

An extended formulation of physical exergy

Pierfrancesco Palazzo

TechnipRome, Italy

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ABSTRACT

The mechanical aspect of entropy-exergy relationship, together with the thermal aspect usually considered, leads to an extended formulation of physical exergy based on both maximum useful work and maximum useful heat that are the outcome of available energy of a thermodynamic system.

This approach suggests that a mechanical entropy can be studied, in addition to the already used thermal entropy, with respect to work interaction due to volume variation. The mechanical entropy is related to energy transfer by means of work and it is complementary to the thermal entropy that accounts energy transfer by means of heat. Furthermore, the paper proposes a definition of exergy based on Carnot cycle that is reconsidered in the case the inverse cycle is adopted and, as a consequence, the concept that work depends on pressure similarly as heat depends on temperature, is pointed out. Then, the logical sequence to get mechanical exergy expression to evaluate work withdrawn from available energy is demonstrated. On the basis of the mechanical exergy, the mechanical entropy set forth is deduced in a general form valid for any process.

Finally, the extended formulation of physical exergy is proposed, that summarizes the contribution of either heat and work interactions and related thermal exergy as well as mechanical exergy that both result as the outcome from the available energy of the system interacting with an external reference environment (reservoir). The extended formulation contains an additional term that takes into account the volume, and consequently the pressure, that allows to evaluate exergy with respect to the reservoir characterized by constant pressure other than constant temperature. The conclusion is that the extended physical exergy takes into account the equality of pressure, other than equality of temperature, as a further condition of mutual stable equilibrium state between system and reservoir.

Keywords

thermal entropy, mechanical entropy, total entropy, thermal exergy, mechanical exergy, physical exergy

1. Introduction

The first purpose of the present paper is to revisit entropy property with respect to the canonical thermodynamic processes and to propose an extended nomenclature that highlights the mechanical aspect of entropy, complementary to the thermal aspect and the definitions already existing in classical thermodynamics literature. The second purpose, on the basis of entropy structure and its extended definition as well as the thermal and mechanical aspects of entropy-exergy relationship, is to propose an extended formulation of physical exergy. This extended physical exergy

would be suitable to evaluate either the maximum net useful work and the maximum net useful heat of a system, being both the outcome of available energy, considering the role of pressure, other than temperature, in the evaluation of work and heat interactions in combination with an external reference system or reservoir in the sense defined by Gyftopoulos and Beretta [1]. The formulation already established in literature is based on mutual stable equilibrium state between system and reservoir due to temperature equality only. The novelty of the paper is that, being equality of

pressure a further condition of mutual stable equilibrium state, pressure too is considered in formulation of the extended physical exergy. The pressure is accounted in the additional term of this formulation, by means of the mechanical entropy related to volume. This is based on the relationship existing between entropy and exergy, either for heat interaction (thermal exergy based on thermal entropy) and for work interaction (mechanical exergy based on mechanical entropy). In order to simplify this analysis and to define the particular case it refers to, the following assumptions have been adopted: the system is considered as simple according to the terminology reported in literature [1]; the system consists in a perfect and single-phase homogeneous gas; the system is closed (no bulk-flow interactions); the state equation for ideal gas is applicable; there are no phase changes or chemical and nuclear reaction mechanisms inside the system; the existence of an external reference system that behaves as a reservoir is assumed [1]; the analysis is focused on stable equilibrium states; the kinetic and potential energy of the system are neglected. On the basis of these assumptions, chemical exergy will be out of the domain of present study and reference will be made to physical exergy only.

The hypothesis that thermodynamic processes are reversible will be assumed in order to demonstrate that the conclusions of this analysis can be deduced from the behaviour and the properties of the system, here assumed to be ideal as a particular case, and are complementary to those existing in literature. Anyway, these conclusions can be considered as general and remain valid also in case irreversible phenomena occur in the system. The methodological schema leading to the formulation of the extended physical exergy is represented in Fig 1.

2. Thermal and mechanical entropy

As it is reported in literature, entropy property is related to the second law and the thermal aspect of thermodynamic systems behaviour and properties. An investigation on the mechanical aspect can also be accomplished with an analysis of a thermodynamic processes considered as ideal without thermal and mechanical irreversibilities. In particular, the isothermal reversible process is here evaluated in which the internal energy of a

system with no chemical and nuclear reactions and constant amount of constituents is formulated by the classical expression of thermodynamic potential known as Euler relation:

$$U = TS - PV + \mu n \quad (1)$$

which implies that the variation of internal energy alongside a reversible isothermal process is as follows for a single-phase system without chemical reactions:

$$dU = d(TS) - d(PV) = \delta Q + \delta W = 0 \quad (2)$$

where δQ and δW both represent positive energy received into the system, by convention for reference transfer direction. Due to the relationship of internal energy to temperature only for perfect systems, that makes the variation of internal energy equal to zero and considering that temperature remains constant for the isothermal process under analysis, being the state equation valid on the isothermal process:

$$PV = \bar{R}T = \text{const} \quad (3)$$

the following result is obtained:

$$dU = T \cdot dS = 0 \Leftrightarrow dS = 0 \quad (4)$$

that is valid if and only if entropy remains constant whereas it should change due to heat interaction. This is an apparent inconsistency that can be resolved if S is intended to be the total entropy. In fact, it is here assumed that total entropy is the result of contribution of entropy due to heat interaction, related to temperature, and entropy due to work interaction, related to pressure. Another consideration addresses to the adiabatic reversible process, namely isoentropic, that is accomplished at constant thermal entropy while temperature and pressure change according to the following formula:

$$S(T, P) = C_p \ln \frac{T}{T_0} - \bar{R} \ln \frac{P}{P_0} \quad (5)$$

thus, thermal entropy variation related to heat interaction is null depending on a compensation effect due to the combination of either temperature and pressure variations.

The above considerations in the special case of isothermal reversible process suggest that both

internal energy and entropy remain constant while a heat-to-work conversion occurs isothermally due to equal quantities of heat and work interactions between the system and the reservoir. Nevertheless, the heat interaction implies a transfer of entropy, therefore a transfer of entropy under “thermal” form requires an entropy conversion into “mechanical” form in order to render the balance of (total) entropy equal to zero as required by the expression (4). Therefore, it can be deduced that this mechanical form of entropy is associated to work interaction by means of pressure and volume variation. Mechanical entropy is complementary to and does not contradict the classical expression of entropy calculated alongside an isothermal reversible process that corresponds to the thermal entropy associated to heat interaction only.

This analysis suggests that (total) entropy can be considered constituted by two components, namely “thermal entropy” that is constant in adiabatic (isoentropic) reversible process where work interaction only occurs and a “mechanical entropy” that is constant in isovolumic reversible process where heat interaction only occurs. In addition, it can also be deduced that entropy, that appears in the expression of internal energy represents the thermal component of entropy (or thermal entropy) that thus results consistent with the properties requested to comply with the above behaviour.

The relationship between entropy and exergy (see Figure 2) represents the basis for assuming and proving that thermal and mechanical components set forth for entropy can be retrieved in exergy property as well.

3. Thermal entropy and thermal exergy

The definition of exergy (or availability as also reported in literature), here considered for the scope of the present analysis, is the one based on heat and work interactions; in particular, it is here discussed the exergy formulated as the maximum net useful work obtained from the available energy on the basis of the thermodynamic efficiency of the Carnot direct cycle operating between the variable temperature T of system A and constant temperature T_R of reservoir R considered as the external reference system:

$$dEX^{THERMAL} = \delta W_{REV}^{NET} = \quad (6a)$$

$$= \delta W_{REV}^{CONVER} + \delta W_{REV}^{TRANSF} \quad (6b)$$

where δW_{REV}^{CONVER} is the net amount of work resulting as the balance of a direct cycle that converts the available heat at a temperature T into work, by means of a cyclic machinery in combination with the reservoir at temperature T_R ;

δW_{REV}^{TRANSF} is the net amount of available energy, transferred by means of a work interaction in a cyclic machinery, resulting from system volume variation (cyclic machinery is an ideal device that returns to its initial state at the end of whatsoever process it accomplish). For the sake of generality, heat and work interactions are considered occurring either successively or simultaneously and both result from generalized available energy of a simple system as defined by Gyftopoulos and Beretta [1]. Therefore, in differential terms:

$$dEX^{THERMAL} = \delta W_{REV}^{NET} = \quad (7a)$$

$$= \eta_{id}^{CARNOT-DIRECT} \cdot \delta Q^{HT} + \delta W_{REV}^{TRANSF} = \quad (7b)$$

$$= \frac{\delta W}{\delta Q_{ISOTHERMAL}^{HT}} \cdot \delta Q^{HT} - P \cdot dV + P_R \cdot dV = \quad (7c)$$

$$= \left(1 - \frac{T_R}{T}\right) \cdot \delta Q^{HT} + \left(1 - \frac{P_R}{P}\right) \cdot \delta W^{HP} \quad (7d)$$

which δQ^{HT} represents the infinitesimal heat interaction along the process at temperature T different from the temperature T_R of the reservoir; δW^{HP} is the infinitesimal work interaction at high pressure P alongside the process.

The formula (7d) corresponds to the already known classical definition of physical exergy [2,3]. This expression is used to define the exergy that is here identified by the superscript “THERMAL” according to the definition reported in literature [2-4] as pointed out above. In finite terms, and considering that $\delta W^{HP} = -PdV$:

$$EX^{THERMAL} = W_{10} = \quad (8a)$$

$$= \int_0^1 \left(1 - \frac{T_R}{T}\right) \delta Q^{HT} + \int_0^1 \left(1 - \frac{P_R}{P}\right) \delta W^{HP} = \quad (8b)$$

$$= Q_{10}^{HT} - T_R \int_0^1 \frac{\delta Q^{HT}}{T} + W_{10}^{HP} + P_R \cdot (V_1 - V_0) \quad (8c)$$

where: W_{10} is the maximum net useful work output from the generalized available energy [1] as the result of interaction between the system and the reservoir; Q_{10}^{HT} is the heat interaction from higher isothermal curve at T to lower isothermal curve at T_R (as a particular case, heat interaction can occur alongside an isovolumic process); W_{10}^{HP} is the work interaction from higher isothermal curve at T to lower isothermal curve at T_R ; the sum of Q_{10}^{HT} and W_{10}^{HP} can also be expressed as:

$$Q_{10}^{HT} + W_{10}^{HP} = U_1 - U_0 = C_V (T_1 - T_0) \quad (9)$$

that represents the equivalence with the amount of heat interaction only in the isovolumic process between two different temperatures. Thus, thermal exergy can also be associated to a sequence of isovolumic-isothermal process connecting the generic state 1 with stable equilibrium state 0 of the composite of system and reservoir. The integration function in the expression of thermal exergy (8c) represents, in infinitesimal terms, the definition of entropy as per Clausius formulation or, as here proposed, the thermal component of entropy property identified by the superscript "THERMAL", and therefore:

$$EX^{THERMAL} = W_{10} = (U_1 - U_0) - T_R \cdot (S_1^{THERMAL} - S_0^{THERMAL}) + P_R \cdot (V_1 - V_0) \quad (10)$$

as the result of combination of the system and the reservoir at constant temperature T_R and constant pressure P_R . This formulation is also consistent with the formulation presented by Gyftopoulos and Beretta [1], deduced from the definition of generalized available energy with respect to an external reference system at constant temperature

T_R and constant pressure P_R that behaves as a reservoir.

The expression of thermal exergy represents the maximum net useful work available and withdrawable from generalized available energy of a system in a thermodynamic state respect the stable equilibrium state with the reservoir. In other terms, this expression highlights the fraction of internal energy that is converted into work correlated to the temperature level with respect to an external reference environmental system considered as a thermal and mechanical reservoir or heat and work reservoir.

4. Mechanical entropy and mechanical exergy

The correlation between thermal entropy and thermal exergy clarified so far suggests to investigate the mechanical aspect of entropy-exergy relationship to attempt the evaluation of the concept of exergy related to work. In other terms, the relation between entropy and exergy above highlighted from thermal point of view suggests that, based on the existence of the mechanical component of entropy previously assumed, a formulation of a "mechanical" component of physical exergy, that depends on the pressure level of internal energy and work interaction with the reservoir, can be investigated. This assumption derives by the fact that equality of pressure between the system and the reservoir, other than temperature, is a condition for stable equilibrium state of the composite system-reservoir.

Now that we have defined exergy formulated by the direct cycle as thermal exergy which highlights the role of temperature in heat-to-work conversion, we may now search a definition of mechanical exergy that is expressed by the inverse cycle with the intent of evaluating the role of pressure in the opposite conversion, that is, in a work-to-heat conversion. Also for the mechanical aspect, the general formulation of exergy, in infinitesimal terms, derives from the relationship built around the Carnot cycle and its expression of thermodynamic efficiency.

The Carnot cycle used in the formulation of thermal exergy is defined in literature as a symmetric cycle consisting of four processes, each pair of which is of the same type (isodiabatic) as represented in Fig 3.

If the working system is a perfect gas, then the alternating politropic (isentropic) processes provide the following property to the cycle 0-1-1C-0C in Figure 3:

$$\frac{V_1}{V_0} = \frac{V_{1C}}{V_{0C}}; \frac{P_1}{P_0} = \frac{P_{1C}}{P_{0C}}; \frac{T_1}{T_0} = \frac{T_{1C}}{T_{0C}} \quad (11)$$

from which it may be inferred that since the ends of the processes are proportional, the work interaction between the system and the external environment (reservoir) is the same both along the isentropic compression from 0 to 1 and in isentropic expansion from 1C to 0C. As a result, the balance of the work interaction between the system and the reservoir along the isentropic processes alone is null, and the balance contribution over the whole cycle is due exclusively to the isothermal processes along which heat and work is exchanged simultaneously in directly proportional and equal amounts. This property enables to express the thermodynamic efficiency of the Carnot cycle of a closed non bulk-flow system both in terms of heat and work interactions, as described in the graphs in Figure 4. The efficiency can be expressed either in terms of heat only and in terms of work only due to the equality of amounts of heat and work interactions alongside the isothermal process:

$$\begin{aligned} \eta_{id}^{CARNOT-DIRECT} &= \frac{W}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{Q^{HT}} = \\ &= \frac{W^{HP} - W^{LP}}{W^{HP}} = \frac{Q^{HT} - Q^{LT}}{Q^{HT}} \end{aligned} \quad (12a)$$

As regard the inverse cycle, if the roles of used heat Q^{HT} and utilized total work W are replaced by used work W^{HP} and utilized total heat Q , the following expression applies (that does not correspond to the Coefficient of Performance reported in literature),

$$\begin{aligned} \eta_{id}^{CARNOT-INVERSE} &= \frac{Q}{W^{HP}} = \frac{Q^{HT} - Q^{LT}}{W^{HP}} = \\ &= \frac{Q^{HT} - Q^{LT}}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{W^{HP}} = \eta_{id}^{CARNOT-DIRECT} \end{aligned} \quad (12b)$$

As may be noted, since there is a linear proportionality between the two expressions, due to the identity of two of the terms, it may be inferred that the meaning of used heat Q^{HT} in the direct cycle corresponds to the meaning of used work W^{HP} in the inverse cycle as well as the meaning of the utilized total work W in the direct cycle corresponds to the meaning of the utilized total heat Q in the inverse cycle, as shown in Figure 4. The conclusion is that the efficiency of Carnot cycle, that depends on isothermal process only, does not change if inverse cycle is compared to direct cycle. In fact:

$$\eta_{id}^{CARNOT-INVERSE} = \frac{Q}{W_{ISOTHERMAL}^{HP}} = \quad (13a)$$

$$= \frac{W}{Q_{ISOTHERMAL}^{HT}} = 1 - \frac{T_0}{T} = \eta_{id}^{CARNOT-DIRECT} \quad (13b)$$

Now that we have defined exergy formulated by the direct cycle as thermal exergy which highlights the role of temperature in heat-to-work conversion, we may now define as mechanical exergy the exergy that may be expressed by the inverse cycle. In this case, the role of pressure in the opposite conversion, that is, from work into heat, is due to the pressure level of work interaction alongside the higher temperature (and higher pressure) isothermal process of inverse Carnot cycle. As a consequence, the general definition of mechanical exergy that represents, in this case, the maximum net useful heat obtained from the available energy, in infinitesimal terms may be expressed by the following relationship:

$$dEX^{MECHANICAL} = \delta Q_{REV}^{NET} = \quad (14a)$$

$$= \delta Q_{REV}^{CONVER} + \delta Q_{REV}^{TRANSF} \quad (14b)$$

where δQ_{REV}^{CONVER} is the net amount of heat resulting as the balance of an inverse cycle that converts available work at a pressure P into heat, by means of a cyclic machinery in combination with the reservoir at pressure P_R ; δQ_{REV}^{TRANSF} is the net amount of available energy, transferred by means of heat interaction in a cyclic machinery, resulting

from system thermal entropy variation (cyclic machinery is an ideal device that returns to its initial state at the end of whatsoever process it accomplishes). For the sake of generality, work and heat interactions are considered occurring either successively or simultaneously and both result from generalized available energy as defined by Gyftopoulos and Beretta [1]. Therefore, in differential terms:

$$dEX^{MECHANICAL} = \delta Q_{REV}^{NET} = \quad (15a)$$

$$= \eta_{id}^{CARNOT-INVERSE} \cdot \delta W^{HP} + \delta Q_{REV}^{TRANSF} = \quad (15b)$$

$$= \frac{\delta Q}{\delta W_{ISOTHERMAL}^{HP}} \cdot \delta W^{HP} + T dS - T_R dS = \quad (15c)$$

$$= \left(1 - \frac{T_R}{T}\right) \cdot \delta W^{HP} + \left(1 - \frac{T_R}{T}\right) \cdot \delta Q^{HT} \quad (15d)$$

in which: δW^{HP} represents the infinitesimal work interaction along the process at the pressure P different from the pressure P_R of reservoir. The role of pressure here corresponds to the role of temperature with respect to heat in thermal exergy; it is noteworthy that the second term of formula (15d) corresponds to the definition of thermal exergy.

The formulation of thermal exergy (7d) is now reversed to define the mechanical exergy, identified by the superscript "MECHANICAL" that is not referred to potential and kinetic energy; in fact, in this case potential exergy and kinetic exergy definitions have already been adopted as components of exergy [2-4]. After replacing work with heat, mechanical exergy is formulated as follows:

$$dEX^{MECHANICAL} = \delta Q_{REV}^{NET} = \delta Q_{REV}^{CONVER} = \left(1 - \frac{T_R}{T}\right) \cdot \delta W^{HP} \quad (16)$$

by integrating, the expression in finite terms is:

$$EX^{MECHANICAL} = Q_{10} = \int_0^1 \left(1 - \frac{T_R}{T}\right) \cdot \delta W^{HP} = W_{10}^{HP} - T_R \int_0^1 \frac{\delta W^{HP}}{T} \quad (17)$$

where: Q_{10} is the maximum net useful heat output from the generalized available energy [1] as the result of interaction between the system and the reservoir; W_{10}^{HP} is the work interaction from higher isothermal curve at T , and in correspondence of the point at P , to lower isothermal curve at T_R (as a particular case, work interaction can occur alongside an isentropic process); W_{10}^{HP} can also be expressed as:

$$W_{10}^{HP} = U_1 - U_0 = C_V \cdot (T_1 - T_0) \quad (18)$$

that represents the equivalence with the amount of work interaction only in the isentropic process between two different temperatures. Thus, mechanical exergy can also be associated to a sequence of isentropic-isothermal process connecting the generic state 1 with stable equilibrium state 0 of the composite of system and reservoir. If the state equation applicable to ideal gas $PV = RT$ is used with the proper substitutions, the mechanical exergy can be written as follows:

$$EX^{MECHANICAL} = Q_{10} = (U_1 - U_0) - \bar{R} T_R \int_0^1 \frac{\delta W^{HP}}{PV} \quad (19)$$

The integrand function $\frac{\delta W^{HP}}{PV}$ depending on the integration operator symbol \int_0^1 is formally

similar to the integrand function $\frac{\delta Q^{HT}}{T}$ that represents the definition of entropy property as per Clausius formulation, and in particular thermal entropy according to the definition here proposed. On the basis of this formal analogy applied to work interaction, it is now possible to define a "mechanical entropy" by means of the following expression:

$$dS^{MECHANICAL} = \frac{\delta W^{HP}}{PV} \quad (20)$$

where the factor $\frac{1}{PV}$ would represent the integrating factor of the infinitesimal work δW^{HP} and makes the integration function an exact differential function. In fact, going back to the expression of mechanical exergy (19) set forth, and considering that:

$$\delta W^{HP} = -PdV$$

it is now possible to write:

$$\begin{aligned} EX^{MECHANICAL} &= Q_{10} = \\ &= (U_1 - U_0) - \bar{R}T_R \int_0^1 \frac{\delta W^{HP}}{PV} = (U_1 - U_0) + T_R \int_0^1 \bar{R} \frac{dV}{V} = \\ &= (U_1 - U_0) + T_R \cdot (\bar{R} \ln V_1 - \bar{R} \ln V_0) \end{aligned} \quad (22)$$

that relates to the work interaction with environmental system (mechanical reservoir); therefore:

$$EX^{MECHANICAL} = (U_1 - U_0) + P_R V_R \cdot (\ln V_1 - \ln V_0) \quad (23)$$

In order to complete the proposed analogy, if reference is made to the integrating function of equation (22), the thermal entropy according to Clausius formulation is as follows:

$$dS^{THERMAL} = \frac{\delta Q^{HT}}{T} \quad (24)$$

whereas the mechanical entropy is formulated as:

$$dS^{MECHANICAL} = \frac{\bar{R} \delta W^{HP}}{PV} = \frac{\bar{R} dV}{V} \quad (25)$$

$$S^{MECHANICAL} = \bar{R} \ln V + c \quad (26)$$

Thus, being $dS^{MECHANICAL}$ an exact differential function, then $S^{MECHANICAL}$ is a state property and can be adopted as the formal definition of mechanical entropy. It depends on the state property volume and therefore it behaves as a state property as well. Furthermore, since volume is additive, it can be proved that mechanical entropy is additive as well.

As Regarding the dimensional analysis, since logarithmic function is dimensionless, then the dimension of mechanical entropy is related to \bar{R} and is Joule / Kgmol °K that is identical to thermal entropy dimension.

The formulation of mechanical exergy (23) adopts the concept of maximum heat obtainable from a system and highlights the “exergetic content of work” that depends on the pressure level of work interaction with respect to the reservoir. In fact, it can be noted that the property pressure, alongside the isothermal process, appears in the expression of the mechanical exergy above formulated by the relationship with volume. The expression is formally similar to the one related to the thermal exergy but the reference pressure P_R appears in the expression (23). The equality of pressure is a condition of mutual stable equilibrium state between system and reservoir at constant P_R in addition to the equality of temperature T_R .

The higher the range of pressures alongside the high temperature isothermal process, the higher the heat at high temperature while Carnot cycle efficiency remains constant, and therefore the higher the mechanical exergy. In other terms, the same difference between higher and lower temperature of Carnot cycle is not affected by the position of the cycle with respect to volume while mechanical exergy is, as illustrated in Fig 5. Indeed, for an isothermal reversible process,

$$\frac{P_1}{P_0} = \left(\frac{V_0}{V_1} \right) \quad \text{and} \quad V_0 = V_1 + c \quad (27)$$

where c is constant; therefore:

$$\frac{P_1}{P_0} = 1 + \frac{c}{V_1} \quad (28)$$

$$\begin{aligned} W_{ISOTHERMAL}^{HT} &= P_0 V_0 \ln \left(\frac{P_1}{P_0} \right) = P_0 V_0 \ln \left(1 + \frac{c}{V_1} \right) = \\ &= \bar{R} T_0 \ln \left(1 + \frac{c}{V_1} \right) = Q_{ISOTHERMAL}^{HT} \end{aligned} \quad (29)$$

Mechanical exergy depends on the pressure range of work interaction amount alongside the isothermal process and therefore depends on the

initial and final volumes ratio whereas volumes difference ΔV remains constant as shown in Fig 5.

The physical meaning of mechanical exergy expresses the specific heat of the inverse cycle in the sense of total heat exchanged by the system with the reservoir over the whole cycle, similarly to thermal exergy that represents the specific work of the direct cycle with the same meaning. The relation of exergy to both temperature and pressure is also due to the property of Carnot cycle where isothermal process realizes either heat-to-work (direct) conversion and work-to-heat (inverse) conversion.

5. Extended physical exergy

The definition of thermal entropy and mechanical entropy, deduced and formulated from thermal exergy and mechanical exergy respectively, is here adopted to extend the concept of physical exergy to the work interaction other than heat interaction between the system and the reservoir. By virtue of the concept of interconvertibility conceived by Gaggioli [5-7], the available energy of a system results in two outcomes: available work or maximum net useful work

- that can be evaluated as thermal exergy
- available heat or maximum net useful heat that can be evaluated as mechanical exergy

The extended physical exergy here proposed is therefore implicated with thermal exergy underpinned by the efficiency of Carnot direct cycle and the high temperature heat and with the mechanical exergy underpinned by the efficiency of Carnot inverse cycle and the high pressure work, whereas external environment is adopted as reservoir.

The internal energy formulated in differential terms:

$$dU = T \cdot dS - P \cdot dV = \delta Q + \delta W \quad (30)$$

can be now expressed as: (31)

that can be transformed, by using the state equation, in the following form:

$$dU = T \cdot (dS^{THERMAL}) - T \cdot (dS^{MECHANICAL}) =$$

$$= T \cdot (dS^{THERMAL} - dS^{MECHANICAL}) = \delta Q + \delta W \quad (32)$$

where:

$$dS^{TOTAL} = dS^{THERMAL} - dS^{MECHANICAL} \quad (33)$$

that, associated to the temperature, takes into account either heat and work interactions that contribute to the variations of internal energy.

The expression (32) can be also written as:

$$dU = T \cdot (dS^{TOTAL}) = \delta Q + \delta W \quad (34)$$

and in finite terms, considering that U is a state property that depends on two independent variables:

$$U = U(S, V) = T \cdot (\Delta S^{TOTAL}) \quad (35)$$

If internal energy balance of system and reservoir is used to express the physical exergy, it follows that:

$$EX^{PHYSICAL} = (U - U_0) - Q_R - W_R \quad (36)$$

where:

Q_R is the minimum heat interaction with the reservoir at constant temperature T_R ;

W_R is the minimum work interaction with the reservoir at constant pressure P_R ;

Thus the energy balance is:

$$EX^{PHYSICAL} = \Delta U^{SYSTEM} + \Delta U^{RESERVOIR}$$

and considering the reservoir as a thermal reservoir at constant temperature T_R and as a mechanical reservoir at constant pressure P_R , then

$$EX^{PHYSICAL} = (U - U_0) - T_R \cdot \Delta S^{TOTAL} + P_R \cdot \Delta V \quad (37)$$

and therefore it can be deduced, substituting the expressions (10) and (23), that:

$$EX^{PHYSICAL} = (U - U_0) - T_R (S^{THERMAL} - S_0^{THERMAL}) + T_R (S^{MECHANICAL} - S_0^{MECHANICAL}) + P_R (V - V_0) \quad (38)$$

or, using the expression of mechanical entropy:

$$EX^{PHYSICAL} = (U - U_0) - T_R (S^{THERMAL} - S_0^{THERMAL}) +$$

$$+ \bar{R}T_R (\ln V - \ln V_0) + P_R (V - V_0) \quad (39)$$

that can be considered as the formulation of the extended physical exergy expressed by means of the contributions of thermal exergy and mechanical exergy.

By using the state equation $P_R V_R = \bar{R}T_R$, the above can be also written as:

$$EX^{PHYSICAL} = (U - U_0) - T_R (S^{THERMAL} - S_0^{THERMAL}) + P_R V_R \ln \frac{V}{V_0} + P_R (V - V_0) \quad (40)$$

The term $\bar{R}T_R (\ln V - \ln V_0)$ or $P_R V_R \ln \frac{V}{V_0}$ of the

above expressions can be defined as an "entropic-mechanical" term that takes into account the entropy conversion that occurs alongside the isothermal reversible process as pointed out in the previous sections. The entropy conversion balance takes into account the mechanical entropy, other than thermal entropy, that is included in the above entropic-mechanical term of the extended formulation.

The symbol $EX^{PHYSICAL}$, instead of W , is proposed for identifying physical exergy to generalize its meaning that here addresses either to maximum work and maximum heat.

A results on of the method here adopted is the identification and the definition of thermal entropy and mechanical entropy that constitute the two components of the total entropy and represent the contributions to entropy balance. In particular, the already known expression of entropy (5) is also expressed as:

$$\Delta S^{THERMAL} = C_V \ln \frac{T}{T_0} + \bar{R} \ln \frac{V}{V_0} \quad (41)$$

that refers to thermal entropy related to heat interaction alone: the sum of terms (24) and (25) confirms this expression for canonical thermodynamic reversible processes, namely isothermal and adiabatic. On the other side, the procedure here described isolates and highlights the term:

$$\Delta S^{MECHANICAL} = \bar{R} \ln \frac{V}{V_0} \quad (42)$$

that, alone, represents the mechanical entropy related to work interaction. Furthermore, the total entropy, resulting from the addition of thermal and mechanical components of entropy, resolves the apparent inconsistency that thermal entropy would be constant in an isothermal reversible process that requires heat interaction by means of thermal entropy exchange, as pointed out in relation (4). In fact, a consequence deduced from the definition of total entropy is that Euler equation, in the particular case of ideal system and isothermal reversible process, now results in finite terms:

$$\Delta U = Q + W = T \cdot \Delta S^{TOTAL} = 0 \quad (43)$$

that is verified being valid the (33); in fact:

$$\Delta S_{ISOTHERMAL}^{THERMAL} = C_V \ln \frac{T}{T_0} + \bar{R} \ln \frac{V}{V_0} \quad (44)$$

$$\Delta S_{ISOTHERMAL}^{MECHANICAL} = \bar{R} \ln \frac{V}{V_0} \quad (45)$$

$$\Delta S_{ISOTHERMAL}^{TOTAL} = \bar{R} \ln \frac{V_1}{V_0} - \bar{R} \ln \frac{V_1}{V_0} = 0 \quad (46)$$

and confirms that $\Delta U = 0$ for an isothermal reversible process since $\Delta S^{TOTAL} = 0$.

In the case of adiabatic reversible (isoentropic) process, the following applies:

$$\Delta S_{ADIABATIC}^{THERMAL} = 0 \quad (47)$$

$$\Delta S_{ADIABATIC}^{MECHANICAL} = \bar{R} \ln \frac{V}{V_0} \quad (48)$$

$$\Delta S_{ADIABATIC}^{TOTAL} = -\bar{R} \ln \frac{V}{V_0} \quad (49)$$

that demonstrates the existence of the relationship between pressure, that changes with volume,

and total entropy also in case the thermal entropy is null due to the absence of heat interaction.

The definition of mechanical exergy associated to work interaction that depends on pressure and mechanical entropy that depends on volume implies that physical exergy should be accounted also by evaluating heat converted from work other than work converted from heat. Furthermore, the higher the pressure of work, the higher the capability in converting work into heat. Therefore, the extended physical exergy takes into account the equality of pressure, other than equality of temperature, as a further condition of mutual stable equilibrium state between system and reservoir.

To Finalize the discussion about this method, the formulation of the extended physical exergy is expressed by the equation (39) or (40) that, being an additive property, can also be Formulated as:

$$EX^{PHYSICAL} =$$

$$= (U - U_0)^{THERMAL} - T_R \cdot (S^{THERMAL} - S_0^{THERMAL}) + P_R \cdot (V - V_0) + \quad (50a)$$

$$+ (U - U_0)^{MECHANICAL} + T_R \cdot (S^{MECHANICAL} - S_0^{MECHANICAL}) \quad (50b)$$

where:

$(U - U_0)^{THERMAL}$ is the variation of internal energy due to heat interaction only (in particular, alongside an isovolumic process), and $(U - U_0)^{MECHANICAL}$ is the variation of internal energy due to work interaction only (in particular, alongside an isoentropic process). Being the internal energy additive, it follows that both contributions to internal energy due to heat and work interaction can occur successively or simultaneously along any process. The term (50a) of extended physical exergy represents the thermal exergy calculated alongside an isovolumic-isothermal process; on the other side, the term (50b) represents the mechanical exergy calculated alongside an isoentropic-isothermal process, therefore physical exergy can be expressed by the of the two components namely thermal exergy and mechanical exergy:

$$EX^{PHYSICAL} = EX^{THERMAL} + EX^{MECHANICAL} \quad (51)$$

It is noteworthy that, even if it is composed of two components, the extended formulation does not depend on a particular process adopted for its definition, thus it can be considered as a general formulation valid for whatever process, reversible or irreversible, connecting two different thermodynamic states.

The extended physical exergy has been deduced under the assumption that all processes are reversible. Anyway, in case irreversible processes are considered, the extended physical exergy is lower and the inequality symbol should appear in the expression (39) and (40) of physical exergy.

For a more clear understanding of the physical meaning of the entropic-mechanical additional term appearing in the extended formulation, reference can be made to the adiabatic reversible process as a particular case. This process is characterized by null variation of thermal entropy (due to absence of heat interaction) in the sense here pointed out, and a not null variation of mechanical entropy. As a consequence of the extended formulation, if the adiabatic reversible process is evaluated in terms of exergy, the maximum net useful work is accounted in terms of its capability to be converted (not transferred) to make available a maximum net useful heat, and therefore, the exergy calculation displays a lower amount. From a different standpoint, the entropic-mechanical part behaves as a reduction term that takes into account the amount of work interaction undergoing the (reversible) entropy conversion occurring alongside the isothermal process related to the reservoir thermodynamic conditions, that renders this work not more useful to be converted back into heat interaction. The Figure 6 shows the physical interpretation of the entropic-mechanical term; the areas included inside the dashed lines connecting the points R-2-3 that represent the work amount that is lost alongside the isothermal process in the direction of increasing pressure (and decreasing volume) and therefore not more convertible into useful heat. It is indeed this consequence that can be underlined as the novelty deriving from considering the mechanical aspect, other than the thermal one, that is implied in the inverse cycles governing, as an example of engineering and industrial applications, the heating pumps and refrigeration systems.

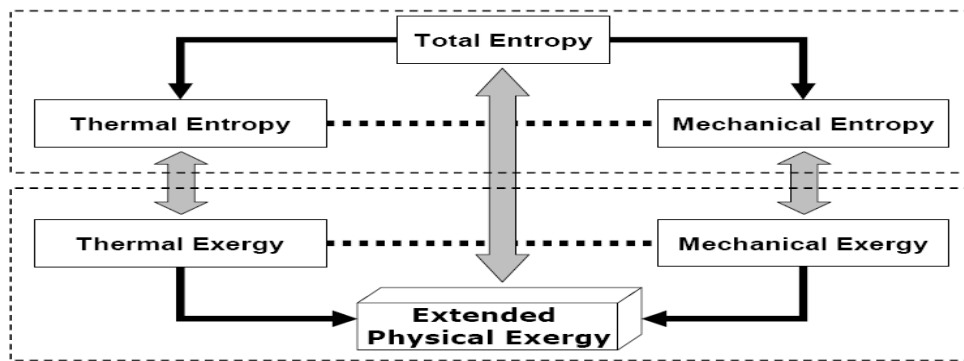


Fig. 1: Methodological scheme

$$S = S^{THERMAL} - S^{MECHANICAL}$$

Related to
Temperature
Related to
Pressure

↑

Entropy-Exergy relationship

↓

$$EX^{PHYSICAL} = EX^{THERMAL} + EX^{MECHANICAL}$$

Fig. 2: Thermal and mechanical contributions to entropy property

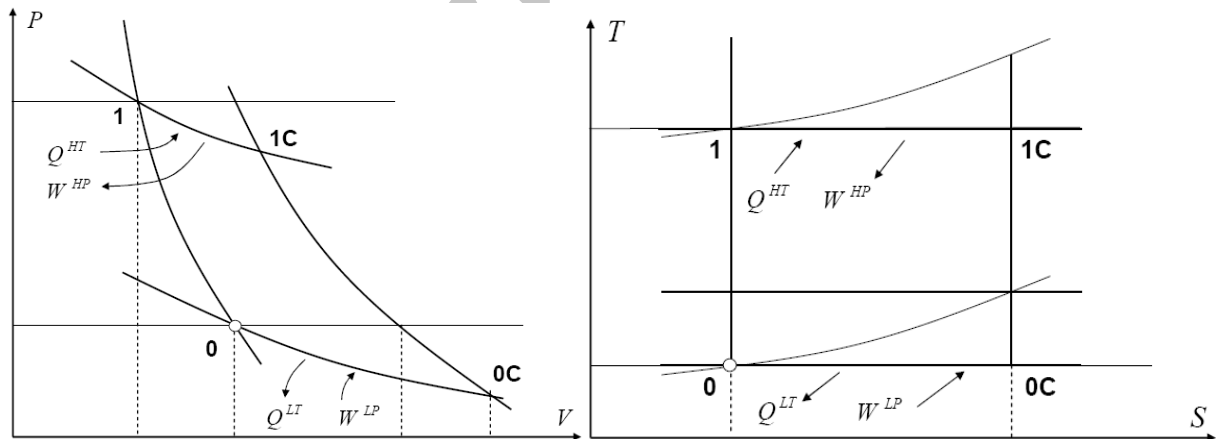


Fig. 3: Property of a symmetric cycle

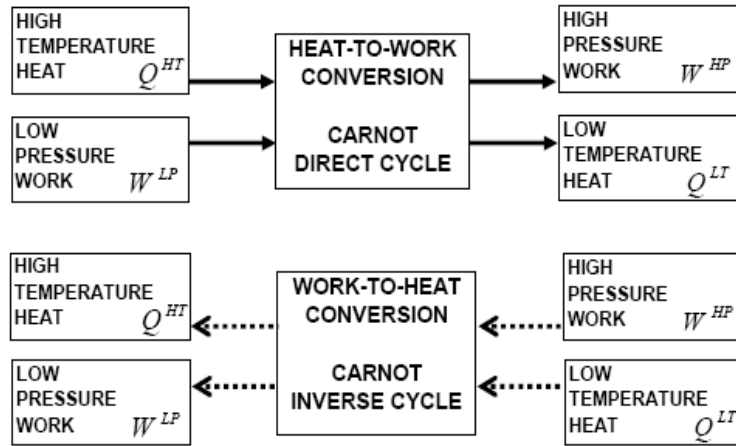


Fig. 4: conversions in a symmetric cycle

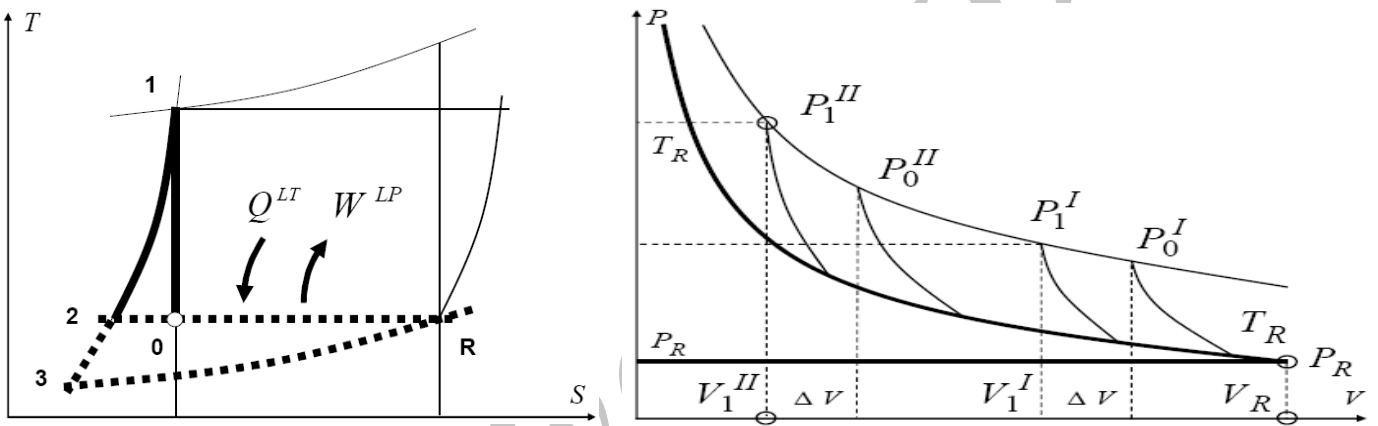


Fig. 5: mechanical exergy related to pressure

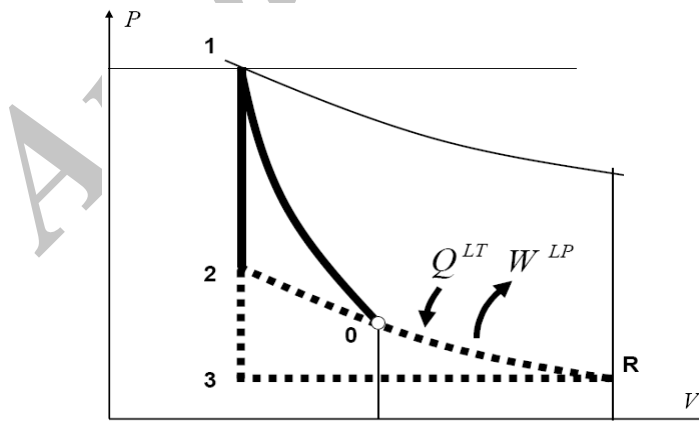


Fig. 6: Physical meaning of entropic- mechanical term

6. Conclusions

The basic and related conclusions of the present study are not in contrast with the principles and conceptions existing in thermodynamics and represent the tentative to propose a more complete approach to availability definitions already reported in literature that remains the theoretical ground of this analysis.

To summarize, the extended physical exergy formulated in the present study is constituted by either available work and heat. It is here calculated by evaluating exergy resulting from both heat and work interactions, or, in other terms, by the evaluation of maximum net useful work from available heat and maximum net useful heat from available work, both being the output of available energy due to the interconvertibility of heat into work and work into heat. In fact, taking as a reference what already stated by Gaggioli relevant to the concept of interconvertibility [5-7], "useful work is not better than useful heat and either one can be converted to the other"; furthermore, the available energy of a system, with respect to a reservoir, "can be obtained as net useful work or, equivalently, as net useful heat or as any combination of the two". Therefore, net useful work and heat are both different forms of the available energy: the extended formulation of physical exergy here proposed is based on this assumption and addresses to second law process for the evaluation of work, other than heat, as the result of interactions inside the composite of the system and the reservoir.

Looking forward to the possible future development in theoretical research, removing the assumptions adopted to simplify the present analysis, the extended physical exergy would comply with open systems bulkflow and real processes. Moreover, as far as the real systems are concerned, proving that pressure has a role in the concept of exergy for ideal systems, where internal energy is determined by temperature only, a fortiori it could be deduced that the extended physical exergy would be affected by pressure, other than temperature, in the more general case of a real system, where intermolecular interactions depend on volume.

A further extension of the present approach consists in considering the equality of chemical potential as a further condition for mutual stable

equilibrium between the system and the reservoir, other than the equality of temperature and pressure. Thus a possible theoretical development would be the investigation about the definition of entropy also based on chemical potential other than on temperature and pressure and therefore the formulation of a chemical entropy and chemical exergy to complete the properties.

Finally, the necessary evolution in the theoretical research would be the generalisation to all systems, large and small, in all states, in particular for nonequilibrium to be consistent and in compliance with the today thermodynamics conceptual structure.

Nomenclature

C_v	specific heat under constant volume ($J \cdot kg^{-1} \cdot K^{-1}$)
$EX^{MECHANICAL}$	mechanical exergy (J)
$EX^{THERMAL}$	thermal exergy (J)
P	pressure (MPa)
Q	total heat interaction over the whole Carnot cycle (J)
Q^{HT}	high temperature heat (J)
Q^{LT}	low temperature heat (J)
\bar{R}	universal gas constant ($J \cdot kgmol^{-1} \cdot K^{-1}$)
$S^{MECHANICAL}$	mechanical entropy ($J \cdot kg^{-1} \cdot K^{-1}$)
$S^{THERMAL}$	thermal entropy ($J \cdot kg^{-1} \cdot K^{-1}$)
T	absolute temperature (K)
U	internal energy (J)
V	volume (m^3)
W	total work interaction over the whole Carnot cycle (J)
W^{HP}	high pressure work (J)
W^{LP}	low pressure work (J)

Greek symbols

$\eta_{id}^{CARNOT-DIRECT}$	Carnot direct cycle efficiency
$\eta_{id}^{CARNOT-INVERSE}$	Carnot inverse cycle efficiency

$$\varepsilon = \frac{\gamma - 1}{\gamma}$$

$$\gamma = \frac{C_P}{C_V}$$

Superscripts

<i>HP</i>	high pressure
<i>HT</i>	high temperature
<i>LP</i>	low pressure
<i>LT</i>	low temperature
CONVER	conversion
TRANSF	transfer

Subscripts

0	stable equilibrium state with reservoir
1	generic thermodynamic state
<i>R</i>	reservoir

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Biography



"**Pierfrancesco Palazzo** was graduated with a Master Degree in Mechanical Engineering from the Department of Mechanical and Aeronautical Engineering, University of Roma 1 "La Sapienza" in Italy. He has been studying about general aspects of thermodynamics, energy processes, exergy method and thermoeconomic analysis and the related applications and participated to international congresses. At present he is an engineering manager in Technip, a world leader in project management, engineering and construction for the energy industry operating in the on-shore, off-shore and subsea segments.