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

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Author's contribution

This whole work was carried out by the authors PP.

Original Research Article

ABSTRACT

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

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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);

$id:$ ideal; $K:$ ratio of C_p over C_v; $P:$ pressure (Pa); $Q:$ heat (J);

$\overline{R}:$ 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)

Greek symbols

$\eta:$ cycle efficiency; $\varepsilon:$ $\dfrac{K-1}{K}$

Superscripts and Subscripts

$DIR:$ direct cycle; $INV:$ inverse cycle; $id:$ ideal; $HP:$ high pressure;
$HT:$ high temperature; $LP:$ low pressure; $LT:$ low temperature;
$M:$ mechanical; $T:$ thermal; $R:$ reservoir

1. PREMISE

The present study constitutes the second and conclusive part of a theoretical analysis aimed at generalizing the canonical formulation of physical exergy property. The first part of this study, already published by the Author [1], proves that the physical exergy is expressed by means of the thermal and mechanical contributions relating to useful heat, depending on the pressure difference between system and isobaric reservoir and useful work, depending on the temperature difference between system and isothermal reservoir. In this perspective, useful work is the result of Carnot cycle direct conversion and useful heat is the result of Joule cycle inverse conversion. Both useful work and useful heat are the outcome of conversion process of available energy of a system interacting with a "generalized reservoir" at constant temperature and constant pressure and behaving as isothermal and isobaric independent reservoirs.

2. INTRODUCTION

Physical exergy is defined as the maximum net useful work and heat flowing through the boundaries of and within a system interacting with a reservoir in stable equilibrium state. Reversible ideal processes constitute exergy losses determining physical exergy. Irreversible interactions and transport phenomena determine exergy destruction [2]. Being additive and non-negative, physical exergy is suitable to account for the balance of contributions, coming from each subsystem, to the total amount of the overall composite as proved by Gaggioli [3]. The assertion that "work is not better than heat" as equivalent and inter-convertible forms of interaction has been conceived by Gaggioli [3,4,5] so that "no distinction between heat and work" is necessary. Hence, physical exergy can be withdrawn in the form of useful work or useful heat or any combination, no matter the process connecting the initial and final states of the system [3,4,5,6]. The intention is here to

formulate thermal exergy, relating to useful work and mechanical exergy, relating to useful heat, as additive and non-negative components. These contributions are combined in a formulation of the generalized physical exergy of a system interacting with a "generalized reservoir" - constituted by independent isothermal and isobaric reservoirs - according to the following expression:

$$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M} \tag{1}$$

The aim is to demonstrate the procedure leading to the formulation of EX_{REV}^{T} and EX_{REV}^{M} and to demonstrate that the generalized physical exergy $EX^{PHYSICAL}$ is an additive and non-negative state property as well. The configuration adopted is constituted by a system A and two independent reservoirs at constant temperature (isothermal) and constant pressure (isobaric) here referred to as "generalized reservoir" each defined according to the conditions and constraints specified by Gyftopoulos and Beretta [7].

3. METHOD OF DUALISM AND SYMMETRY

As far as method is concerned, a dual perspective, induced by the thermal and mechanical aspects and by the correlations existing between them is assumed in order to discuss the two components of physical exergy directly correlated to temperature and pressure as well as to heat and work interactions between a system and a reservoir.

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

The procedure demonstrated here does not intentionally address to the entropy property in order to base arguments on the concept of physical exergy defined solely by means of ideal cycles generalized for any real non-cyclic process. This approach relies on the rationale that entropy can be derived from energy and exergy which should be previously defined as reported in the literature [7].

The assumptions adopted in the present Second Part remain unchanged with respect to those posited in the First Part of this study [1].

4. DUALISM IN PHYSICAL EXERGY

The existence of useful heat and useful work, both resulting from available energy, constitutes the dualism that features the concept of physical exergy and its components [2,3,4,5]. Of these, the calculation of useful heat or useful work can be obtained by evaluating heat interaction only alongside an isovolumic reversible process and work interaction only alongside an adiabatic reversible process. These two processes are adopted to accomplish the whole process in sequence connecting any two states by separated contributions. More in general, indeed any two different states in a bi-dimensional diagram related to any couple of thermodynamic properties can always be connected by two consecutive portions of any type of polytropic elaboration since they constitute a system of two equations with two variables as follows:

$$PV^m = a \quad \text{and} \quad PV^n = b \tag{2}$$

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

In particular, the evaluation of work interaction addresses the pressure level at which work itself is exchanged with respect to the pressure of the reservoir. Since the Joule cycle is characterized by an expression of efficiency that depends on pressure only and by virtue of its properties [1], it can be adopted to replicate the formal method used to evaluate heat interaction by means of the Carnot cycle that depends on temperature only.

The efficiency of the Joule cycle becomes the evaluation factor of the available energy of a system A interacting with a reservoir R by means of the work transmitted alongside an adiabatic expansion or compression process. Fig. 1 illustrates out an elementary portion of the expansion adiabatic reversible process curve producing an elementary work quantity released, at constant pressure, as an input of the Joule inverse cycle that converts, at constant pressure, this elementary quantity of work into an elementary quantity of useful heat. This mechanism is similar to the one used to evaluate the exergetic content associated to the amount of heat utilising the efficiency of the Carnot direct cycle that converts, at constant temperature, an elementary quantity of heat, along an isovolumic process, into an elementary quantity of useful work as also represented in Fig. 1.
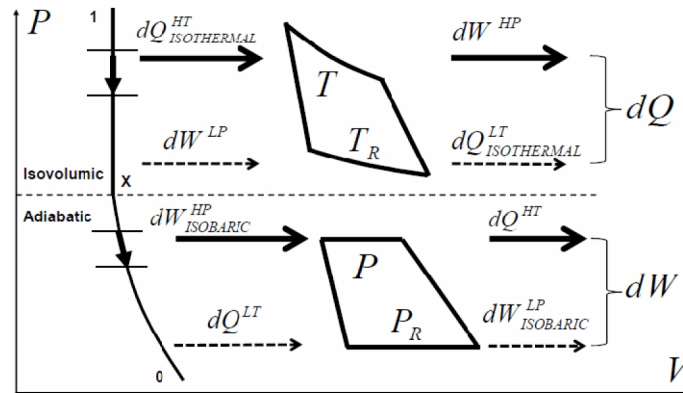

Fig. 1. Isovolumic-Adiabatic process (1-X-0) connecting any two states

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

Elementary useful work associated with thermal exergy:

$$dEX_{REV}^T = dW = \eta_{id}^{CARNOT \cdot DIR} \cdot dQ_{ISOTHERMAL}^{HT}$$

$$= \left(1 - \frac{T_R}{T}\right) \cdot dQ_{ISOTHERMAL}^{HT} \tag{3}$$

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

Elementary useful heat associated with mechanical exergy:

$$dEX_{REV}^{M} = dQ = \eta_{id}^{JOULE \cdot INV} \cdot dW_{ISOBARIC}^{HP}$$

$$= \left[1 - \left(\frac{P_R}{P} \right)^{\frac{K-1}{K}} \right] \cdot dW_{ISOBARIC}^{HP} \tag{4}$$

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

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 constituting proof that physical exergy is a state property. Nevertheless, by way of further confirmation, this method has a close analogy with the one proposed by Kotas [8] 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 mathematical integration thought the whole process corresponds to the thermal and mechanical conversion processes that occur at high temperature (isothermal) and high pressure (isobaric) respectively. Therefore, useful work and useful heat, corresponding to specific work and specific heat are represented by the area enclosed within the Carnot and Joule cycles respectively. The model of the ideal system and reversible processes is here adopted because it represents the theoretical limit corresponding to "maximum net" useful work and or useful heat expressed by physical exergy and in particular by its thermal and mechanical components [1].

5. SYMMETRY IN PHYSICAL EXERGY

The formulation of physical exergy, in infinitesimal terms, derives from the relationship built around the efficiency of the Carnot cycle. Such a 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 [1,8,9],

$$dEX_{REV}^{T} = dW$$

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

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

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 the Carnot direct cycle appearing in the above equations, can be written as follows,

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

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

while, for 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 (which does not correspond to the Coefficient of Performance reported in the literature) [10,11].

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

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

Due to the linear proportionality of the two expressions and the identity of two of the terms, the meaning of used heat Q^{HT} in the direct cycle thus corresponds to the meaning of used work W^{HP} in the inverse cycle; vice-versa, the meaning of utilized total work W in the direct cycle corresponds to the meaning of utilized total heat Q in the inverse cycle, thus constituting a symmetry in Carnot cycle thermo-mechanical conversion. The applicability of this conclusion is also confirmed by the properties of the Carnot cycle that remain unchanged for real systems characterized by a state equation that differs from the one describing the ideal systems here assumed [12,13,14].

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 the related mechanical exergy can be set 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] which may be expressed, in infinitesimal terms by the following relationship [1,8,9]:

$$dEX_{REV}^{M} = dQ$$

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

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

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.

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

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

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

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

From a formal standpoint the result is the same as the one obtained for the Carnot cycle. In fact for the Joule direct cycle,

$$\eta_{id}^{JOULE \cdot DIR} = \frac{W}{Q^{HT}} = \frac{Q^{HT} - Q^{LT}}{Q^{HT}}$$

$$= -\frac{1}{\varepsilon} \frac{W^{HP} - W^{LP}}{Q^{HT}} = \frac{W^{HP} - W^{LP}}{W^{HP}} \qquad (12)$$

In which 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:

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

$$= \frac{Q^{HT} - Q^{LT}}{-\varepsilon Q^{HT}} = \frac{W^{HP} - W^{LP}}{-\varepsilon W^{HP}} = \frac{1}{\varepsilon} \eta_{id}^{JOULE \cdot DIR} \tag{13}$$

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

$$\frac{\eta_{id}^{JOULE \cdot DIR}}{\eta_{id}^{JOULE \cdot INV}} = \varepsilon = const \tag{14}$$

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

6. 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 of but not limited to, the isovolumic and adiabatic sequence (or in the opposite sequential order, adiabatic and isovolumic). These two processes are respectively characterized by an exchange, with the reservoir of heat interaction only and work interaction only and can therefore be assumed as components of physical exergy [1]. Hence, 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 expressing the net useful heat and net useful work respectively. To summarize the arguments of the 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 no longer necessary due to the proportionality of respective efficiency. This ensures that the physical exergy equation is generally valid for any 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.

In finite terms, the formal expression of the thermal exergy related to the isovolumic process depending on temperature represented in Fig. 1 is derived by integrating Equation (5a) or (8a):

$$EX_{REV}^{T} = \int\limits_{ISOVOLUMIC} dEX_{ISOTHERMAL}^{T} = \int\limits_{ISOVOLUMIC} \eta_{id}^{CARNOT} \cdot dQ_{ISOTHERMAL}^{HT}$$

$$= \int\limits_{ISOVOLUMIC} \left(1 - \frac{T_R}{T}\right) \cdot dQ_{ISOTHERMAL}^{HT} \tag{15}$$

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

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

$$EX_{REV}^{M} = \int\limits_{ADIABATIC} dEX_{ISOBARIC}^{M} = \int\limits_{ADIABATIC} \eta_{id}^{JOULE} \cdot dW_{ISOBARIC}^{HP}$$

$$= \int\limits_{ADIABATIC} \left[1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}}\right] \cdot dW_{ISOBARIC}^{HP} \tag{16}$$

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

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

$$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M} = \Delta U^{SYSTEM} + \Delta U^{RESERVOIR} \tag{17}$$

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

The thermal exergy of the isovolumic process:

$$EX_{REV}^{T} = \int\limits_{X}^{1} dQ_{ISOTHERMAL}^{HT} - T_R \int\limits_{X}^{1} \frac{dQ_{ISOTHERMAL}^{HT}}{T}$$

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

$$= \int\limits_{X}^{1} C_V dT - T_R \int\limits_{X}^{1} \frac{C_V dT}{T} = \left(U_1 - U_X\right) - T_R C_V \int\limits_{X}^{1} \frac{dT}{T} \tag{18}$$

thermal exergy is therefore expressed as:

$$EX_{REV}^T = W_{REV}^{CONVER} + W_{REV}^{TRANSF} = \Delta U_Q^{SYSTEM} + \Delta U_Q^{RESERVOIR}$$

$$= \left(U_1 - U_X\right) - C_V T_R \left(\ln T_1 - \ln T_X\right) + Q_R \tag{19}$$

where $Q_R = -\overline{R} T_R \left(\ln V_1 - \ln V_0\right)$ represents the amount of heat interaction - over the entire process (isovolumic-adiabatic or adiabatic-isovolumic) - delimited between initial state 1 and final state 0, which does not undergo conversion into useful work because it is directly released to the thermal reservoir with a corresponding reversible energy transfer $\Delta U_Q^{RESERVOIR}$.

The mechanical exergy of the adiabatic process:

$$EX_{REV}^M = \int_0^X dW_{ISOBARIC}^{HP} - \int_0^X \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}} dW_{ISOBARIC}^{HP}$$

$$= \int_0^X dW_{ISOBARIC}^{HP} - \int_0^X \left(\frac{P_R}{P}\right) \cdot \left(\frac{P_R}{P}\right)^{-\frac{1}{K}} dW_{ISOBARIC}^{HP}$$

considering that $\left(\dfrac{P_R}{P}\right)^{-\frac{1}{K}} = \dfrac{V_R}{V}$ applies to the adiabatic process:

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

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

$$= -\int_0^X PdV + P_R V_R \int_0^X \frac{dV}{V}$$

$$= \left(U_X - U_0\right) + P_R V_R \left(\ln V_X - \ln V_0\right) \tag{20}$$

mechanical exergy is therefore expressed as:

$$EX_{REV}^M = Q_{NET}^{CONVER} + Q_{NET}^{TRANSF} = \Delta U_W^{SYSTEM} + \Delta U_W^{RESERVOIR}$$

$$= \left(U_X - U_0\right) + P_R V_R \left(\ln V_X - \ln V_0\right) + W_R \tag{21}$$

where $W_R = P_R\left(V_1 - V_0\right)$ 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, which does not undergo conversion into useful heat because it is directly released to the mechanical reservoir with a corresponding reversible energy transfer $\Delta U_W^{RESERVOIR}$.

Finally, the sum of the two contributions - EX_{REV}^T, Equation (19) and - EX_{REV}^M, Equation (21) constitutes the formulation of physical exergy. Since the state equation $P_R V_R = \overline{R} T_R$ is applicable and since $V_X = V_1$ and if the work exchanged with the mechanical reservoir at pressure P_R is also considered, the formulation is:

$$
\begin{aligned}
EX^{PHYSICAL} &= EX_{REV}^T + EX_{REV}^M \\
&= W_{REV}^{CONVER} + Q_{NET}^{CONVER} + W_{REV}^{TRANSF} + Q_{NET}^{TRANSF} = \Delta U_{W,Q}^{SYSTEM} + \Delta U_{W,Q}^{RESERVOIR} \quad (22)
\end{aligned}
$$

$$
\begin{aligned}
EX^{PHYSICAL} &= EX_{REV}^T + EX_{REV}^M = \left(U_1 - U_0 \right) \\
&\quad - C_V T_R \left(\ln T_1 - \ln T_0 \right) + P_R V_R \left(\ln V_1 - \ln V_0 \right) \\
&\quad - \overline{R} T_R \left(\ln V_1 - \ln V_0 \right) + P_R \left(V_1 - V_0 \right)
\end{aligned} \quad (23)
$$

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

With respect to canonical exergy formulation, the term $P_R V_R \left(\ln V_1 - \ln V_0 \right)$ represents the additional addendum taking into account exergy in the form of useful heat. This generalized formulation expresses the physical exergy resulting from the dualism related to the equivalence of useful heat or useful work. The additional addendum makes maximum net useful heat equal to maximum net useful work, as postulated according to the concept of equivalence. In effect, useful work, calculated between two arbitrary states along any adiabatic reversible process is not equal to the useful heat alongside any other process connecting the same initial and final states (with an invariable difference of internal energy) [1]. Nevertheless, this equality is restored if the useful heat is converted into useful work which is therefore identical to the one initially calculated alongside the adiabatic process. This rationale is valid provided the inversion of useful work with useful heat is in accordance with the concepts of equivalence and inter-convertibility. Thus, this final equation, including the additional term is the result of the dualism characterized by the equivalence and the symmetry related to the inter-convertibility of the mechanical exergy into thermal exergy and the thermal exergy into mechanical exergy. In other words, the former is the mechanical exergy of thermal exergy and the latter is the thermal exergy of mechanical exergy or in more synthetic terms, the exergy of exergy.

It is worth noting that if the isovolumic-adiabatic (or adiabatic-isovolumic) process, connecting two generic states of the system is replaced by an isobaric-isothermal (or isothermal-isobaric) process between the same two states in Fig. 2, then the resulting

expression of physical exergy is identical for the two different dual processes. The proof is given below considering that, in the isobaric and isothermal processes, in which the thermo-mechanical conversion occurs, heat and work interactions are simultaneous (and not sequential), hence physical exergy must be evaluated as the result of both thermal exergy and mechanical exergy combined together through the same process.
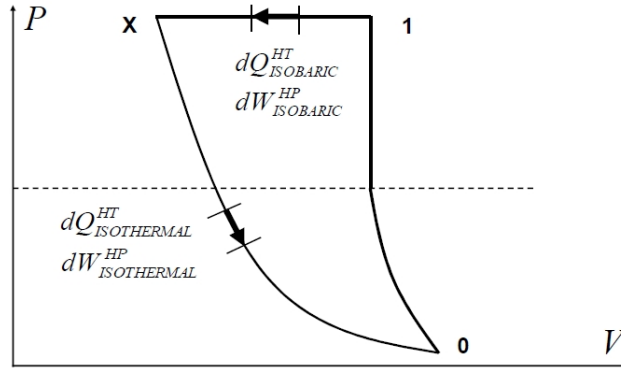

Fig. 2. Isobaric-Isothermal process (1-X-0) connecting any two states

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

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

by the equation (5b), becomes:

$$EX^T_{ISOBARIC} = C_P(T_1 - T_X) - \int_1^X \left(\frac{T_R}{T}\right) \cdot C_P dT$$

$$= (U_1 - U_X)^T - \overline{R}T_R(\ln V_1 - \ln V_X) - C_V T_R(\ln T_1 - \ln T_X) \tag{24}$$

and the mechanical exergy calculated by Equation (8b), considering that $dW^{HP}_{ISOBARIC} = -(P - P_R) \cdot dV$, becomes:

$$EX^M_{ISOBARIC} = \int_1^X dW^{HP}_{ISOBARIC} - \int_1^X \left(\frac{P_R}{P - P_R}\right)^{\frac{K-1}{K}} dW^{HP}_{ISOBARIC}$$

$$= (U_1 - U_X)^M + P_R V_R(\ln V_1 - \ln V_X) + P_R(V_1 - V_X) \tag{25}$$

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

$$EX^T_{ISOTHERMAL} = \overline{R}T(\ln V_X - \ln V_0) - \overline{R}T_R(\ln V_X - \ln V_0) \tag{26}$$

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

$$EX_{ISOTHERMAL}^{M} = -\overline{R}T \left(\ln V_X - \ln V_0 \right)$$
$$+ P_R V_R \left(\ln V_X - \ln V_0 \right) + P_R \left(V_X - V_0 \right) \tag{27}$$

The sum of the addenda expressed by Equations (24), (25), (26) and (27) is identical to Equation (23): this result confirms that the generalized physical exergy does not depend on any particular process and is therefore a state property that can indeed be considered as a formulation valid for any process connecting two different thermodynamic states. Furthermore, the definitions of the two components of exergy are valid for cyclical and non-cyclical processes between any two thermodynamic states, so that 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:

$$EX^{PHYSICAL} = EX_{REV}^{T} + EX_{REV}^{M} = W_{REV}^{NET} + Q_{REV}^{NET}$$
$$= W_{REV}^{CONVER} + W_{REV}^{TRANSF} + Q_{REV}^{CONVER} + Q_{REV}^{TRANSF} \tag{28}$$

where "CONVER" identifies the useful work W_{REV}^{CONVER} or heat Q_{REV}^{CONVER} resulting from reversible "REV" conversion of heat or work respectively; "TRANSF" identifies the nonuseful work or heat directly transferred to the reservoir, hence:

NET = CONVER + TRANSF = USEFUL + NONUSEFUL = NET USEFUL

and work W_{REV}^{NET} or heat Q_{REV}^{NET} are according to the canonical definition here reported as outset of Section 2.

The procedure adopted in the present analysis is based on thermo-mechanical conversion cycles and leads to a definition of the components contributing to the physical exergy expressed by Equation (27). Nevertheless, it should be noted that this equation corresponds to and is consistent with, the formulation of physical exergy derived using a different procedure based on entropy property [15].

7. CONCLUSIONS

To summarize the results of the whole study, a formulation of generalized physical exergy in relation to pressure, together with temperature is proposed and takes into account the combination of work interaction and heat interaction between a system and a generalized reservoir [1]. 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 cycle which converts work into heat in isobaric processes, and the Carnot cycle which converts heat into work in isothermal processes.

The assumption that the system is ideal (perfect gas) and that 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 may however be considered as general and remain valid even for real systems characterized by a more general form of state equation for which the validity of Carnot's theorem is proven [12,13,14]. This expression remains valid for the criterion of exergo-environmental or exergo-economic analysis based on the concepts of "avoidable/unavoidable" and "endogenous/exogenous" exergy destruction [16,17], unaffected by this generalized definition of physical exergy which, on the other side, deals with exergy losses with respect to the control volume comprising the composite of system and reservoir. The results of the present research are applicable by way of example, to 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 – which cannot be considered as equivalent from the exergy method perspective and therefore require specific analysis to assess an optimized configuration of the system producing the input power. Another example is the exergy method applied to the design of Compressed Air Energy Storage (CAES) systems for Liquefied Natural Gas (LNG) liquefaction and regasification plants [18].

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 revisit and extension elaborated by Gaggioli [4,5], encompass the chemical potential and maximum work obtainable from an (open) chemical system, as also described by Kotas [7]. From another standpoint, Gyftopoulos and Beretta debate the equality of chemical potential (total potential) as an additional necessary condition for mutual stable equilibrium between system and reservoir, together with the equality of temperature. The conclusion is that the perspective envisaged by these Authors, considering the importance of chemical processes in industrial production and the environmental context, may suggest a topic for a more far-reaching investigation of chemical exergy and its components, as well as the related implications for the whole framework of the generalized exergy concept [19].

COMPETING INTERESTS

Author has declared that no competing interests exist.

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