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On the Reference State for Exergy when Ambient Temperature Fluctuates*

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Abstract

Exergy (availability) is the amount of mechanical work that could be produced by reversible processes. This notion is revisited in the case when ambient temperature fluctuates. Simple examples are first considered, and then a theoretical approach is developed. It results that the most reliable way for combining entropy and total energy into an *exergy* function is a linear combination where entropy is multiplied by a **constant** temperature. It results that ambient air has non-zero exergy, but that exergy is surely conserved in ideal reversible processes. This approach is relevant for studying some recent problems in solar energy and building engineering.

Keywords: Solar energy, building, dead state, thermodynamics, second law, heat storage.

1. Introduction

Our planet faces two major challenges, both related to energy: peak oil and global warming. This induces a growing interest in solar energy for all kinds of purposes (electricity, heating or cooling), as well as in energy savings, for instance for improving the energy efficiency of buildings. Buildings can indeed be seen as complex open energetic systems that, like solar-powered systems, need to be optimized. Second law analysis, based on either entropy- or exergy-balances, is a very powerful tool for optimizing systems (Bejan, 1996). Analysis of irreversibilities helps first to explain why the efficiency of actual processes is less than the maximal limit (typically the Carnot efficiency); second to identify the components or sub-processes mainly responsible for those efficiency losses; and, third to propose solutions.

Entropy and exergy (also called availability) mainly differ by their relation to ambient temperature. Up to an additive constant which is arbitrary, entropy only depends on the state of the system under consideration; entropy does not involve ambient temperature. Exergy can be defined in two ways. Energetically, it is the maximal mechanical work that can be extracted from a system, *i.e.* the amount of work potentially produced by reversible processes operated between that system and ambient air. Formally, exergy is total energy minus entropy multiplied by ambient temperature. In most thermodynamic textbooks introducing exergy, *e.g.* (Obert, 1960; Spanner, 1964; Bejan, 1988; Szargut et al., 1988; Borel, 2005) among numerous works, both definitions are equivalent. Considering ambient temperature, there is however a great difference between textbooks and the real climate: in textbooks physico-chemical characteristics of ambient air (pressure, composition, and especially temperature) are fixed, but in reality they fluctuate. For instance ambient temperature fluctuates over tens of Kelvin.

Solar-powered processes are strongly related to ambient air, buildings as well. For such systems, climatic fluctuations are extremely important because they directly influence the magnitude of what is commonly called *thermal losses* (more exactly heat dissipated from process/building to ambient air), also because some processes are directly based on those fluctuations. One very good and simple example is night ventilation: over-ventilating a building at night lowers the temperature of the building itself and reduces the energy consumed for air-conditioning the next day (Yang and Li, 2008). On the other hand, in all textbooks ambient air occurs as the *neutral* heat source (or the *dead state*) with respect to which exergy is defined and where exergy vanishes.

Climatic fluctuations thus raise several questions. How must exergy be defined when outdoor characteristics, especially ambient temperature, fluctuate? Must ambient air always have zero exergy whatever its characteristics? Or should not exergy be defined with respect to a fixed reference, just like other thermodynamic quantities? Exergy analyses considering transient behaviors in fluctuating ambient conditions (at least temperature) are very scarce, most are reported in the recent review of Torio et al. (2009), and they do not address these questions. Sakulpipatsin et al. (2008) investigated the errors resulting from evaluating the exergy of indoor air under certain simplifying assumptions. They consider variations of pressure, composition and temperature. Following the method of Szargut et al. (1988), Göğüs et al. (2002) derived the equations for open systems involving kinetic energy and obtained non-dimensional exergetic functions. Implicitly, all these authors make the *dead state* exactly follow the fluctuations of ambient (outdoor) conditions, so that exergy always cancels out for ambient air. In their transient exergy analysis of a solar still, Torchia-Nuñez et al. (2008) adopt an intermediate position: they take a fixed reference for entropy and altogether multiply entropy by the fluctuating ambient temperature; fluctuations of the latter thus result in exergy changes (see their equation 20). Oppositely, in their exergy analysis of an experimental heat-storage with phase-change material, Koca et al. (2008) define exergy only with respect to a constant reference temperature.

However, none of those studies has explicitly developed the thermodynamic framework they refer to, or the consequences of their assumptions. In the present energy context, this point becomes important. Solar-powered air-

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conditioning emerges as a new technology (Henning, 2007). Research programs develop where different solar-powered air-conditioners are tested in different climates and will eventually be compared in terms of exergy efficiency (Lucas et al., 2008). It is then important to build a thermodynamic framework robust enough for these comparisons not to be biased by fluctuations in ambient air properties, and more generally for establishing an exergy function that is reliable for process optimization. The present article aims at these goals and is organized as follows. First, the two ways for introducing exergy are reviewed. Then two simple examples dealing with equilibration with ambient air, and conversion of heat into mechanical work are studied (two important notions for the exergy concept). Possible paradoxes are highlighted. In the third part, theoretical derivations are developed for these two situations as well as for cyclic operation. Both possible references, fluctuating and fixed, are explored. The two resulting expressions of exergy balances are analyzed in the light of basic rules of second law analyses; conclusions are drawn. Finally, the present approach is related to some practical applications.

2. Energy, entropy and exergy

Consider a unit mass of some material, characterized by its specific total energy e_{tot} (total energy=kinetic + potential + internal energy) and its specific entropy s. This material is surrounded by ambient air, assumed to have constant characteristics especially constant temperature T_a. When that material is in thermodynamic equilibrium with ambient air in terms of pressure, temperature and composition, its characteristics e_{tot} and s take the index 0. If the only heat exchanged is between that material and ambient air (the material receives q_a), then the maximal amount of work, w_{max}, that can be produced while that material reversibly equilibrates with ambient air is given by: $w_{max} = e_{tot} - e_{tot0} + q_a$, with: $s - s_0 + q_a / T_a = 0$. One finally obtains:

$$w_{max} = e_{tot} - e_{tot0} - T_a(s - s_0)\,. \qquad (1)$$

Now, consider the energetic characteristics of that material: velocity (for kinetic energy), vertical position (for potential energy), internal energy and entropy. It is well known that each of them is defined only up to an additive constant, and that this constant is arbitrary. Usually these constants are chosen so that any system in thermodynamic equilibrium with ambient air has zero total energy and zero entropy. On the other hand, since the right-hand-side (RHS) of Eq. (1) is a linear combination of state functions, it also is a state function, called exergy and denoted b. Like any thermodynamic function, exergy can be defined differentially:

$$\mathrm{d}b = \mathrm{d}e_{tot} - T_a \mathrm{d}s \qquad (2)$$

For the sake of simplicity, temperature changes are mainly considered in the following. More general cases and conclusions are mentioned when relevant, but not in detail. This will however be sufficient for our demonstration while avoiding cumbersome derivations. When only temperature changes are involved (*e.g.*, no pressure changes), total energy appearing in the expressions above can be replaced by internal energy or by enthalpy h. If in addition the specific heat c_p is taken as a constant, one has:

$$h = c_p(T - T_0)\,;\; s = c_p \mathrm{Ln}(T / T_0) \qquad (3)$$

where T_0 is the reference temperature. As mentioned above the choice of T_0 is arbitrary it can be $T_0 = T_a$. This leads to the following expression of exergy:

$$b = c_p[(T - T_a) - T_a \mathrm{Ln}(T / T_a)] \qquad (4)$$

Now what happens when ambient temperature fluctuates?

3. Two examples

3.1. Matter equilibrating with ambient air

One kilogram of liquid water, initially at 100°C (373.15K), is cooled down to ambient temperature T_a. In the first step two values of T_a, 40 and 20°C (313.15 and 293.15K), are considered *independently*, *i.*e. assuming that ambient temperature is constant during the cooling process. As final state is equilibrium with ambient air ($h_f = b_f = 0$), the initial values of enthalpy and exergy obviously are respectively the amount of heat released by water, and the amount of work potentially produced by Carnot cycles operated between that kilogram of water and ambient air (the *maximal achievable work*). In terms of changes from case 1 to case 2, Table 1 shows that water releases 33% more heat, while the maximal achievable work (the initial exergy) increases by 81%. Indeed, in case 2 the virtual Carnot cycles are operated with a cold source at lower temperature, see Figure 1. Their efficiency, η_C, increases when T_a is lowered ($\eta_C = 1 - T_a / T_w$). Both effects, more heat to process and higher efficiency, induce that large increase in initial exergy. The second step (case 3) consists of assuming that ambient temperature decreases steadily from 40 to 20°C while that kilogram of water cools down from 100°C to 20°C (final temperature for both water and ambient air). If Eq. (4) were blindly applied, *i.e.* if any occurrence of T_a in Eq. (4) were time-dependent, then the exergy of water would be 21.4 kJ initially, and zero at the end of the process. What about the work achievable by Carnot cycles? Note that the question can be answered only once the time dependences of water temperature $T_w(t)$ and ambient temperature $T_a(t)$ are related to each other. If both temperatures are linearly correlated, *i.e.* if the relation: $\frac{T_w(t) - T_{w,i}}{T_f - T_{w,i}} = \frac{T_a(t) - T_{a,i}}{T_f - T_{a,i}}$ is always fulfilled, then one obtains, after some algebra, an analytical expression for the maximal achievable work:

$$w_{max} = c_p(T_{w,i} - T_{a,i})\left(1 - \frac{T_f}{T_{w,i} - T_f}\mathrm{Ln}\frac{T_{w,i}}{T_f}\right) \qquad (5)$$

In our case, the numerical value is 28.5 kJ; it differs from the initial exergy of water for both cases considered in Table 1. Moreover, when compared to Eq. (4), this analytical expression of w_{max} cannot be correlated to any exergy content. Lastly, another correlation between $T_a(t)$ and $T_w(t)$ would lead to another expression of w_{max}.

As a summary of this first simple example, a function that looks like exergy and includes fluctuations of ambient temperature can easily be defined, see Eq. (4); however, changes in this function cannot be correlated to maximal achievable work. The former only depend on the initial and final conditions while the latter depends on how the system and ambient temperatures are correlated **during** the considered transformation, *i.e.* is path-dependent. This shows that the two notions fundamentally differ.

Table 1. Initial Enthalpy and Exergy [in kJ] of one Kilogram Liquid Water at 100°C, for two Values of T_a.

Case	T_a	h_i	b_i
1	40°C	251	21.4
2	20°C	335	38.8

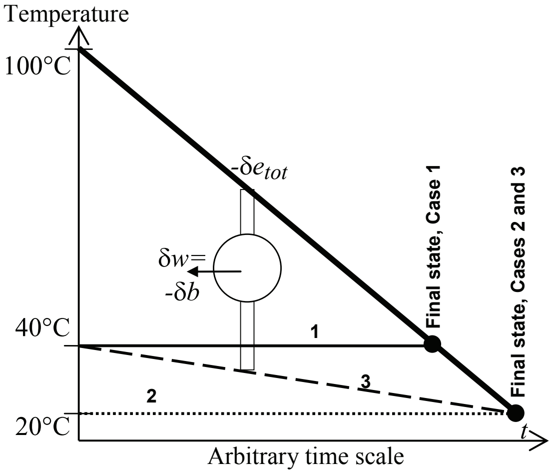

Figure 1. Schematic Representation of Reversible Cycles Operated between Matter being Cooled (bold line) and External Air either at T_a=40°C (case 1, solid line), or at T_a=20°C (case 2, dotted line), or Decreasing from 40 to 20°C (case 3, dashed line).

3.2. Heat delivered at given temperature

A given and small amount of heat, say one Joule, is delivered at given temperature, say 126.85°C, in an environment where ambient temperature fluctuates between 20°C and 40°C, for instance periodically like frequently met in nature. The amounts of heat q and entropy s are perfectly known (resp. 1 J, and 2.5 mJ.K^{-1}), but not of exergy because this one seems to depend on the value of ambient temperature at the moment when heat is delivered. According to $b = q - T_a(t).s$, exergy would lie between 0.217 and 0.267 J.

However, keeping in mind the notion of **maximal** achievable work leads to another answer. Indeed, it is perfectly allowed to think of associating the Carnot cycle to an ideal heat storage, *i.e.* infinitely large and equipped with infinite heat transfer areas. The function of that storage consists of, first receiving heat from the Carnot cycle exactly whenever required, and second releasing that heat toward ambient air exactly at the moment when the ambient temperature is the most favorable for the process, its minimum in the present case. No process can produce more work than this association. The maximal achievable work is now unambiguously defined by $q - T_{a,opt}.s$, which indeed is the upper limit of the range mentioned above.

As a summary of this second example, a function exergy which is the maximal achievable work can be defined also when ambient temperature fluctuates. It refers to the concept of ideal heat storage (infinitely large and with infinite heat transfer areas) implemented between the reversible process and ambient air. Involving heat storage into the notion of ideal process reduces the fluctuations of ambient temperature to only one value, the one most favorable to the process.

The same approach can be applied to other characteristics of ambient air, pressure and composition, leading to the notion of the *most favorable characteristics of ambient air*.

4. Theoretical approach

In order to analyze the consequences of fluctuating characteristics of ambient air, the present approach reconsiders the fundaments of any occurrence of T_a in Eq. (4). Even if temperature changes are the main focus here, it can easily be seen that neither the principle nor the conclusions are affected by kinetic or potential energy. Moreover, the approach can easily be generalized to other fluctuations (pressure, composition).

4.1. About zero exergy for ambient air

The RHS of Eq. (4) displays three occurrences of ambient temperature, but with only two origins. Two occurrences, $(T - T_a)$ and $\mathrm{Ln}(T / T_a)$, stem from the additive constants used for defining enthalpy and entropy, *i.e.* the role played by the constant temperature T_0 in Eqs. (3). This role consists of fixing the arbitrary additive constants h_0 and s_0, which are the values of enthalpy and entropy for a given reference state (temperature, pressure, compositions, electrical potential). Considering that h_0, s_0, and therefore also T_0 are **constant**, Eq. (4) should be rewritten as:

$$b = c_p[(T - T_0) - T_a \mathrm{Ln}(T / T_0)] \tag{6}$$

This is what Torchia-Nuñez et al. (2008) did "*in order to calculate entropy variations and not absolute entropy*". More generally, Eq. (6) is a simplified form of Eq. (1) where total energy also is defined up to an additive constant corresponding to the reference state, e_{tot0}. The reference state used for defining total energy and entropy is always arbitrary. Why should it then stick to ambient temperature when defining exergy? Is this necessary?

Let us open here a parenthesis and return to the case of ambient air with constant physico-chemical characteristics, like in textbooks. It is then very convenient to chose these characteristics as reference, *i.e.* $T_0 = T_a$, $P_0 = P_a$, etc. This is the so-called *dead state*. That choice makes many formulae much simpler. For instance, in the example given in Section 3.1, exergy at the final state (equilibrium with ambient air) is always zero and the maximal achievable work equates to the initial value of exergy. What would happen with another reference? The maximal achievable work would then be equal to the change between initial and final values; the last column of Table 1 would be referred as

$(b_i - b_f)$ instead of b_i only, but the numerical values would be exactly the same. The only change introduced by choosing a reference state different from ambient air is that exergy analyses must consider exergy *variations* instead of *absolute values* of exergy, just as is done with all other thermodynamic quantities (enthalpy, free energy, Gibbs energy, entropy, etc.). Consequently, the reference state **may** differ from ambient, and exergy does not necessarily cancel out for ambient air. This feature does not prevent exergy analyses to correctly evaluate exergy losses.

Even when ambient air is assumed not to vary, the reference state may differ from it, as long as the reference remains constant. The latter condition still applies to second law analyses in real climate conditions: any reference is constant. As ambient air surely fluctuates, both are forcedly different. When the process involves other quantities than temperature, *e.g.* pressure or compositions, their reference values must also be taken as constant.

4.2. Exergy is a linear combination of total energy and entropy

The third occurrence of T_a in Eq. (4) stems from the combination of total energy e_{tot} (which is conserved) and entropy s (which is not conserved and whose source term – entropy production- has a prescribed sign). That combination yields exergy in Eqs. (1) and (2). When ambient temperature fluctuates, must entropy be multiplied by the actual (fluctuating) ambient temperature (non-linear combination) or by a constant reference temperature (linear combination)? Most authors take the first option (Szargut et al., 1988; Sakulpipatsin et al., 2008; Torchia-Nuñez et al., 2008). Let us denote that non-linear combination as b_{nl}:

$$b_{nl} = e_{tot} - e_{tot0} - T_a(t).(s - s_0) \tag{7}$$

Differentiation yields:

$$\mathrm{d}b_{nl} = \mathrm{d}e_{tot} - T_a(t).\mathrm{d}s - \mathrm{d}T_a(t).(s - s_0) \tag{8}$$

As shown in Section 2 [Eq. (2)], the elementary amount of maximal work achievable by a reversible process operated between a system undergoing the changes (de_{tot}, ds) and ambient air at $T_a(t)$ is $\delta w_{max} = \mathrm{d}e_{tot} - T_a(\mathrm{t}).\mathrm{d}s$. This is not an exact differential, its integral over a time interval $[t_i, t_f]$, $w_{max} = \int_{t_i}^{t_f} \mathrm{d}e_{tot} - T_a(\mathrm{t}).\mathrm{d}s$, is path-dependent. Oppositely, the function b_{nl} can be specified at any moment and its variation during the time interval $[t_i, t_f]$ only depends on the initial and final values: $\Delta b_{nl} = b_{nl}(t_f) - b_{nl}(t_i)$. Even when the notion of state function is extended to b_{nl} (b_{nl} depends on both states, that of the system and that of ambient temperature) this function fundamentally differs from maximal achievable work, the latter being path-dependent and the former not. It can be seen from Eq. (8) that the difference $w_{max} - \Delta b_{nl}$ is $\int_{t_i}^{t_f} (s - s_0).\mathrm{d}T_a$, *i.e.* the integral of the product of entropy (s-s_0) by the change rate of ambient temperature dT_a, a product written as $c_p.\mathrm{Ln}(T / T_{ref}).\mathrm{d}T_a$ by Torchia-Nuñez et al. (2008) in their equation 20. That integral, which takes a form unknown in thermodynamics, depends on the respective evolutions of the system's entropy s and of ambient temperature T_a along the time interval under consideration. Like w_{max}, it is path-dependent. Lastly, its sign cannot be known *a priori*, so that it cannot be interpreted as irreversibility. It thus turns out that the difference between maximal achievable work and the function b_{nl} is irreducible. This fundamental difference explains the discrepancy observed in Section 3.1 case 3 and demonstrates that that this discrepancy is not an accident but is intrinsic to the non-linear construction of function b_{nl} and to the underlying definition of maximal achievable work.

Let us open here a second parenthesis. If, like in Section 3.1 and oppositely to the conclusions of Section 4.1, also e_{tot0} and s_0 were time-dependent following ambient temperature, then straightforward algebra shows that the integral discussed above would write:

$$\int_{t_i}^{t_f} \left[s - s_0(t) + \left(\frac{\partial e_{tot0}}{\partial T} \right)_{T=T_a} - T_a.\left(\frac{\partial s_0}{\partial T} \right)_{T=T_a} \right].\mathrm{d}T_a \tag{9}$$

Obviously, the conclusions of the paragraph above apply to this integral as well.

Let us now follow the second option: exergy is a linear combination of total energy and entropy, where the latter is multiplied by a constant temperature T_{ref}. This yields the function b_l:

$$b_l = e_{tot} - e_{tot0} - T_{ref}.(s - s_0) \tag{10}$$

T_{ref} surely differs from ambient temperature: one is constant, the other fluctuates. Differentiation yields $\mathrm{d}b_l = \mathrm{d}e_{tot} - T_{ref}\mathrm{d}s$. First, d$b_l$ depends only on system changes; b_l really is a function of state. Second, db_l is exactly the maximal achievable elementary work δw_{max} as given by Eq. (2), except that here the reversible cycles are operated with a heat source at T_{ref} instead of $T_a(t)$. Integration over any period maintains the identity between Δb_l and the so-defined w_{max}.

As a conclusion of this section, combining energy and entropy with the help of actual (fluctuating) ambient temperature yields a function which first is not rigorously a state function, second surely cannot be interpreted as a maximal achievable work, and third introduces a quantity unknown in thermodynamics. On the other hand, combining energy and entropy with the help of a constant temperature T_{ref} unambiguously yields a state function which is the maximal work achievable by reversible cycles using a heat source/sink at T_{ref}. If T_{ref} is *a priori* arbitrary, it will be shown in the next section that one specific value of ambient temperature is the most meaningful for exergy analyses. For the sake of convenience in the following T_{ref} is equated to the temperature T_0 of Section 3.1.

4.3. Exergy analysis of a generic process

In order to make a sensible choice for T_0, an exergy analysis of a general process is now developed. For the sake of clarity, the present approach is restricted to simple processes that receive power from one source, produce one utility, and exchange heat with ambient air. The power source and utility are both described by two fluxes, energy e_x and entropy s_x, where the index x is p (power) or u (utility). The ratio $r_x = s_x / e_x$ is usually constant. For instance, for work: $r_x = 0$; for heat exchange at T_x: $r_x = T_x^{-1}$; and so forth. Fluxes are positive when supplied to the process, negative otherwise. We consider fluctuating ambient temperature. As a consequence of these fluctuations, at least one component of the machine (*e.g.* the condenser of an air-conditioner, or the evaporator of a heat-pump) cannot be at steady-state. This induces changes in the total energy and entropy contents of the whole machine (*E* and *S*) and *E* and *S* fluctuate. With all those elements, the instantaneous energy and entropy balances generically write:

$$e_p + q_a + e_u = \dot{E} \tag{11}$$

$$s_p + \frac{q_a}{T_a} + s_u + \dot{P}_S = \dot{S} \tag{12}$$

Introducing the ratios r_x into these equations and integrating them on time yields:

$$E_p + \int q_a \mathrm{d}t + E_u = \int \dot{E} \mathrm{d}t \tag{13}$$

$$r_p E_p + \int \frac{q_a}{T_a} \mathrm{d}t + r_u E_u + \int \dot{P}_S \mathrm{d}t = \int \dot{S} \mathrm{d}t \tag{14}$$

At this point, it must be noticed that ambient temperature on Earth is fundamentally ruled by two periodicities: first the daily period, which is the most important, and second the yearly one. It results that if the integration period is sufficient long (typically two or three of the characteristic periods corresponding to the process under study), the RHS of Eqs. (13) and (14) become negligible compared to the different terms on the left hand sides (LHS). In the case of exact periodicity both RHS vanish; they may thus be neglected without any loss of generality. Two ways of combining energy and entropy into exergy are now followed, in order to see which approach is the most reliable in terms of process optimization, the final purpose of any second law analysis.

4.3.1. Non-linear combination

Entropy is multiplied by the instantaneous ambient temperature $T_a(t)$. The combined equation [(11)-$T_a(t)$·(12)] is rewritten as:

$$(1 - T_a r_p) e_p = (T_a r_u - 1) e_u + T_a \dot{P}_S + (\dot{E} - T_a \dot{S}) \tag{15}$$

where e_p, e_u, $\dot{P}_S$, $\dot{E}$, $\dot{S}$, and T_a are time-dependent. The term on the left hand side looks like a rate of exergy supplied to the process. The RHS consists of three terms:

- The first one is related to the process utility; it looks like a rate of produced exergy.
- The second one is the product of the rate of entropy production and the ambient temperature $T_a(t)$; it looks like an exergy loss.
- The third one looks like the change rate of the exergy content of the machine itself.

Note that the utility e_u, and $(T_a r_u - 1)e_u$ are prescribed functions of time (*e.g.* the cooling load of an air-conditioner installed in a given building submitted to a given climate), they do not depend on the design of the machine. Optimization consists of minimizing the energy supplied over a long period of time for a prescribed utility. Let us accept that minimizing the integral E_p is equivalent to minimizing the integral of $(1 - T_a r_p) e_p$. Introducing the two above-mentioned integrals as F_u and F_p, integration of Eq. (15) yields:

$$F_p = F_u + \int T_a \dot{P}_S \mathrm{d}t - \int T_a \dot{S} \mathrm{d}t \tag{16}$$

According to Eq. (16), the process would be optimized when the quantity $\int T_a \dot{P}_S \mathrm{d}t - \int T_a \dot{S} \mathrm{d}t$ is minimized. These two integrals are now analyzed. In the first one the rate of entropy production $\dot{P}_S$ is multiplied by ambient temperature T_a. This means that entropy productions occurring when ambient temperature is high are more weighted than those occurring when ambient temperature is low. Such a weighting function contradicts the basis of entropy analysis where any irreversibility has the same significance regardless of the moment when it occurs.

The second integral involves the product of ambient temperature T_a by the change rate of the entropy content in the machine $\dot{S}$. Even in periodic operation $-\int T_a \dot{S} \mathrm{d}t$ does not cancel out ($\int \dot{S} \mathrm{d}t$ does). Actually that integral depends on the phase difference between the entropy content in the machine and ambient temperature, a notion which is unknown in the field of process optimization. It then becomes a very complex question to see how the design of the machine influences that phase difference in order to optimize the process. What about its sign? $-\int T_a \dot{S} \mathrm{d}t$ should rather be negative. Indeed, if one thinks of what happens in the exchanger where heat is transferred between the machine and ambient air, then $\dot{S}$ is very likely to be positive when T_a is high, negative when T_a is low. Beyond this surmise, its sign is however unknown *a priori*. Lastly, there is no relation between $-\int T_a \dot{S} \mathrm{d}t$ and irreversibility, and this integral has no reason to cancel out for reversible processes when $\dot{P}_S$ does. It can be seen from this last remark that the above-defined function *F* is not even conserved by reversible processes.

4.3.2. Linear combination

The second approach uses the linear combination [(11)-T_0·(12)]. This yields:

$$(1 - T_0 r_p) e_p = (T_0 r_u - 1) e_u + (\frac{T_0}{T_a} - 1) q_a + T_0 \dot{P}_S + (\dot{E} - T_0 \dot{S}) \tag{17}$$

Time integration with periodic operation yields:

$$(1 - T_0 r_p) E_p = (T_0 r_u - 1) E_u + T_0 \int \dot{P}_S \mathrm{d}t + \int (\frac{T_0}{T_a} - 1) q_a \mathrm{d}t \tag{18}$$

First note that multiplying Eq. (12) by a constant temperature immediately has two positive consequences: the entropy content of the machine is no longer involved in the second-law balance after integration; and, all the sources of irreversibility (entropy production) are exactly equivalent. Moreover, the LHS can exactly be interpreted as an exergy supply (*i.e.* the maximal work that could be achieved by reversible processes out of the energy supply E_p), provided the reversible processes are operated with a source at reference temperature T_0, see Sections 3.2 and 4.2. The same applies to the first term on the RHS. Eq. (18) thus can be written:

$$B_p = B_u + T_0 \int \dot{P}_S \mathrm{d}t + \int (\frac{T_0}{T_a} - 1) q_a \mathrm{d}t \,, \tag{19}$$

where the function B can be called *exergy*.

The RHS of the second-law balance (19) involves the term $\int (\frac{T_0}{T_a} - 1) q_a \mathrm{d}t$ that does not occur when ambient temperature is constant. Indeed, assuming constant ambient temperature permits to state $T_0 = T_a$, and make that term cancel out. When ambient temperature fluctuates, can that term be interpreted as a loss of exergy, as an irreversibility?

First, considering that ambient temperature fluctuates with limited amplitude around an average value, it is rather easy to fix the sign of the quantity $b_a = (T_0 / T_a - 1) q_a$. If the process of interest rejects heat to ambient ($q_a<0$; *i.e.* for work engines, air-conditioners, refrigerators, etc.), choosing T_0 so that $T_0 \le \mathrm{Min}(T_a(t))$ is sufficient for b_a to always be positive. If the process of interest receives heat from ambient ($q_a>0$; *i.e.* for heat-pumps), choosing T_0 so that $T_0 \ge \mathrm{Max}(T_a(t))$ is also sufficient for b_a to always be positive. It thus can be stated that both b_a and its time integral B_a are always positive. Moreover, $b_a = (1 - T_0 / T_a)(-q_a)$ can directly be interpreted as the work produced by a reversible cycle operated between two sources at T_0 and T_a and receiving $-q_a$ from the latter source [If $T_a>T_0$ and $q_a<0$, the reversible cycle receives ($-q_a$) at T_a and rejects ($-q_a - b_a$) at T_0; if $T_0>T_a$ and $q_a>0$, the reversible cycle receives ($q_a + b_a$) at T_0 and rejects q_a at T_a]. This development shows that B_a can be interpreted as a flux of exergy. This flux must be called *the exergy received by ambient air*. Does this flux of exergy necessarily flow through the process, or could it be avoided? In the latter case, it would then be uselessly lost, destroyed, and thus could correspond to an irreversibility.

At this point, two notions already mentioned in Section 3.2 are invoked: 1) exergy is the *maximal* achievable work; and, 2) a heat storage can be installed between the process and ambient air. The first point helps defining unambiguously T_0. For an exergy analysis not to introduce a heat source that would not exist in the real process, T_0 must belong to the fluctuation domain of ambient temperature. Then, for exergy to be the maximal achievable work, T_0 must take the value of ambient temperature which is the most favorable to the process, *i.e.* $T_0 = \mathrm{Min}(T_a(t))$ in cases where $q_a<0$; or $T_0 = \mathrm{Max}(T_a(t))$ in cases where $q_a>0$. If one now thinks of heat storage between the process and ambient air, there are two limit cases: no storage and ideal heat storage. Ideal heat storage has been described in Section 3.2, it is infinitely large, equipped with infinite heat transfer areas, and maintained at T_0. Compared to the case without heat storage, a heat storage, even of finite size, permits reducing the amount of heat rejected toward ambient air during the moments when T_a is high and increasing that amount of heat while T_a is low. The design of that heat storage directly affects the integral $B_a = \int (\frac{T_0}{T_a} - 1) q_a \mathrm{d}t$. At the ideal limit, heat is exchanged with ambient air only when $T_a = T_0$, and B_a vanishes.

In these conditions, the most efficient process that can be imagined associates a reversible machine ($\dot{P}_S = 0$) AND an ideal heat storage ($B_a=0$), so that Eq. (19) becomes $B_p = B_u$. In other words, an ideal process can be imagined that exactly conserves this function exergy. Referring to that ideal process, the quantity B_a (which is strictly positive for any real process) can indeed be interpreted as an exergy loss, which exactly adds to the other exergy losses. That exergy loss B_a is specific to processes surrounded by a fluctuating environment. It does not result from irreversible processes occurring inside the heat-storage (these are accounted for in $T_0 \dot{P}_S$), but from absence or finiteness of heat-storage between process and ambient air. Indeed, no real heat-storage can store heat without any increase of its temperature nor release the stored heat toward ambient air in an infinitely short period and without any temperature difference. This remark shows how this irreversibility is related to the design of the whole process and can be included into an optimization procedure aiming at minimizing exergy losses (including B_a). Lastly, B_a is maximal when there is no heat-storage.

4.3.3. *Conclusions from the analysis*

Balances on periodic operation show that:

- Defining exergy by the non-linear combination [(11)-$T_a(t)$·(12)] yields a function that is not conserved in reversible processes. The residue, the rightmost integral in Eq. (16), involves the phase difference between ambient temperature and entropy content of the machine and thus can be positive as well as negative. As no prescribed sign can be attributed to that residue, it cannot be interpreted as a loss of exergy. Moreover, adopting that non-linear combination induces that entropy productions are weighted according to the value of ambient temperature at the moment when they occur, in full contradiction with the principle that all entropy productions are equivalent.
- Defining exergy by the linear combination [(11)-T_0·(12)] yields a function that exactly equates a maximal achievable work (the fundamental meaning of *exergy*) and that is exactly conserved for one ideal process. This ideal process associates reversibility with ideal heat-storage. With respect to this ideal heat-storage, 1) T_0 occurs as the value of ambient temperature which is the most favorable for the process, 2) a specific exergy loss emerges from the analysis that is due to heat exchanges with fluctuating ambient air. This second definition of exergy opens the question of implementing a heat-storage between the process and ambient air and gives tools for studying

such heat-storages. Therefore it can perfectly be applied to practical cases such as those presented in Section 5.

Could this linear combination be reduced to the standard exergy as defined by Szargut et al. (1988)? Not exactly. Standard conditions result from conventions (*e.g.* 0°C and 100kPa for IUPAC, but 20°C and 101.325kPa for NIST). The reference state introduced herein is the *most favorable ambient condition*. This reference state is then strongly related, first to the climate where the process under study is operated -or simulated-, and second to the process itself (for instance, the reference will not be the same for air-conditioning and heat-pumping, see above). Note that this strong relation to the pair process+climate (which is absent from the notion of standard exergy) is often claimed as a fundamental feature of the concept of exergy.

4.3.4. Generalization

The analysis developed above can easily be extended to processes exchanging pressure work and mass with ambient air, the pressure and/or composition of which is fluctuating. Ideal storages implemented between the process under study and ambient air can also be imagined. Then, similar to the most favorable ambient temperature, most favorable values can be defined for, respectively, ambient pressure and ambient compositions. The reference state is then defined by the set of those most favorable values (temperature, pressure, composition), even if they do not occur at the same moments. Indeed, the different ideal storages may be operated independently, and do not have to be charged or discharged simultaneously.

5. Practical applications

Here are four practical examples where a heat-storage is implemented between ambient air and process, two in the field of solar energy, and two in the field of thermal sciences applied to buildings.

5.1. Solid-sorption solar-powered ice-maker

Solar-powered ice-makers operated with the adsorption pair activated carbon + methanol were tested by Boubakri et al. in Morocco during the late eighties-early nineties (1992). The concept of those ice-makers is basically described in Figure 2. It is worth noticing that the condenser is cooled by ambient air at daytime, while the adsorber is cooled by ambient air at nighttime. More exactly, two moments are especially important: 1) mid-afternoon, say around 4 p.m., when condensation takes end; and, 2) just before sunrise, say around 7 a.m., when adsorption takes end. Ambient temperature is very often warmer around 4 p.m. than around 7 a.m. If ambient air were as fresh around 4 p.m. as around 7 a.m., then the adsorptive refrigeration cycle would be more efficient. That difference in ambient temperature was already pointed out as a source of irreversibility (Pons, 2004). Independently, Boubakri had proposed the concept of storing some fresh water in a well-insulated box every morning and use that fresh water for supplying the condenser with extra-cooling at 4 p.m. This would complement the desorption-condensation process and increase the amount of processed refrigerant without any extra solar input (Boubakri, 2003). Water is then refreshed during the next night. This is exactly the concept of heat-storage as above-described.

5.2. Solar-powered air-conditioner

ZAE-Bayern is a well-known research center in the field of liquid sorption chillers. The principle of liquid sorption cycles is rather similar to solid sorption, except that operation is continuous: the desorber/generator receives solar heat (same role as A-Day in Figure 2) while the absorber, a separate component, releases heat (same role as A-Night). Readers are referred to the textbook of Alefeld and Radermacher (1994) for more details. ZAE-Bayern recently tested a solar-powered lithium bromide + water unit designed for conditioning air in offices and laboratories. The heat rejected by the condenser and absorber is released toward ambient air via a dry air cooler **plus** a latent heat storage containing phase change material installed in series (Mehling et al., 2008). During diurnal operation, this latent heat storage reduces the cooling temperature by 4°C, which improves the cycle performance; the stored heat is rejected to ambient air during the night. This is again the same use of heat-storage.

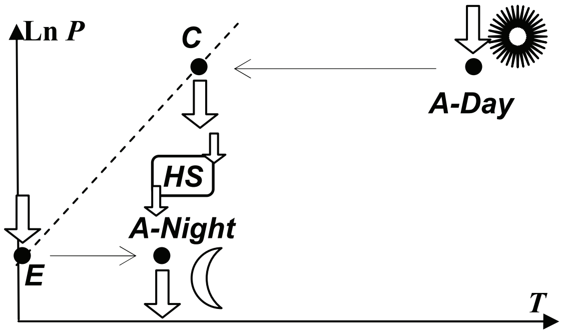

Figure 2. Solid-Sorption Cycle of Solar-Powered Ice-Maker. During Daytime, the Adsorber (A-Day) receives Solar Heat and desorbs Refrigerant Vapor while the Condenser (C) is cooled by Ambient Air. At Nighttime, the Adsorber (A-Night) is cooled by Ambient Air and adsorbs Refrigerant Vapor while the Evaporator (E) receives Heat from Freezing Water. A Heat Storage (HS) can receive Part of the Heat released by the Condenser, and release it at Night to Ambient Air.

5.3. Night ventilation

Nowadays an increasing interest focuses on night ventilation as a means for reducing the energy consumed by air-conditioners. Night ventilation can be applied during periods when outdoor temperature lies under comfort conditions at nighttime and above at daytime. It consists of ventilating, if not over-ventilating, a building at nighttime in order to reduce the temperature of its own thermal mass, so that thermal inertia delays the temperature rise inside the building on the next day, and consequently delays the moment when air-conditioners need to be switched on. Night ventilation consists of controlling the heat exchanges with outdoor air according to the ambient temperature. This is again the same concept, but here the role of heat storage day-night is played by the building itself. Maximal efficiency is obtained when there is no more need for air-conditioning at daytime, *i.e.* when the entire diurnal cooling load is released at night. For approaching this ideal configuration, the balance between thermal mass and ventilation intensity becomes a question of interest (Yang and Li, 2008).

5.4. Air-to-earth heat exchange

While the three previous examples are concerned with the day-night alternation, the fourth one is concerned with the summer-winter alternation in building engineering. It is well known that the ground temperature fluctuates much less than ambient air temperature, and thus can play the role of long-term heat-storage. Air-to-earth heat exchangers use the ground as a heat capacity for pre-conditioning fresh air before the latter is to be processed in the air handling unit: pre-cooling in summertime, and pre-heating in wintertime. This technique, which is currently tested in many experiments and may reduce energy consumption in buildings, uses again the same heat-storage concept. However, in this application the whole heat-storage cycle is very long: one year. Nevertheless, for the function exergy to be unambiguously defined, only one value of reference temperature T_0 must be used.

5.5. Comments

It is far beyond the scope of the present study to study whether such heat storages are worthwhile or not. Some features can however be noticed. Most of the time, the heat storage is used not for replacing but rather for complementing direct heat transfer between the process and ambient air. In all cases, the heat-storage is used for postponing heat transfer toward moments when ambient temperature is relatively favorable, *i.e.* for reducing the quantity $\int (\frac{T_0}{T_a} - 1) q_a \mathrm{d}t$. Moreover, it can also be observed that the presence of heat storage enhances the efficiency of the process itself, either via non-linearity (like in sorption units) or via thresholds (like for comfort conditions), so that the internal irreversibility $T_0 \int \dot{P}_S \mathrm{d}t$ is also reduced. Eq. (19) gives the framework where both effects can be compared and optimized.

6. Conclusion

The present work studies how exergy must be defined in cases when ambient conditions fluctuate. It results from this study, first, that the reference state (where exergy cancels out) must be fixed and constant; second, that exergy must be a linear combination of total energy and entropy, *i.e.* entropy multiplied by a constant temperature. Moreover, the full meaning of exergy is recovered when the reference consists of the ambient characteristics (temperature, and if relevant pressure and composition) which are the most favorable to the process under investigation. Indeed, only the so-constructed exergy function is conserved in reversible processes; only this function can be interpreted as maximal achievable work; only this function permits processes to be optimized via minimization of exergy losses, especially those due to fluctuations of ambient air. It must also be mentioned that several cases of heat-storage implemented between a process or a building, and ambient air are currently under study in order to reduce energy consumption. The exergy function constructed with that constant reference (and not with dynamic reference) offers a comprehensive and robust second-law framework for analyzing processes involving such heat-storages.

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Nomenclature

b	Specific exergy [$\mathrm{J \cdot kg^{-1}}$] or flux of exergy [W]
B	Exergy [J]
c_p	Specific heat [$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$]
e_{tot}	Specific or flux of total energy [$\mathrm{J \cdot kg^{-1}}$, W]
E	Total energy in the machine [J]
f, F	*Ad hoc* functions
h	Specific enthalpy [$\mathrm{J \cdot kg^{-1}}$]
P_S	Entropy production [$\mathrm{J \cdot K^{-1}}$]
r	Ratio of entropy by energy [$\mathrm{K^{-1}}$]
q	Heat flux [W]
T	Temperature [K]
t	Time [s]
s	Specific or flux of entropy [$\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$, $\mathrm{W \cdot K^{-1}}$]
S	Total entropy in the machine [$\mathrm{J \cdot K^{-1}}$]
w	Mechanical work [W]

Dotted quantities of E, P_S, and S are time derivatives.

Indexes

0	Reference
a	Ambient air
f	Final
i	Initial
l	Linear
max	Maximal
nl	Non-linear
p	Power
ref	Reference
u	Utility
w	Water

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