

Dualisms and Symmetries in Physical Exergy Property and Generalized Formulation Related to the Carnot and Joule Cycles

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ABSTRACT

The aim of the present study is to propose a generalized formulation of physical exergy property of a system interacting with a generalized reservoir constituted by independent reservoirs at constant temperature and constant pressure. The components of physical exergy are the thermal exergy and the mechanical exergy representing the contributions due to the useful work and useful heat as outcome of the available energy related to a composite system-reservoir and converted by means of the Carnot and Joule cycles. The demonstration of the generalized formulation, and its additive property, utilizes the method constituted by the categories of dualism and symmetry adopted to prove that work depends on pressure as well as heat depends on temperature when a system is interacting with independent isobaric reservoir and isothermal reservoir.

Keywords: Available energy, useful work, useful heat, Carnot cycle, Joule cycle, thermal exergy, mechanical exergy, generalized physical exergy, isothermal reservoir, isobaric reservoir, generalized reservoir

DEFINITIONS, ACRONYMS, ABBREVIATIONS

A	generic system
C_p	specific heat at constant pressure ($J \cdot kg^{-1} \cdot K^{-1}$)
C_v	specific heat at constant volume ($J \cdot kg^{-1} \cdot K^{-1}$)
EX	exergy (J)
K	ratio of C_p over C_v
P	pressure (Pa)
Q	heat (J)
$\bar{R}$	universal gas constant ($J \cdot kg^{-1} \cdot K^{-1}$)
T	absolute temperature (K)
U	internal energy (J)
V	volume ($m^3 \cdot kg^{-1}$)
W	work (J)

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36 Greek symbols

37

38 η cycle efficiency

39 $\varepsilon \quad \frac{K-1}{K}$

40

41 Superscripts and Subscripts

42

43 *DIR* direct cycle

44 *INV* inverse cycle

45 *id* ideal

46 *HP* high pressure

47 *HT* high temperature

48 *LP* low pressure

49 *LT* low temperature

50 *M* mechanical

51 *T* thermal

52 *R* reservoir

53

54 1. PREMISE

55

56 The present study constitutes the second and conclusive part of a theoretical analysis aimed
57 to generalize the canonical formulation of physical exergy property. The first part of this
58 study, already published by the Author [1], proves that the physical exergy is expressed by
59 means of the thermal and mechanical contributions relating to useful heat, depending on the
60 pressure difference between system and isobaric reservoir, and useful work, depending on
61 the temperature difference between system and isothermal reservoir. In this perspective,
62 useful work is the result of Carnot cycle direct conversion and useful heat is the result of
63 Joule cycle inverse conversion, being useful work and heat the outcome of conversion of
64 available energy of a system interacting with a “generalized reservoir” at constant
65 temperature and constant pressure and behaving as isothermal and isobaric reservoirs. Due
66 to its additivity, physical exergy is suitable to account for the contribution of all subsystems to
67 the useful heat and useful work, conceived as equivalent and inter-convertible forms of
68 interaction [2,3,4,5]. On the basis of this scenario, the intention is here to formulate the
69 thermal exergy and mechanical exergy as components combined to express the generalized
70 formulation of physical exergy related to a “generalized reservoir” constituted by an
71 isothermal and isobaric reservoir.

72

$$73 \quad EX^{PHYSICAL} = EX_{REV}^T + EX_{REV}^M \quad (1)$$

74

75 The aim is here to demonstrate the procedure leading to the formulation of EX_{REV}^T and

76 EX_{REV}^M and to demonstrate that the generalized physical exergy $EX^{PHYSICAL}$ as an additive
77 state property.

78

79 2. METHOD OF DUALISM AND SYMMETRY

80

81 As far as the method is concerned, a dual perspective, induced by the thermal and
82 mechanical aspects and by the correlations existing between them, is assumed in order to

83 discuss the two components of physical exergy directly correlated to temperature and
84 pressure as well as to heat and work interactions between a system and a reservoir.

85 The principle of symmetry, formulated in geometry to govern the correspondence of two or
86 more elements and a reference entity, is adopted to analyze the properties of exergy
87 quantity and the thermodynamic cycles used for its definition taking temperature and
88 pressure as “reference entities for symmetry”.

89 The procedure here demonstrated does not intentionally addresses to the entropy property
90 in order to base the arguments on the concept of physical exergy defined solely by means of
91 the ideal cycles that can be generalized for any real non-cyclic process. This approach relies
92 on the rationale that entropy can be derived from energy and exergy which should be prior
93 defined as reported in the literature [6]. The assumptions adopted in this second part remain
94 unchanged with respect to those posited in the first part of this study [1].
95

96 **3. DUALISM IN PHYSICAL EXERGY**

97
98 The existence of useful heat and useful work, both resulting from available energy,
99 constitutes the dualism that features the concept of physical exergy and its components
100 [2,3,4,5]. Thereof, the calculation of useful heat or useful work can be obtained by evaluating
101 the heat interaction only and to work interaction only: hence, isovolumic reversible process,
102 determined by heat interaction only, and adiabatic reversible process, determined by heat
103 interaction only, are adopted to sequentially accomplish the whole process connecting any
104 two states by separated contributions. More in general, in fact, any two different states in a
105 bi-dimensional diagram related to any couple of thermodynamic properties can always be
106 connected by two consecutive portions of any type of polytropic process as they constitute a
107 system of two equation with two variables as follows:

$$108 \quad PV^m = a \quad \text{and} \quad PV^n = b \quad (2)$$

109 where m, n are real numbers and a, b are variable parameters.

110 In particular, the evaluation of work interaction addresses to the pressure level at which work
111 itself is exchanged with respect the pressure of the reservoir. Being the Joule cycle
112 characterized by the expression of efficiency that depends on pressure only, as
113 demonstrated [1], it can be adopted to replicate the formal method used to evaluate heat
114 interaction by means of the Carnot cycle that depends on temperature only.

115 The efficiency of Joule cycle becomes the evaluation factor of available energy of a system
116 A interacting with a reservoir R by means of the work transmitted alongside an adiabatic
117 expansion or compression process. The Figure 1 points out an elementary portion of the
118 expansion adiabatic reversible process curve that produces an elementary work quantity
119 released, at constant pressure, as an input of the Joule inverse cycle that converts, at
120 constant pressure, this elementary quantity of work into an elementary quantity of useful
121 heat. This mechanism is similar to the one used to evaluate the exergetic content associated
122 to heat amount by means of the efficiency of the Carnot direct cycle that converts, at
123 constant temperature, an elementary quantity of heat, along an isovolumic process, into an
124 elementary quantity of useful work as also represented in Figure 1.
125

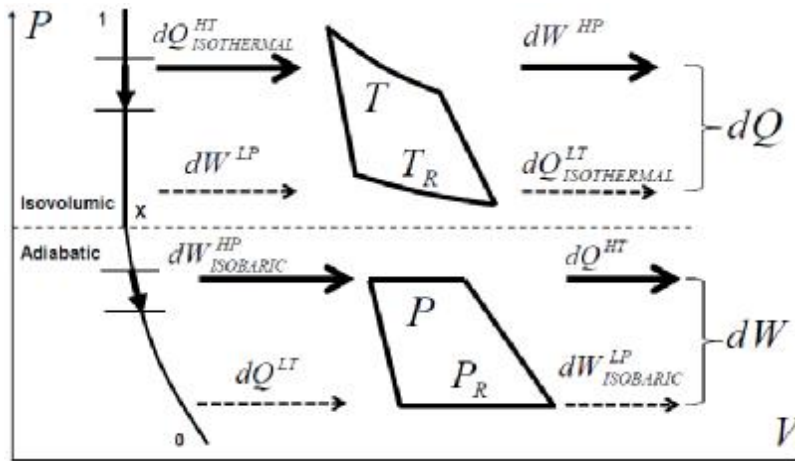


Figure 1 – Isovolumic-Adiabatic process (1-X-0) connecting any two states

The mathematical formulations of these two definitions, in infinitesimal terms, are reported here after.

Elementary useful work associated to the thermal exergy:

$$dEX^T = dW = \eta_{id}^{CARNOT \cdot DIR} \cdot dQ_{ISOTHERMAL}^{HT} = \left(1 - \frac{T_R}{T}\right) \cdot dQ_{ISOTHERMAL}^{HT} \quad (3)$$

that expresses the elementary quantity of useful work that can be extracted from an elementary quantity of heat available at a constant temperature;

Elementary useful heat associated to mechanical exergy:

$$dEX^M = dQ = \eta_{id}^{JOULE \cdot INV} \cdot dW_{ISOBARIC}^{HP} = \left[1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}}\right] \cdot dW_{ISOBARIC}^{HP} \quad (4)$$

that expresses the elementary quantity of useful heat that can be extracted from an elementary quantity of work available at a constant pressure level.

The reason for calculating physical exergy alongside a combined and sequential isovolumic-adiabatic (or adiabatic-isovolumic) process is to isolate the heat interaction and the work interaction with respect to the thermal reservoir and mechanical reservoir. This dual process can always connect any two states so that it constitutes a prove that physical exergy is a state property. Nevertheless, as a further confirmation, this method has a close analogy with the one proposed by Kotas [7] in which the thermal and mechanical components of physical exergy are calculated between any pair of states correlated by an isothermal-isobaric (or isobaric-isothermal) process. This implies that the mathematical integration over the whole process corresponds to the thermal and mechanical conversion process that occur at high

temperature (isothermal) and high pressure (isobaric) respectively. Therefore, the useful work and useful heat, corresponding to specific work and specific heat, are represented by the area enclosed inside the Carnot and Joule cycles respectively. The model of ideal system and the reversible processes is here adopted because it represents the theoretical limit corresponding to the “maximum net” useful work and or useful heat expressed by the physical exergy, and in particular by its thermal and mechanical components [1].

4. SYMMETRY IN PHYSICAL EXERGY

The formulation of physical exergy, in infinitesimal terms, derives from the relationship built around the efficiency of Carnot cycle. Such formulation expresses the role played by temperature in determining the amount of converted thermal energy and heat, which for this reason may be more specifically defined as thermal exergy [1,7,8],

$$dEX^T = dW$$

$$= \eta_{id}^{CARNOT-DIR} \cdot dQ_{ISOTHERMAL}^{HT} = \left(1 - \frac{T_R}{T}\right) \cdot dQ_{ISOTHERMAL}^{HT} \quad (5a)$$

$$= \eta_{id}^{JOULE-DIR} \cdot dQ_{ISOBARIC}^{HT} = \left[1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}}\right] \cdot dQ_{ISOBARIC}^{HT} \quad (5b)$$

in which $dQ_{ISOTHERMAL}^{HT}$ represents the elementary heat exchanged along the isothermal process at the highest temperature T of the Carnot cycle and $dQ_{ISOBARIC}^{HP}$ represents the elementary heat exchanged along the isobaric process at the highest pressure P . In particular, the efficiency of Carnot direct cycle appearing in the above equations, can be written as follows,

$$\eta_{id}^{CARNOT-DIR} = \frac{W}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{Q^{HT}}$$

$$= \frac{W^{HP} - W^{LP}}{W^{HP}} = \frac{Q^{HT} - Q^{LT}}{Q^{HT}} \quad (6)$$

while, the inverse Carnot 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 [9,10]),

$$\eta_{id}^{CARNOT-INV} = \frac{Q}{W^{HP}} = \frac{Q^{HT} - Q^{LT}}{W^{HP}}$$

$$= \frac{Q^{HT} - Q^{LT}}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{W^{HP}} = \eta_{id}^{CARNOT-DIR} \quad (7)$$

Due to the linear proportionality between the two expressions and the identity of two of the terms, then the meaning of used heat Q^{HT} in the direct cycle corresponds to the meaning of used work W^{HP} in the inverse cycle; vice versa, 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, this constituting the symmetry in Carnot cycle thermo-mechanical conversion. The applicability of this conclusion is also confirmed by the properties of Carnot cycle that remain unchanged for real systems characterized by state equation different from the one describing the ideal systems here assumed [11]. Once the exergy formulated by the direct cycle is defined as thermal exergy which highlights the role of temperature in heat-to-work conversion, the definition of mechanical exergy can be set thereof as the exergy expressed by the inverse cycle. In this case, the role of pressure replaces the role of temperature in the opposite conversion, that is, from work into heat. Moreover, input or output heat and work amounts are equal for isothermal or isobaric processes.

On the other side, physical exergy also encompasses the contribution of mechanical exergy [1] that may be expressed, in infinitesimal terms, by the following relationship [1,7,8]:

$$dEX^M = dQ$$

$$= \eta_{id}^{CARNOT-INV} \cdot dW_{ISOTHERMAL}^{HP} = \left(1 - \frac{T_R}{T}\right) \cdot dW_{ISOTHERMAL}^{HP} \quad (8a)$$

$$= \eta_{id}^{JOULE-INV} \cdot dW_{ISOBARIC}^{HP} = \left[1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}}\right] \cdot dW_{ISOBARIC}^{HP} \quad (8b)$$

in which $dW_{ISOTHERMAL}^{HP}$ represents the infinitesimal work exchanged along the isothermal process at the highest temperature T of the Carnot cycle and $dW_{ISOBARIC}^{HP}$ represents the infinitesimal work exchanged through the isobaric process at the highest pressure P . The equations (8a) and (8b) show the elementary work exchanged at high pressure along the higher temperature isothermal curve of the cycle and in which the role of pressure related to work is homologous to and symmetrical with the role of temperature related to heat. Consequently, mechanical exergy would in turn express the relationship between work and pressure that is symmetrical to the relationship between heat and temperature expressed by thermal exergy.

On the basis of the relationship between the Carnot and Joule cycle, the same observations made for the efficiency of direct and inverse Carnot cycle apply to the Joule cycle. However, unlike what occurs along the isothermal curves, such quantities exchanged along the isobaric curves are not equal but differ by one constant,

$$Q^{HT} = C_p \cdot (T_{1J} - T_1); \quad W^{HP} = \bar{R} \cdot (T_1 - T_{1J}) \quad (9)$$

$$\frac{W^{HP}}{Q^{HT}} = -\frac{\bar{R}}{C_p} = -\frac{C_p - C_v}{C_p} = -\left(1 - \frac{1}{K}\right) = \frac{1 - K}{K} = -\varepsilon \quad (10)$$

$$W^{HP} = -\varepsilon Q^{HT} \Rightarrow Q^{HT} = -\frac{1}{\varepsilon} W^{HP} \quad (11)$$

From the formal stand point the result is the same as that obtained for the Carnot cycle. In fact, for the Joule direct cycle,

$$\begin{aligned} \eta_{id}^{JOULE-DIR} &= \frac{W}{Q^{HT}} = \frac{Q^{HT} - Q^{LT}}{Q^{HT}} \\ &= -\frac{1}{\varepsilon} \frac{W^{HP} - W^{LP}}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{W^{HP}} \end{aligned} \quad (12)$$

where the contribution of heat and work is due exclusively to the isobaric processes along which heat and work is converted and exchanged simultaneously in directly proportional amounts.

Thus the following applies to the Joule inverse cycle:

$$\begin{aligned} \eta_{id}^{JOULE-INV} &= \frac{Q}{W^{HP}} = \frac{Q^{HT} - Q^{LT}}{W^{HP}} \\ &= \frac{Q^{HT} - Q^{LT}}{-\varepsilon Q^{HT}} = \frac{W^{HP} - W^{LP}}{-\varepsilon W^{HP}} = \frac{1}{\varepsilon} \eta_{id}^{JOULE-DIR} \end{aligned} \quad (13)$$

Hence, the ratio between direct cycle and inverse cycle efficiencies is in turn constant,

$$\frac{\eta_{id}^{JOULE-DIR}}{\eta_{id}^{JOULE-INV}} = \varepsilon = const \quad (14)$$

The fact that there is a constant relationship between the efficiency of the direct and inverse Joule cycles means that, for both cycles, the efficiency is characterized by identical expressions except for a constant factor, which establishes a linear proportionality. This makes it possible to replicate, for the Joule cycle, the same symmetry between thermal exergy and mechanical exergy as that demonstrated for the Carnot cycle.

5. THERMAL AND MECHANICAL CONTRIBUTIONS TO PHYSICAL EXERGY

As previously assumed, a thermodynamic process connecting any two states can always be composed by means of any two independent processes consisting in, but not limited to, the sequence of isovolumic and adiabatic (or, in the opposite sequential order, adiabatic and isovolumic). These two processes are characterized by the exchange, with the reservoir, of heat interaction only and work interaction only respectively and therefore can be assumed as components of physical exergy [1]. Hence, the resulting (total) physical exergy can be derived from the sum of the contributions due to the thermal exergy calculated for the isovolumic process and the mechanical exergy calculated for the adiabatic process that express the net useful heat and net useful work respectively. To summarize the arguments of previous sections:

- (i) dualism: useful work is the thermal exergy calculated for an isovolumic process; useful heat is the mechanical exergy calculated for an adiabatic process;

(ii) symmetry: thermal exergy is useful work related to temperature; mechanical exergy is useful heat related to pressure.

The distinction between direct and inverse cycle is not more necessary due to the proportionality of respective efficiency. This ensures that physical exergy equation features general validity for whatever total process and heat and or work interaction directions with respect to the reservoir, from the initial state to the final state of the whole process.

The formal expression in finite terms of the thermal exergy related to isovolumic process depending on temperature represented in Figure 1 is derived by integrating the equation (5a) or (8a):

$$\begin{aligned}
 EX^T &= \int_{ISOVOLUMIC} dEX_{ISOTHERMAL}^T = \int_{ISOVOLUMIC} \eta_{id}^{CARNOT} \cdot dQ_{ISOTHERMAL}^{HT} \\
 &= \int_{ISOVOLUMIC} \left(1 - \frac{T_R}{T}\right) \cdot dQ_{ISOTHERMAL}^{HT} \quad (15)
 \end{aligned}$$

This equation expresses the maximum net useful work converted from heat interaction at a given temperature along an isovolumic process.

The formal expression in finite terms of the mechanical exergy related to adiabatic process depending on pressure is deduced by integrating the equations (5b) or (8b):

$$\begin{aligned}
 EX^M &= \int_{ADIABATIC} dEX_{ISOBARIC}^M = \int_{ADIABATIC} \eta_{id}^{JOULE} \cdot dW_{ISOBARIC}^{HP} \\
 &= \int_{ADIABATIC} \left[1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}}\right] \cdot dW_{ISOBARIC}^{HP} \quad (16)
 \end{aligned}$$

This equation expresses the maximum net useful heat converted from work interaction at a given pressure along an adiabatic process.

Upon combining useful work and useful heat for whatever process, the physical exergy is defined as resulting from the sum of its two components and is formulated by the relation:

$$EX^{PHYSICAL} = EX^T + EX^M = \Delta U^{SYSTEM} + \Delta U^{RESERVOIR} \quad (17)$$

This expression can be further developed by using the formulation (15) and (16) set forth by calculating the thermal exergy of isovolumic process and the mechanical exergy of adiabatic process.

Thermal exergy of isovolumic process:

$$EX^T = \int_X^1 dQ_{ISOTHERMAL}^{HT} - T_R \int_X^1 \frac{dQ_{ISOTHERMAL}^{HT}}{T}$$

being $dQ_{ISOTHERMAL}^{HT} = C_V dT$ in the last expression :

$$= \int_X^1 C_V dT - T_R \int_X^1 \frac{C_V dT}{T} = (U_1 - U_X) - T_R C_V \int_X^1 \frac{dT}{T} \quad (18)$$

therefore the thermal exergy is expressed as:

$$EX^T = W_{REV}^{CONVER} + W_{REV}^{TRANSF} = \Delta U_Q^{SYSTEM} + \Delta U_Q^{RESERVOIR} \\ = (U_1 - U_X) - C_V T_R (\ln T_1 - \ln T_X) + Q_R \quad (19)$$

where $Q_R = -\bar{R}T_R (\ln V_1 - \ln V_0)$ represents the amount of heat interaction, over the entire process (isovolumic-adiabatic or adiabatic-isovolumic) delimited between the initial state 1 and the final state 0, that does not undergo conversion into useful work because it is directly transferred to the thermal reservoir.

Mechanical exergy of adiabatic process:

$$EX^M = \int_0^X dW_{ISOBARIC}^{HP} - \int_0^X \left(\frac{P_R}{P} \right)^{\frac{K-1}{K}} dW_{ISOBARIC}^{HP} \\ = \int_0^X dW_{ISOBARIC}^{HP} - \int_0^X \left(\frac{P_R}{P} \right) \left(\frac{P_R}{P} \right)^{\frac{1}{K}} dW_{ISOBARIC}^{HP} \\ \text{considering that } \left(\frac{P_R}{P} \right)^{\frac{1}{K}} = \frac{V_R}{V} \text{ applies to the adiabatic process:}$$

$$= \int_0^X dW_{ISOBARIC}^{HP} - P_R V_R \int_0^X \frac{dW_{ISOBARIC}^{HP}}{P V}$$

being $dW_{ISOBARIC}^{HP} = -PdV$ in the last expression :

$$= -\int_0^X PdV + P_R V_R \int_0^X \frac{dV}{V} \\ = (U_X - U_0) + P_R V_R (\ln V_X - \ln V_0) \quad (20)$$

therefore the mechanical exergy is expressed as:

$$EX^M = W_{NET}^{CONVER} + W_{NET}^{TRANSF} = \Delta U_W^{SYSTEM} + \Delta U_W^{RESERVOIR} \\ = (U_X - U_0) + P_R V_R (\ln V_X - \ln V_0) + W_R \quad (21)$$

where $W_R = P_R (V_1 - V_0)$ represents the amount of heat interaction, over the entire process (isovolumic-adiabatic or adiabatic-isovolumic) delimited between the initial state 1 and the

342 final state 0, that does not undergo conversion into useful heat because it is directly
 343 transferred to the mechanical reservoir.
 344

345 Finally, the sum of the two contributions EX^T , Equation (19) and EX^M , Equation (21)
 346 constitutes the formulation of physical exergy. Being applicable the state equation
 347 $P_R V_R = \bar{R}T_R$ and being $V_X = V_1$ and if the work exchanged with the mechanical reservoir at
 348 pressure P_R is also considered, the formulation is:
 349

$$\begin{aligned}
 350 \quad EX^{PHYSICAL} &= EX^T + EX^M = (U_1 - U_0) \\
 351 \quad &- C_V T_R (\ln T_1 - \ln T_0) + P_R V_R (\ln V_1 - \ln V_0) \\
 352 \quad &- \bar{R}T_R (\ln V_1 - \ln V_0) + P_R (V_1 - V_0) \quad (22)
 \end{aligned}$$

353
 354 This generalized formulation is “hybrid” in the sense that it conforms to the canonical one if
 355 the term $P_R V_R$ is equal to the term $\bar{R}T_R$, that is, a unique, or a dual, external system
 356 behaves as a thermal reservoir and mechanical reservoir where $P_R V_R = \bar{R}T_R$.

357 The term $P_R V_R (\ln V_1 - \ln V_0)$ represents, with respect to the canonical exergy formulation,
 358 the additional addendum that takes into account the exergy in the form of useful heat. This
 359 generalized formulation expresses the physical exergy resulting from the dualism related to
 360 the equivalence of useful heat or useful work. This additional addendum makes the
 361 maximum net useful heat equal to the maximum net useful work, as postulated according to
 362 the concept of equivalence. In effect, useful work, calculated between two arbitrary states
 363 laying on an adiabatic reversible process, is not equal to the useful heat alongside any other
 364 process connecting the same initial and final states (with invariable difference of internal
 365 energy) [1]. Nevertheless, this equality is restored if the useful heat is converted into useful
 366 work that therefore results identical to the one initially calculated alongside the adiabatic
 367 process. This rationale is valid provided the inversion of useful work with useful heat
 368 according to the concept of inter-convertibility. Thus, physical exergy, including the additional
 369 term, constitutes the expression of the equivalence and inter-convertibility of useful heat into
 370 useful work and useful work into useful heat. This final equation results from the dualism
 371 characterized by the equivalence and the symmetry related to the inter-convertibility of the
 372 mechanical exergy into thermal exergy and the thermal exergy into mechanical exergy.
 373 Differently, the first is the mechanical exergy of thermal exergy and the second is the thermal
 374 exergy of mechanical exergy or, in a more synthetic term, the exergy of exergy.
 375

376 It is noteworthy that if the isovolumic-adiabatic (or adiabatic-isovolumic) process, connecting
 377 two generic states of the system, is replaced by an isobaric-isothermal (or isothermal-
 378 isobaric) process between the same two states in Figure 2, then the resulting expression of
 379 physical exergy is identical for the two different dual processes. The prove is here after
 380 attained considering that, in the isobaric and isothermal processes where the thermo-
 381 mechanical conversion occur, heat and work interactions are simultaneous (and not
 382 sequential), hence physical exergy must be evaluated as the result of both thermal exergy
 383 and mechanical exergy combined together through the same process.
 384

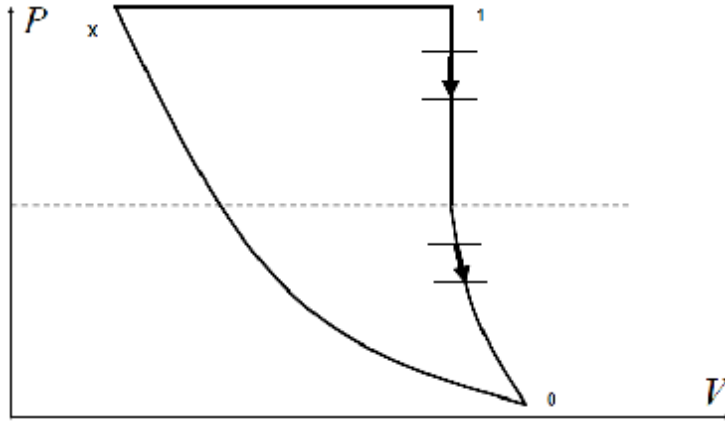


Figure 2 – Isobaric-Isothermal process (1-X-0) connecting any two states

With reference to the isobaric process and the associated Joule cycle, considering that:

$$dQ_{ISOBARIC}^{HT} = C_P d(T - T_R); \quad \left(\frac{P_R}{P} \right)^{\frac{K-1}{K}} = \frac{T_R}{T}; \quad \frac{V_1}{V_X} = \frac{T_1}{T_X} \quad \text{then the thermal exergy,}$$

calculated by the equation (5b), becomes:

$$\begin{aligned} EX_{ISOBARIC}^T &= C_P (T_1 - T_X) - \int_1^X \left(\frac{T_R}{T} \right) \cdot C_P dT \\ &= (U_1 - U_X)^T - \bar{R} T_R (\ln V_1 - \ln V_X) - C_V T_R (\ln T_1 - \ln T_X) \end{aligned} \quad (23)$$

and the mechanical exergy calculated by the equation (8b), considering that $dW_{ISOBARIC}^{HP} = -(P - P_R) dV$, becomes:

$$\begin{aligned} EX_{ISOBARIC}^M &= \int_1^X dW_{ISOBARIC}^{HP} - \int_1^X \left(\frac{P_R}{P} \right)^{\frac{K-1}{K}} dW_{ISOBARIC}^{HP} \\ &= (U_1 - U_X)^M + P_R V_R (\ln V_1 - \ln V_X) + P_R (V_1 - V_X) \end{aligned} \quad (24)$$

With reference to the isothermal process and the associated Carnot cycle, considering that $dQ_{ISOTHERMAL}^{HT} = \bar{R} T (\ln V_X - \ln V_0)$ and $dW_{ISOTHERMAL}^{HP} = -P V (\ln V_X - \ln V_0)$ the thermal exergy calculated by the equation (5a) becomes:

$$EX_{ISOTHERMAL}^T = \bar{R} T (\ln V_X - \ln V_0) - \bar{R} T_R (\ln V_X - \ln V_0) \quad (25)$$

and the mechanical exergy calculated by the equation (8a), also considering that $dW_{ISOTHERMAL}^{HP} = -(P - P_R) dV$, becomes:

$$EX_{ISOTHERMAL}^M = -\bar{R} T (\ln V_X - \ln V_0)$$

$$+ P_R V_R (\ln V_X - \ln V_0) + P_R (V_X - V_0) \quad (26)$$

The sum of the addenda expressed by the Equations (23), (24), (25), (26) is identical to the Equation (22): this result confirms that the generalized physical exergy does not depend on any particular process and therefore it is a state property that indeed can be considered as a formulation valid for whatever process connecting two different thermodynamic states. Moreover, the definitions of the two components of exergy are valid for cyclical and non-cyclical processes between any two thermodynamic states, therefore the generalized physical exergy, resulting from the algebraic sum of two additive state properties, is additive as well. The expression of the generalized physical exergy set forth can also be represented in terms of useful work and useful heat in compliance with the initial definition:

$$\begin{aligned} EX^{PHYSICAL} &= EX_{REV}^T + EX_{REV}^M = W_{REV}^{NET} + Q_{REV}^{NET} \\ &= W_{REV}^{CONVER} + W_{REV}^{TRANSF} + Q_{REV}^{CONVER} + Q_{REV}^{TRANSF} \end{aligned} \quad (27)$$

6. CONCLUSIONS

To summarize the results of the study, a generalized formulation of physical exergy in relation to pressure, together with temperature, is proposed taking into account the combination of work interaction and heat interaction between system and a generalized reservoir [11]. This conclusion is derived from the concept of equivalence and inter-convertibility of useful work and useful heat conceived by Gaggioli and is obtained by expressing the specific work of the Joule and Carnot cycles, which convert work into heat in isobaric processes and heat into work in isothermal processes. The specific work and specific heat resulting from thermo-mechanical conversions constitute one of the general canonical definitions of thermal exergy and mechanical exergy constituting the physical exergy expressed by the formulation here proposed.

The assumption that the system is ideal (perfect gas) and the processes are reversible has been posited in order to demonstrate that the results of this analysis can be deduced to formulate the theoretical maximum amount of physical exergy. Such conclusions can however be considered as general and remain valid even for real systems and processes characterized by irreversible phenomena occurring inside the system itself, as also confirmed in [12] in which the validity of Carnot's theorem is proven for a more general form of state equation. This expression remains valid for the criterion of exergo-environmental or exergo-economic analysis founded on the concepts of "avoidable/unavoidable" and "endogenous/exogenous" exergy destruction [13,14], that are not affected by this generalized definition of physical exergy that, on the other side, deals with exergy losses with respect to the control volume comprising the composite of system and reservoir. The applicability of the results of the present research is given, as an example, by the evaluation of the different impact in plant design if two shafts deliver the same output power – higher torque and lower speed or lower torque and higher speed – that cannot be considered as equivalent from the exergy method perspective and therefore require specific analysis to assess the optimized architecture of the system producing the input power. Another example is the exergy method applied to the design of Compressed Air Energy Storage (CAES) systems to the Liquefied Natural Gas liquefaction and regasification plants [15].

A possible future research development may be the application to open steady-state flow systems. In a wider approach, Gibbs' equations, considered as the historical basis of the extension elaborated by Gaggioli [4,5], encompass the chemical potential and maximum work that can be obtained from an (open) chemical system, as also described by Kotas [7].

461 From another standpoint, Gyftopoulos and Beretta debate the equality of chemical potential
462 (total potential) as an additional necessary condition for mutual stable equilibrium between
463 system and reservoir, together with the equality of temperature. The conclusion is that the
464 perspective envisaged by these Authors, considering the importance of chemical processes
465 in industrial production and the environmental context, may suggest a topic for a more far-
466 reaching investigation of chemical exergy and its components, as well as the related
467 implications for the whole framework of the generalized exergy concept [16].
468

469 **COMPETING INTERESTS**

470
471 Author has declared that no competing interests exist.
472

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