination of two state functions, enthalpy and entropy, unambiguously makes it a state function. Moreover, the changes of the so-defined function $b$ do equal the work potentially produced by reversible cycles operated between the system and an external source, provided this external source is at the fixed temperature $T_{e0}$. Note that this reference temperature $T_{e0}$ essentially differs from the external temperature $T_e$: the former is constant, the latter fluctuates. Note also that $T_{e0}$ and $T_0$ do not need to be equal. However, equality makes things more convenient and is assumed in the following.

Now two questions arise:

1/ What should be the value of $T_0$?

2/ With this definition of exergy, the exergy of ambient air is (almost) never zero: $b$ vanishes only at the moments when $T_e(t) = T_0$. Has the non-zero exergy of heat received or supplied by ambient air a thermodynamic meaning?

These two questions are addressed in the next subsections.

5.2 Choice of $T_0$

Keeping in mind that exergy should be the amount of work produced by reversible cycles operated between the considered system and ambient air, then $T_0$ must be somehow related to external temperature. In the academic case of constant external temperature, the work produced by reversible cycles surely is maximal. The idea of maximizing the work produced reversibly is a guide for choosing the value given to $T_0$ when external temperature fluctuates. One can consider the period over which the different fluxes (energy, entropy and exergy) are to be integrated and choose for $T_0$ the value of the external temperature that maximizes that reversible work, i.e. that which is the most favourable to the process.

When the process rejects heat toward ambient air (i.e. engines and cooling machines), then the most favourable value is the minimum of external temperature observed over the integration period; when the process receives heat from ambient air (i.e. heat pumps), then the most favourable is the maximum of external temperature.
As the present study was first motivated by solar-powered air-conditioning, we are interested in the minimum of external temperature. The lowest external temperature observed in our meteorological data for Ouagadugu was 288.5K. As a consequence, in Part 1 of this work the exergy of solar radiation was calculated with $T_0=T_0=288.5K$ (denoted $T_0$).

5.3 Thermodynamic meaning of non-zero exergy of ambient air

Let us now consider again the reversible engine represented in Figures 1 to 3. It rejects heat to ambient air, the temperature of which is larger than $T_0$ (apart from rather short moments), never less. According to eq. (7), heat at external temperature $T_e(t)>T_0$ contains exergy. Can a thermodynamic meaning be given to this amount of exergy in ambient air?

For answering this question (and remembering that the definition of exergy involves reversible processes only, not real processes), let us introduce a special storage, ideally maintained at the temperature $T_0$. Ideally this heat storage can reject all the heat it contains toward ambient air when the external temperature $T_e(t)$ just equals its own temperature $T_0$. As temperature is the same on both sides, the latter heat exchange would be reversible. Now, instead of rejecting heat toward ambient air at temperature $T_e(t)>T_0$, the engine can reject heat toward that heat storage. As a consequence, the engine efficiency $\eta$ is enhanced and more work is produced. Equivalently, it can be said that the heat rejected at $T_e(t)$ is extra processed down to $T_0$, adding thus some more work production. This development is schematically represented in Figure 4.

Equipping the process with this ideal storage obviously maximizes its work production. Symmetrically, without this storage, cycle efficiency is reduced and the produced work is less than maximum: in other words the heat rejected to ambient air at $T_e(t)$ still contains exergy which is uselessly lost (instead of being processed down to $T_0$). The absence of that storage thus induces an exergy loss which, like any other irreversibility, reduces efficiency.

The same can be said, mutatis mutandis, when considering a cooling process, an air-conditioner for instance.

Usually, exergy losses are attributed to a given component, process, or sub-process. In the present case, an exergy loss, i.e. an irreversibility, appears due to the fact that a component is not implemented in the process. This is exactly what can be called a systemic irreversibility, see [11,12]. In ref. [12,13], the analysis of an adsorptive solar-powered ice machine which rejects heat partly between 10am and 4pm and partly during the night leads to similar conclusions.

Whether it is worth or not to install such a heat storage in a given process obviously lies far beyond the scope of the present study. It is just one benefit of the present approach to open such a question and to give part of the answer (the loss due to the production. Symmetrically, without this storage, cycle efficiency is reduced and the produced work is less than maximum: in other words the heat rejected to ambient air at $T_e(t)$ still contains exergy which is uselessly lost (instead of being processed down to $T_0$). The absence of that storage thus induces an exergy loss which, like any other irreversibility, reduces efficiency.

The same can be said, mutatis mutandis, when considering a cooling process, an air-conditioner for instance.

Usually, exergy losses are attributed to a given component, process, or sub-process. In the present case, an exergy loss, i.e. an irreversibility, appears due to the fact that a component is not implemented in the process. This is exactly what can be called a systemic irreversibility, see [11,12]. In ref. [12,13], the analysis of an adsorptive solar-powered ice machine which rejects heat partly between 10am and 4pm and partly during the night leads to similar conclusions.

Whether it is worth or not to install such a heat storage in a given process obviously lies far beyond the scope of the present study. It is just one benefit of the present approach to open such a question and to give part of the answer (the loss due to the
absence of storage, which is also the upper limit of the gain a real heat storage can bring).

6. CONCLUSION

The present study addresses the problem of how the second law, especially exergy analyses, can account for the fluctuations of ambient air (external) temperature, a natural phenomenon. The analysis is very simple, but it clearly demonstrates that if defined with respect to a fluctuating external temperature, exergy has no thermodynamic meaning. Exergy must then be defined with respect to a fixed temperature. From the thermodynamic point of view, it makes sense to give that constant temperature the value of external temperature which is the most favourable to the considered process over the period under consideration (most favourable = minimum for an engine or a cooling machine, and = maximum for a heat pump). When such a choice is done, then the exergy contained in the heat fluxes received by ambient air appears as a systemic exergy loss caused by the decision not to install a heat storage between the system and the external heat source.

Acknowledgment: This work was done in the framework of the ORASOL project, financed by the French ANR program PREBAT and coordinated by Dr. F. Lucas (LPBS, Univ. La Réunion, France).

REFERENCES


