



Performance Optimization of the Carnot and Joule Cycles and Relationship with the Formulation of Physical Exergy Property

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Author's contribution

Author PP designed the study and wrote all revisions of the manuscript. Assumptions, method, proofs and conclusions were elaborated by author PP solely. Author read and approved the final version.

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ABSTRACT

The present theoretical study proposes an analysis, underpinned by the basic foundations reported in the literature, aimed at establishing a generalization of the relationship between cyclic thermo-mechanical conversion processes and the physical exergy property defined for a system interacting with two different and independent reservoirs. The outcome of the study is the demonstration that physical exergy expresses both useful work or useful heat, if these interactions undergo conversion when withdrawn from a system. The approach to conversion consists in comparing the efficiency of (ideal) Carnot and Joule cycles leading to the argument that the Joule cycle is the one performing at maximum efficiency between two constant pressures, similarly to the Carnot cycle performing at maximum efficiency between two constant temperatures. In terms of specific (per cycle) work or heat of Carnot and Joule cycles, the study proves that the roles of temperature and pressure are opposed as evidenced by a performance optimization analysis for the two cycles. Interactions between a system and two independent reservoirs undergoing isothermal and isobaric processes respectively are examined in relation to useful work and useful heat. The aim and the novelty of this analysis is to explore the role of the Joule cycle and the pressure of system and isobaric reservoir, which are similar to the role of the Carnot cycle and the temperature of system and isothermal reservoir. This implies a generalized formulation of physical exergy which, for this reason, may be regarded as a temperature-and-pressure-dependent property in

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the general case of a system interacting with two reservoirs. Finally, the expression of the thermal and mechanical components of physical exergy, depending on temperature and pressure, and their relationship with the Carnot and Joule cycles, are envisaged as possible consequences of this analysis representing the basis for future research.

Keywords: Thermo-mechanical conversion; Carnot cycle; Joule cycle; useful work; useful heat; thermal exergy; mechanical exergy; physical exergy; isothermal reservoir; isobaric reservoir.

DEFINITIONS, ACRONYMS, ABBREVIATIONS

C_p	Specific heat at constant pressure ($J \cdot kg^{-1} \cdot K^{-1}$)
C_v	Specific heat at constant volume ($J \cdot kg^{-1} \cdot K^{-1}$)
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)

Greek symbols

η	Cycle efficiency
ε	$\frac{K-1}{K}$

Superscripts and Subscripts

DIR	Direct cycle
id	Ideal
INV	Inverse cycle
Irr	Irreversible
HP	High pressure
HT	High temperature
LP	Low pressure
LT	Low temperature
M	mechanical
T	Thermal
Rev	Reversible
R	Reservoir
←	Input into system
→	Output from system

1. INTRODUCTION

The efficiency determining the specific (per cycle) work of the Carnot ideal cycle characterizes one of the procedures leading to the definition of the physical exergy property [1,2]. Exergy is the “quality” of energy. In more rigorous terms, exergy expresses the maximum net useful work withdrawn, from the available energy, through the interaction of the system with a thermal reservoir at constant temperature [3,4,5,6]. This study attempts to explore, from a wider standpoint, the thermal exergy and mechanical exergy components that constitute the contributions to physical exergy due to: (i) thermal exergy losses determined by reversible heat interactions and irreversible thermal exergy destruction determined by thermal dissipation driven by temperature differences; (ii) mechanical exergy losses associated with reversible work interactions and mechanical exergy destruction determined by irreversible mechanical dissipation due to transport phenomena driven by pressure differences. The aim and novel approach of this analysis lies in exploring the role of the Joule cycle and pressure, similar to the role of the Carnot cycle and temperature, in defining the physical exergy property.

2. ASSUMPTIONS AND METHOD

The following assumptions are posited: (i) the system is closed (non-flow) and consists of an ideal and single-phase homogeneous gas considered as a simple system [7]; (ii) the state equation for ideal gas $PV = n\overline{RT}$ [7] is applicable; (iii) there are no phase changes, chemical or nuclear reactions inside the system; (iv) the kinetic and potential energy associated with the overall mass are not considered.

With regard to method, a dual perspective, induced by the thermal and mechanical aspects and by the correlations existing between them, is adopted in order to discuss the performances of the Carnot and Joule cycles directly correlated to absolute temperature and pressure, as well as to heat and work interactions between the system and reservoir.

The principle of symmetry, formulated in geometry to govern the correspondence of two or more elements and a reference entity, is adopted to analyse the properties of thermodynamic cycles with respect to temperature and pressure, here considered as “reference entities for symmetry”.

3. USEFUL WORK AND USEFUL HEAT

The expression of useful work, constituting the outcome of the available energy of a generic system with respect to a reservoir R at constant temperature [1,2], is based on the temperature level determining the thermal exergy quantity associated with the heat and temperature according to the following canonical formula [6,7]:

$$\begin{aligned} \text{USEFUL WORK} = EX^T = -W^{DIR} &= \left(1 - \frac{T_R}{T}\right) \cdot Q^{HT} = \left(1 - \frac{Q^{LT}}{Q^{HT}}\right) \cdot Q^{HT} \\ &= Q^{HT} - Q^{LT} = -W^{HP} + W^{LP} \end{aligned} \quad (1a)$$

where the product of the efficiency of the Carnot direct ideal cycle times the high temperature heat value Q^{HT} , expresses the specific work of the cyclic direct conversion process representing maximum net useful work in which the maximum value is obtained, if and only if, all interactions and processes are reversible. In general, and also considering non-cyclic processes, useful work can be withdrawn directly in the form of work interaction and or as the result of "inter-conversion" through a direct cycle from useful heat to useful work, no matter what the process, from the initial to the final state, exergy being a state property.

On the basis of the concepts of equivalence and inter-convertibility of useful work and useful heat withdrawn from available energy [5,6], the amount of useful heat is identical to the amount of useful work, so that both constitute the outcome of the (thermal and mechanical) exergy of the system with respect to the (thermo-mechanical) reservoir, characterized by the state of least energy. Thus, useful heat can be withdrawn directly in the form of heat interaction and or as the result of "inter-conversion" through an inverse cycle, of work interaction (useful work) into useful heat, again no matter what the process from the initial to final state exergy being a state property. The concepts of equivalence and inter-convertibility imply an equal amount of useful heat Q^{\rightarrow} or useful work W^{\rightarrow} , and consequently both useful work and useful heat, withdrawn individually or combined together to realize whatever process connecting two states, must undergo a heat-to-work or work-to-heat conversion process to ensure the same amount of Q^{\rightarrow} and W^{\rightarrow} between the two states so that physical exergy behaves as a state property. The proof here proposed concerns the reversible adiabatic and reversible isovolumic processes of an ideal system. The symbology adopted is defined by Gyftopoulos and Beretta [7].

(i) Adiabatic reversible process, from state 1 to state 0 of Fig. 1A, may be accomplished by a sequence of isovolumic-isothermal reversible processes (1X-X0): equivalence requires that $W^{\rightarrow} = Q^{\rightarrow}$ where $W^{\rightarrow} = (U_1 - U_0)$ from state 1 to state 0 of adiabatic process 10 while Q^{\rightarrow} may be calculated by the contributions along the isovolumic-isothermal process (1X-X0) between the same states 1 and 0.

As regard the isovolumic process 1X from state 1 to state X, $Q_{1X}^{\rightarrow} = (U_1 - U_X)$ which is equal to $(U_1 - U_0)$ since U_X and U_0 lie on the same isothermal curve and internal energy U depends on temperature only for ideal systems here assumed. Therefore $(U_1 - U_0) = W^{\rightarrow} = Q_{1X}^{\rightarrow}$.

As regard the isothermal process, $Q_{X0}^{\leftarrow} = W_{X0}^{\rightarrow}$ from state X to state 0 along the isothermal process X0.

The comparison between useful heat and useful work contributions calculated throughout the two different processes connecting the same initial 1 and final 0 states is: $(U_1 - U_0)$

$= (U_1 - U_X) + (U_X - U_0)$ which is $W^{\rightarrow} = Q_{1X}^{\rightarrow} + Q_{X0}^{\leftarrow} = W^{\rightarrow} + Q_{X0}^{\leftarrow} \neq W^{\rightarrow}$ and does not comply with the equality $W^{\rightarrow} = Q^{\rightarrow}$ constituting the initial assumption.

(ii) Isovolumic reversible process, from state 1 to state 0 of Fig. 1A, which may be accomplished by a sequence of adiabatic-isobaric reversible processes (1X-X0): equivalence requires that $Q^{\rightarrow} = W^{\rightarrow}$ where $Q^{\rightarrow} = (U_1 - U_0)$ from state 1 to state 0 along the isovolumic process 10, while W^{\rightarrow} may be calculated by the contributions along the adiabatic-isobaric process (1X-X0) between the same states 1 and 0.

As regard the adiabatic process 1X from state 1 to state X, $W_{1X}^{\rightarrow} = (U_1 - U_X)$.

As regard the isobaric process X0 from state X to state 0 $(U_X - U_0) = W_{X0}^{\leftarrow} + Q_{X0}^{\rightarrow}$.

The comparison between useful work and useful heat contributions leads to: $(U_1 - U_0) = (U_1 - U_X) + (U_X - U_0)$; substituting the differences of internal energy with interactions quantities it is obtained that: $Q^{\rightarrow} = W_{1X}^{\rightarrow} + W_{X0}^{\leftarrow} + Q_{X0}^{\rightarrow}$ and considering that $(U_1 - U_0) = Q^{\rightarrow} = W^{\rightarrow}$ it follows that $Q^{\rightarrow} = W^{\rightarrow} + Q_{X0}^{\rightarrow} \neq Q^{\rightarrow}$ that again does not comply with the $Q^{\rightarrow} = W^{\rightarrow}$ equality constituting the initial assumption.

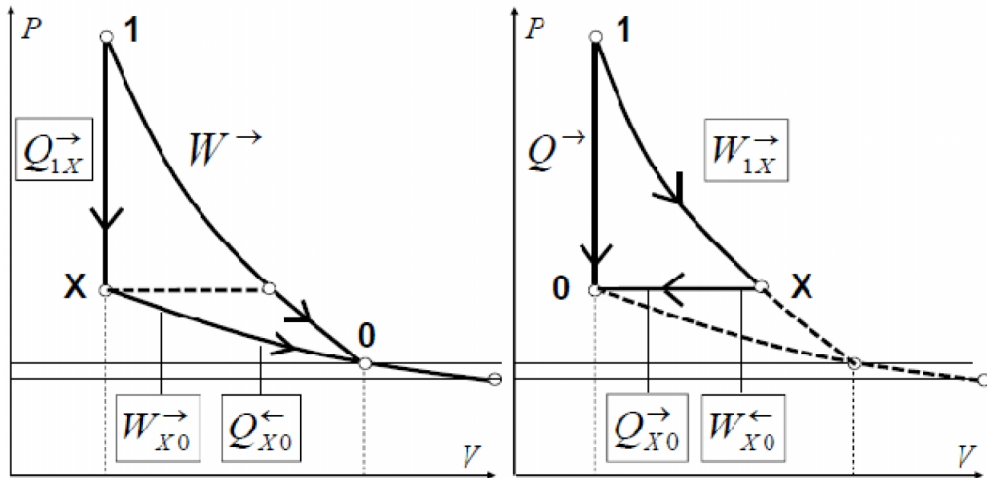


Fig. 1A. Reversible adiabatic and isovolumic processes

In order to resolve the non-compliance demonstrated above, it may be posited that both useful work and useful heat undergo conversion into the other form of assumed equivalent interactions; hence, if a generic process is accomplished by means of a sequence of useful

work and useful heat, a linear combination of thermal exergy and mechanical exergy is suitable to express the equivalence of heat and work interactions by means of the combination of heat-to-work and work-to-heat conversions throughout the whole process from initial to final states. The definition of physical exergy is thus based on the combination of useful work and useful heat as equivalent and inter-convertible forms of interaction between the system and a thermo-mechanical reservoir [6]. This definition can consist of the sum of thermal exergy, as per Equation (1a), and the mechanical exergy by the following Equation (1b), relating to (inverse) cyclic work-to-heat conversion; this Equation (1b) is derived from the Carnot inverse cycle efficiency [8]:

$$\begin{aligned} \text{USEFUL HEAT} = EX^M = -Q^{INV} &= \left(1 - \frac{T_R}{T}\right) \cdot W^{HP} = \left(1 - \frac{Q^{LT}}{Q^{HT}}\right) \cdot W^{HP} \\ &= W^{HP} - W^{LP} = -Q^{HT} + Q^{LT} \end{aligned} \quad (1b)$$

It should be noted that the canonical expression of physical exergy based on Carnot ideal cycle efficiency in Equation (1a) reported in the literature, requires the processes to be reversible and the state equation for ideal systems here adopted $PV = n\bar{R}T$ to be valid. Therefore this state equation will be considered to argue that the performance of both the Carnot and Joule cycles is correlated to the formulation of the physical exergy property as illustrated in the following sections.

4. EFFICIENCY OF THE CARNOT AND JOULE CYCLES

The efficiency of the Carnot cycle is expressed by means of the extreme temperature ratio just as the efficiency of the Joule cycle depends on the extreme pressure ratio. The role of temperature and pressure can be inverted by expressing the efficiency of the Carnot cycle as a function of pressure instead of temperature, and the efficiency of the Joule cycle as a function of temperature instead of pressure. With reference to Fig. 1B, the point X is correlated to $T_{ISOVOLUMIC} = T_{ADIBATIC}$ equality which determines the thermodynamic equivalence of the Carnot and Joule cycles. Indeed, using the temperature and pressure ratios in an adiabatic reversible process [9,10]:

$$\eta_{id}^{JOULE-DIR} = 1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}} = 1 - \frac{T_R}{T_X} = \eta_{id}^{CARNOT-DIR} \quad (2)$$

This result may also be obtained starting from the expression of the Carnot ideal cycle. Indeed, using the pressure and temperature ratios in an isovolumic reversible process, the following is obtained:

$$\eta_{id}^{CARNOT-DIR} = 1 - \frac{T_Y}{T} = 1 - \left(\frac{P_R}{P}\right)^{\frac{K-1}{K}} = \eta_{id}^{JOULE-DIR} \quad (3)$$

which is identical to Equation (2). Both Equation (2) and Equation (3) express the equality of the efficiency of the two cycles under specific temperature conditions. In fact, with reference

to Joule cycle 1J-2J-3J-4J, Equation (2) is valid if the Carnot cycle operates between T_X and T_R while Equation (3) is valid if the Carnot cycle operates between T and T_Y . Nowhere is made reference to the efficiency of the Carnot cycle operating between T_X and T_Y since, in such a case, its efficiency would never be equal to the efficiency of the 1J-2J-3J-4J Joule cycle. The proof of this equivalence between Equation (2) and Equation (3) of the two Carnot cycles is that the isovolumic processes 1C-X and Y-3C operate between temperatures with the same ratio since the respective extreme isothermal processes (1C-2J and 4J-3C) are connected by the adiabatic reversible processes operating between the same pressures P and P_R : therefore, T_R/T_X equals T_Y/T deriving from the ratio P/P_R which is constant. The equality between the two thermodynamic efficiencies expresses the bi-univocal relationship between the extreme temperature ratio of the Carnot cycle and the extreme pressure ratio of the Joule cycle. This relationship also establishes the equivalence of the heat-to-work conversion process at constant temperature (and variable pressure), along the isothermal curves, at higher and lower temperature, of the Carnot cycle and to its "dual" process at constant pressure (and variable temperature), along the isobaric curves, at higher and lower pressure, of the Joule cycle. In other words, the process of direct conversion into work, when heat is transmitted at constant temperature and variable pressure (decreasing) or at constant pressure and variable temperature (increasing), is equivalent under the above condition corresponding to the point X in Fig. 1B.

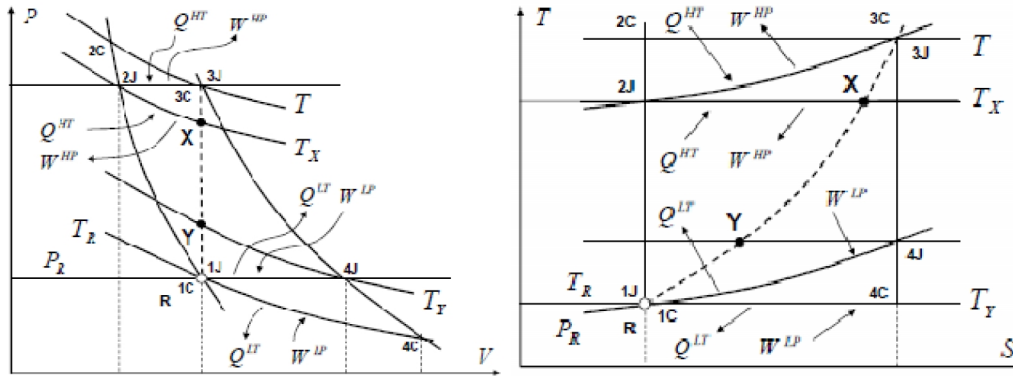


Fig. 1B. Carnot and Joule cycle relationship

The comparison of the two cycles confirms that the ideal Carnot cycle performs the maximum efficiency between two (thermal) reservoirs at constant temperature considering the ideal Joule cycle inscribed inside the Carnot cycle as depicted in Fig. 1B.

The proof of this property is based on the fact that the isothermal process between the states 2C and 3C of the Carnot cycle (considering that $P_{3C} = P_{3J}$) requires the following condition by virtue of the state equation $PV = n\overline{RT}$:

$$P_{3C}V_{3C} = P_{2C}V_{2C} \Rightarrow P_{3J} = \frac{P_{2C}V_{2C}}{V_{3C}} \tag{4}$$

and a reversible adiabatic process between states 3J and 4J of the Joule cycle:

$$\frac{P_{3J}}{P_{4J}} = \left(\frac{T_{3J}}{T_{4J}}\right)^{\frac{-K}{K-1}} \Rightarrow P_{4J} = P_{3J} \left(\frac{T_{3J}}{T_{4J}}\right)^{\frac{-K}{K-1}} \quad (5)$$

substituting the former in the last equation:

$$P_{4J} = P_{2C} \frac{V_{2C}}{V_{3C}} \left(\frac{T_{3J}}{T_{4J}}\right)^{\frac{-K}{K-1}} \quad (6)$$

Assuming T_{3J} and V_{2C} as constant, the Joule cycle can then reach the maximum efficiency in the particular case where it degenerates in the 1C-2C portion of the reversible adiabatic process limited by the higher and lower temperatures that define (maximum) Carnot efficiency; furthermore, the higher the volume, the lower the pressure ratio and hence Joule cycle efficiency.

On the other side, if the Carnot cycle is inscribed inside the Joule cycle, it can be proved that the Joule cycle reaches the maximum efficiency between two (mechanical) reservoirs at constant pressure. In fact, considering the reversible adiabatic process between states 1J and 2J of the Joule cycle:

$$\frac{T_{2J}}{T_{1J}} = \left(\frac{P_{2J}}{P_{1J}}\right)^{\frac{K-1}{K}} = \text{constant by assumption} \quad (7)$$

$$T_{1J} = T_{2J} \left(\frac{P_{2J}}{P_{1J}}\right)^{\frac{1-K}{K}} \quad (8)$$

Isobaric process of the Joule cycle between points 1J and 4J:

$$\frac{T_{4J}}{T_{1J}} = \frac{V_{4J}}{V_{1J}} \Rightarrow T_{4J} = T_{1J} \frac{V_{4J}}{V_{1J}} \quad (9)$$

Upon combining the two above Equations (8) and (9):

$$T_{4J} = T_{2J} \left(\frac{P_{2J}}{P_{1J}}\right)^{\frac{1-K}{K}} \left(\frac{V_{4J}}{V_{1J}}\right) \quad (10)$$

the condition $V_{4J} = V_{1J}$ represents the special case where the Carnot cycle degenerates into the 1J-2J reversible adiabatic process and efficiency is at a maximum since $\frac{T_{1J}}{T_{2J}}$ is the minimum value. For all other values of $V_{4J} \neq V_{1J}$, the efficiency of the Carnot cycle is lower than the efficiency of Joule cycle.

To conclude, the above highlights the fact that the ideal Joule cycle constitutes the cyclic process performing at maximum efficiency in converting heat to work at constant pressure. This result corresponds to the similar fundamental theorem relating to the ideal Carnot cycle performing at maximum efficiency in converting heat to work at constant temperature. These properties suggest a classification of the energy conversion process assuming that the Carnot and Joule cycles are symmetric being constituted by two pair of same polytropic processes. The two cycles represent two different classes of conversion cycle which may be defined as “isothermal conversion” and “isobaric conversion” respectively, no matter the polytropic processes connecting the two isothermal or isobaric processes, and thus may identify “classes of thermodynamically equivalent cycles”.

5. SPECIFIC WORK OF THE JOULE AND CARNOT CYCLES

Specific work is the result of heat and work contributions determined by the interactions between the system and the reservoir throughout whatever cyclic process and constitutes net useful work in the sense of the definition of the exergy property as per Equations.(1a) and (1b). The procedure leading to a description of the mathematical function of specific work depending on temperature and pressure is described below for ideal Joule and Carnot direct cycles. The same conclusions remain valid if reference is made to net useful heat representing the specific heat resulting from the inverse cycles by inverting the direction of all the sequential processes that constitute the two conversion cycles.

6. SPECIFIC WORK OF THE JOULE CYCLE

As far as the Joule ideal cycle is concerned, specific work over the whole cycle can be calculated by means of the following expression [11] which makes reference to Figs. 2A and 2B; the overall work balance is calculated by the contribution throughout the isobaric processes at higher and lower pressures (the two adiabatic processes give no contribution):

$$W = Q^{HT} - Q^{LT} = C_p(T_3 - T_2) - C_p(T_4 - T_1) \quad (11)$$

to render this expression non-dimensional, it is divided by $C_p T_1$:

$$\frac{W}{C_p T_1} = \frac{T_3}{T_1} - \frac{T_2}{T_1} - \frac{T_4}{T_1} + 1 = \frac{T_3}{T_1} - \left(\frac{P_2}{P_1}\right)^{\frac{K-1}{K}} - \frac{\frac{T_3}{T_1}}{\left(\frac{P_2}{P_1}\right)^{\frac{K-1}{K}}} + 1 \quad (12)$$

and adopting the symbolic convention:

$$\tau = \frac{T_3}{T_1}; \beta = \frac{P_2}{P_1}; \varepsilon = \frac{K-1}{K} \tag{13}$$

the above can be rewritten as:

$$\frac{W}{C_p T_1} = 1 + \tau - \beta^\varepsilon - \frac{\tau}{\beta^\varepsilon} \tag{14}$$

This expression of specific work depends on the extreme temperatures and extreme pressures of the Joule cycle. It shows that, for the same higher and lower pressures of the cycle, specific work always increases if T_3 increases (and or T_1 decreases), as shown in Fig. 2A.

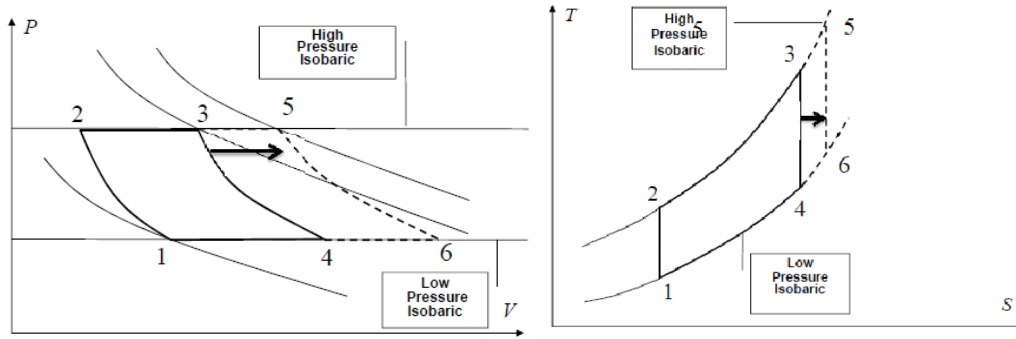


Fig. 2A. Joule cycle: constant extreme pressures and variable higher temperature

To confirm this behaviour, the existence of a minimum or maximum value of specific work function can be investigated by means of the derivation of the analytical non-dimensional specific work function with respect to τ as follows:

$$\frac{d}{d\tau} \left(\frac{W}{C_p T_1} \right) = \frac{d}{d\tau} \left(1 + \tau - \beta^\varepsilon - \frac{\tau}{\beta^\varepsilon} \right) = 1 - \frac{1}{\beta^\varepsilon} = \frac{\beta^\varepsilon - 1}{\beta^\varepsilon} \tag{15}$$

equalizing to zero:

$$\frac{d}{d\tau} \left(\frac{W}{C_p T_1} \right) = 0 \Rightarrow \frac{\beta^\varepsilon - 1}{\beta^\varepsilon} = 0 \Rightarrow \tag{16}$$

$$\Rightarrow \beta^\varepsilon = 1 \Rightarrow \beta = 1 \tag{17}$$

from which it can be deduced that specific work achieves its maximum value, at extreme higher and lower temperature variations, if the cycle's extreme higher and lower pressures are equal. This implies that the cycle degenerates into an isobaric process occurring in two

opposite directions. Hence no maximum or minimum values exist for the above Equation (14) which is thus monotone.

Vice-versa, if T_1 and T_2 (or τ) are fixed and P_1 and/or P_2 (or β) change in the direction of increasing or decreasing volume, as described in Fig. 2B, the specific work function in Equation (14), is no longer monotone. Indeed, if $P_1 = P_2$ then $\beta = 1$ and the specific work is null.

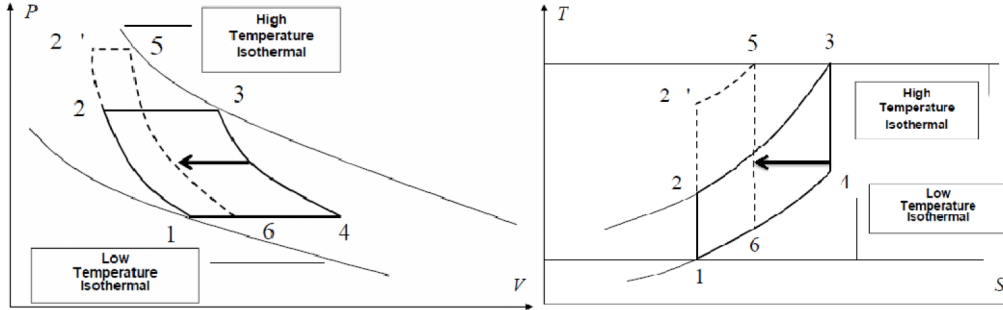


Fig. 2B. Joule cycle: constant extreme temperatures and variable higher pressure

At the same time, if $\left(\frac{P_2}{P_1}\right)^{\frac{K-1}{K}} = \frac{T_3}{T_1}$ or if $\beta^\epsilon = \tau$ which can be written as $\beta = \tau^{\frac{1}{\epsilon}}$ the

specific work is once again null. The Rolle's mathematical theorem is here applied: "a real-valued differentiable function which attains equal values at two distinct points must have a point somewhere between them where the first derivative (the slope of the tangent line to the graph of the function) is zero". By virtue of Rolle's theorem relating to a continuous and derivable function, a relative maximum or minimum value is located in between the two end points where the function itself is null; this value satisfies the following condition:

$$\begin{aligned} \frac{d}{d\beta} \left(\frac{W}{C_p T_1} \right) &= \frac{d}{d\beta} \left(1 + \tau - \beta^\epsilon - \frac{\tau}{\beta^\epsilon} \right) \\ &= \epsilon \beta^{\epsilon-1} + \epsilon \tau \beta^{-\epsilon-1} = 0 \Rightarrow \beta = \tau^{\frac{1}{2\epsilon}} \end{aligned} \tag{18}$$

It is noteworthy that if $\tau = 1$ then $\beta = 1$ necessarily and this implies that the cycle degenerates into one single point.

Fig. 2B shows how the geometry of the Joule cycle changes with a variation of extreme higher pressure while extreme temperatures of the cycle itself remain constant.

7. SPECIFIC WORK OF THE CARNOT CYCLE

With regard to the Carnot ideal cycle, specific work is now analyzed according to the same procedure, beginning with Equation (11), adopted for the Joule ideal cycle. In this case, the

overall work balance is calculated on the contribution throughout the isothermal processes at higher and lower temperatures (the two adiabatic processes give no contribution). With reference to Figs. 2C and 2D:

$$W = Q^{HT} - Q^{LT} = -\left(P_3 V_3 \ln \frac{P_2}{P_3} - P_4 V_4 \ln \frac{P_1}{P_4} \right) \quad (19)$$

The validity of state equation $PV = n\bar{R}T$ is inherent in the definition of physical exergy in Eq. (1a) and therefore can be used to obtain the following:

$$W = -\left(n\bar{R}T_3 \ln \frac{P_2}{P_3} - n\bar{R}T_4 \ln \frac{P_1}{P_4} \right) \quad (20)$$

which, upon dividing the entire expression by $n\bar{R}T_1$ to render the above function non-dimensional and since $T_1 = T_4$, the said Equation (20) becomes:

$$\frac{W}{n\bar{R}T_1} = -\frac{T_3}{T_1} \ln \frac{P_2}{P_3} + \ln \frac{P_1}{P_4} \quad (21)$$

and multiplying the two arguments of the logarithm by $\frac{P_4}{P_4}$ and $\frac{P_2}{P_2}$ respectively, the following is obtained:

$$\frac{W}{n\bar{R}T_1} = -\frac{T_3}{T_1} \ln \frac{P_4}{P_4} \frac{P_2}{P_3} + \ln \frac{P_2}{P_2} \frac{P_1}{P_4} \quad (22)$$

Considering that, for the reversible adiabatic process: $\frac{T_3}{T_4} = \left(\frac{P_3}{P_4} \right)^{\frac{K-1}{K}}$ and $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{K-1}{K}}$

then:

$$\frac{W}{n\bar{R}T_1} = -\frac{T_3}{T_1} \ln \left[\frac{P_2}{P_4} \left(\frac{T_3}{T_4} \right)^{-\frac{K}{K-1}} \right] + \ln \left[\frac{P_2}{P_4} \left(\frac{T_2}{T_1} \right)^{-\frac{K}{K-1}} \right] \quad (23)$$

Being $T_1 = T_4$ and $T_2 = T_3$ respectively, then:

$$\frac{W}{nRT_1} = -\frac{T_2}{T_4} \ln \left[\frac{P_2}{P_4} \left(\frac{T_2}{T_4} \right)^{\frac{K}{K-1}} \right] + \ln \left[\frac{P_2}{P_4} \left(\frac{T_2}{T_4} \right)^{\frac{K}{K-1}} \right] \quad (24)$$

$$\text{Assuming that } \tau = \frac{T_2}{T_4}; \beta = \frac{P_2}{P_4}; \varepsilon = \frac{K-1}{K} \quad (25)$$

the previous equation can be simplified in the form:

$$\frac{W}{nRT_1} = -\tau \ln \beta \tau^{\frac{1}{\varepsilon}} + \ln \beta \tau^{\frac{1}{\varepsilon}} \quad (26)$$

Although this expression of specific work calculated for the Carnot cycle differs from the one calculated for the Joule cycle, it again depends on both extreme temperatures and pressures. This expression demonstrates that, if the extreme cycle temperatures are equal, specific work always increases if P_3 increases and or P_1 decreases as shown in Fig. 2C.

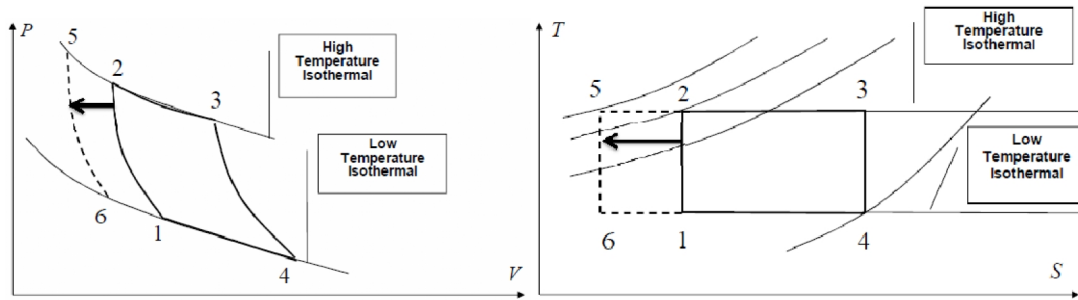


Fig. 2C. Carnot cycle: constant extreme temperatures and variable higher pressure

This behavior can be confirmed by calculating the value of the cycle's extreme pressures determining the maximum value of specific work for the Carnot cycle. The result is:

$$\begin{aligned} \frac{d}{d\beta} \left(\frac{W}{nRT_1} \right) &= \frac{d}{d\beta} \left(-\tau \ln \beta \tau^{\frac{1}{\varepsilon}} + \ln \beta \tau^{\frac{1}{\varepsilon}} \right) \\ &= (1-\tau) \cdot \left(-\frac{\tau^{\frac{1}{\varepsilon}}}{\beta \tau^{\frac{1}{\varepsilon}}} \right) = \frac{1-\tau}{\beta} \end{aligned} \quad (27)$$

equalizing to zero:

$$\frac{d}{d\beta} \left(\frac{W}{nRT_1} \right) = 0 \Rightarrow \tag{28}$$

$$\Rightarrow \frac{1-\tau}{\beta} = 0 \Rightarrow \tau = 1 \tag{29}$$

It can be deduced that, with respect to the Joule cycle, swapping temperature with pressure implies that the Carnot cycle is characterized by a maximum value of specific work if and only if the cycle's extreme temperatures are equal and the cycle itself therefore degenerates into an isothermal process executed in the two directions.

Vice-versa, if the Carnot cycle's extreme pressures are fixed so that β is constant and the cycle's extreme temperatures change by means of ratio τ as shown in Fig. 2D, it is possible to investigate what value of τ will maximize specific work.

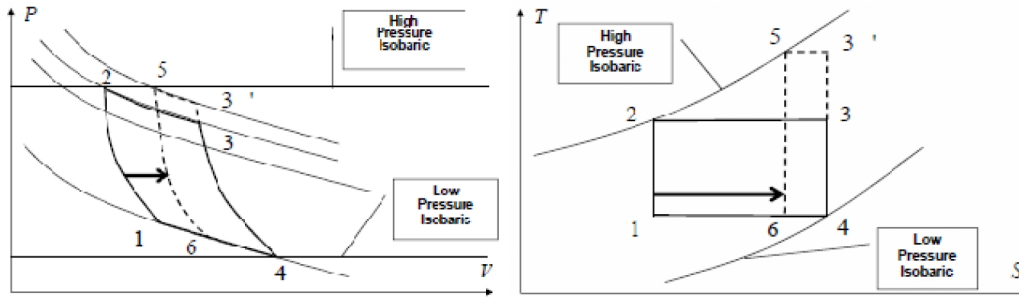


Fig. 2D. Carnot cycle: constant extreme pressures and variable higher temperature

Assuming that $\frac{dW}{nRT_1} = 0$ the following is obtained:

$$\tau \ln \beta \tau^{-\frac{1}{\epsilon}} = \ln \beta \tau^{-\frac{1}{\epsilon}} \tag{30}$$

which is verified if $\tau = 1$ or if $\beta \tau^{-\frac{1}{\epsilon}} = 1$ or if $\tau = \beta^\epsilon$ or if $\beta = \tau^{\frac{1}{\epsilon}}$ and, as will be noted, this last expression equals the corresponding one derived from the Joule cycle.

The equality of the two expressions proves the symmetry of the effect due to temperature ratios and pressure ratios that render null the specific work of the Carnot cycle and Joule cycle respectively and hence the role of temperature and pressure in the two cycles.

Furthermore, also in the Carnot cycle, if specific work is null for two different values of property τ then, by virtue of the Rolle's theorem, there must be at least one value of τ where the specific work function is maximum. This value can be calculated by deriving the non-dimensional expression of specific work, with respect to τ :

$$\begin{aligned} \frac{d}{d\tau} \left(\frac{W}{nRT_1} \right) &= \frac{d}{d\tau} \left(-\tau \ln \beta \tau^{\frac{1}{\varepsilon}} + \ln \beta \tau^{\frac{1}{\varepsilon}} \right) \\ &= \frac{d}{d\tau} \left[(1-\tau) \cdot \ln \beta \tau^{\frac{1}{\varepsilon}} \right] = 0 \end{aligned} \quad (31)$$

which becomes, after calculating the derivative:

$$\frac{\tau-1}{\tau\varepsilon} - \ln \beta \tau^{\frac{1}{\varepsilon}} = 0 \Rightarrow \frac{\tau-1}{\tau} = \ln \frac{\beta}{\tau} \Rightarrow \frac{\tau-1}{\tau} + \ln \tau = \ln \beta \quad (32)$$

This expression provides, for any fixed value of β , the corresponding value of τ to determine the specific work of the Carnot cycle that gives the maximum value of its function. If $\beta=1$, consequently $\tau=1$ in the previous Equation (32); this implies, similarly to the conclusion deduced for the Joule cycle, that the Carnot cycle degenerates into one single point.

Fig. 2D shows the change Carnot ideal cycle geometry for the variation in extreme temperatures while extreme pressures remain constant.

In particular, whatever the Carnot cycle between two constant extreme pressures, work $dW_{ISOTHERMAL}^{HT}$, for an infinitesimal cycle, is characterized by (maximum) specific work that tends to decrease if the adiabatic process of this infinitesimal cycle is adjusted in the direction of the highest or lowest volume range with a consequent the specific work decrease in both cases on the basis of the conclusions reached in the previous sections. Thus, a Joule cycle can be accomplished through an infinite series of infinitesimal Carnot cycle with the result that Joule cycle maximum specific work remains constant if isobaric processes are finite. Vice versa, whatever the Joule cycle between two constant extreme temperatures, the same conclusion is validated for the Carnot cycle.

As a result of the above remarks on performance optimization of the Carnot and Joule cycles, it may be inferred that efficiency and specific work or heat trends, even in the special case of ideal system and reversible processes, are determined by system temperatures and pressures with opposite roles in the two cycles.

8. ISOTHERMAL AND ISOBARIC RESERVOIR

The thermal reservoir and mechanical reservoir [7,12], used to accomplish the lower temperature isothermal process of the Carnot cycle and the lower pressure isobaric process of the Joule cycle respectively, may be constituted by different and independent physical bodies characterized by finite masses undergoing processes while interacting with the system. This implies that the (constant) temperature of the thermal reservoir T_R (at variable pressure) can, as a rule, be different from the (variable) temperature of the mechanical reservoir (at constant pressure); similarly, the constant pressure of mechanical reservoir P_R (at variable temperature) can, as a rule, be different from the variable pressure of the

thermal reservoir (at constant temperature). Hence, the thermal reservoir may be regarded as an isothermal reservoir undergoing an isothermal process at constant temperature and variable pressure and the mechanical reservoir as an isobaric reservoir undergoing an isobaric process at constant pressure and variable temperature.

The Carnot ideal cycle is symmetric [13] and operates between two constant extreme temperatures. In particular, the lower temperature is kept constant by means of an isothermal reservoir at constant temperature T_R . The system pressure, undergoing the lower isothermal process, contributes entirely to the work interaction transmitted to the external system. However, if the system undergoes the additional effect of constant pressure P_R due to interaction with an isobaric reservoir, then the cycle processes are affected by P_R and the efficiency and specific work depend on pressure as well as temperature. In fact, the property of symmetry [13] implies that:

$$V_1 V_3 = V_2 V_4 ; P_1 P_3 = P_2 P_4 ; T_1 T_3 = T_2 T_4 \quad (33a)$$

but, taking into account P_R , equality $P_1 P_3 = P_2 P_4$ becomes:

$$(P_1 - P_R) \cdot (P_3 - P_R) = (P_2 - P_R) \cdot (P_4 - P_R) \quad (33b)$$

so that the property of symmetry is no longer valid. Consequently, the efficiency of the Carnot cycle also depends on the pressure difference, in addition to the temperature difference, between system and reservoir.

On the other side, the Joule ideal cycle, which depends on extreme pressures only, constitutes the pressure-dependent cycle capable of providing the maximum efficiency and maximum specific work with respect to the mechanical reservoir at constant pressure as proved in the previous section. Nevertheless, since the property of symmetry (33a) is no longer valid if the temperature of reservoir T_R is not null and taking into account T_R , equality $T_1 T_3 = T_2 T_4$ becomes:

$$(T_1 - T_R) \cdot (T_3 - T_R) = (T_2 - T_R) \cdot (T_4 - T_R) \quad (33c)$$

so that the property of symmetry is no longer valid and the Joule cycle depends on pressure and temperature as well. The consequence is that, even in this case, if the system undergoes the additional effect of constant temperature T_R due to an isothermal reservoir, then the cycle processes are affected by T_R and the efficiency of the Joule cycle now depends on temperature as well as pressure. Since the property of symmetry is no longer valid if the temperature of reservoir T_R is not null, then the result is that the Joule cycle efficiency depends on the temperature difference, in addition to the pressure difference, between system and reservoir. The result, and the novelty proposed, is that physical exergy may be regarded as a temperature-and-pressure-dependent property in the general case of any system interacting with two independent isothermal and isobaric reservoirs.

9. CONCLUSIONS

The first result achieved by the present study is that the Joule ideal cycle produces maximum efficiency between two constant extreme pressures as does the Carnot ideal cycle between two constant extreme temperatures provided that the two cycles operate under the ideal conditions on which the definition of the exergy property is based. Furthermore, the procedure developed above demonstrates that the Carnot and Joule cycles achieve a maximum of specific work (direct cycle) corresponding to maximum net useful work or a maximum of specific heat (inverse cycle) corresponding to maximum net useful heat. The second result is that, if interacting with the system, isothermal reservoir temperature T_R and isobaric reservoir pressure P_R affect the properties of these two symmetric cycles so that Carnot cycle efficiency depends on both temperature and pressure and, similarly, Joule cycle efficiency depends on both pressure and temperature. These arguments constitute the rationale for adopting the Carnot (direct) ideal cycle to express thermal exergy and the Joule (inverse) ideal cycle to express mechanical exergy as contributions to physical exergy. Indeed, thermal exergy is the maximum net useful work converted from heat withdrawn from a system interacting with an isothermal reservoir and mechanical exergy is the maximum net useful heat converted from work withdrawn from a system interacting with an isobaric reservoir. The result is general and applicable to any cyclic or non-cyclic process.

Considering the equivalence and inter-convertibility of useful work and useful heat, it makes sense to seek a formulation of the exergy property that also takes into account the pressure of the system and isobaric reservoir in addition to the temperature of the system and isothermal reservoir to express physical exergy in a generalized equation related to, and constituted by, thermal and mechanical contributions:

$$EX^{PHYSICAL} = EX_{REV}^T + EX_{REV}^M \quad (34)$$

This definition, relating to the Carnot and Joule cycles, may be extended and applied to systems characterized by arbitrary equation of state [14,15,16], and interacting with multiple reservoirs, representing the basis for future research and the outset of further development leading to a generalization of the concept of physical exergy property.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Moran MJ, Sciubba E. Exergy analysis: principles and practice. Journal of Engineering for Gas Turbine and Power. 1994;116:285-290.
2. Kotas TJ. The Exergy Method of Thermal Plant Analysis. Krieger Publishing Company: FL, USA; 1995.
3. Dunbar WR, Lior N, Gaggioli RA. The component equations of energy and exergy. Journal of Energy Resources Technology. 1992;114:75.
4. Gaggioli RA. Available energy and exergy. International Journal of Applied Thermodynamics. 1998;1(1-4):1-8.

5. Gaggioli RA, Richardson DH, Bowman AJ. Available energy – Part I: Gibbs revisited. *Journal of Energy Resources Technology*. 2002;124:105-115.
6. Gaggioli RA, Paulus DM Jr. Available energy – Part II: Gibbs extended. *Transaction of the ASME. Journal of Energy Resources Technology*. 2002;124:110-115.
7. Gyftopoulos EP, Beretta GP. *Thermodynamics: Foundations and Applications*. Mineola, New York: Dover Publications; 2005.
8. Palazzo P. An Extended Formulation of Physical Exergy. *IMECE*;2010-37824 pp. 559-567; 9 pages doi: 10.1115/IMECE2010-37824. *Proceedings of ASME-IMECE 2010 Congress, Vancouver, British Columbia, Canada*
9. Sandler SI. *Chemical and engineering thermodynamics*. 3rd edn. New York; Wiley; 1999
10. Hatsopoulos GN, Keenan JH. *Principles of general thermodynamics*. Wiley; 1965.
11. Acton O, Caputo C. *Impianti Motori*. Torino; UTET; 1992. ISBN 88-02-04668-9.
12. Gaggioli R. The dead state. *Proceedings of 25th ECOS Conference, Perugia, Italy; 2012*.
13. Acton O, Caputo C. *Introduzione allo Studio delle Macchine*. UTET; 1979. ISBN 88-02-02556-8.
14. Gonzalez-Ayala, Angulo-Brown. Some remarks on Carnot's theorem. *Proceedings of 25th ECOS Conference, Perugia, Italy; 2012*.
15. Agrawal D, Menon VJ. The Carnot cycle with the Van der Waals equation of state. *Eur. J. Physics*. 1990;11;88-90.
16. Tjiang P, Sutanto S. The efficiency of the Carnot cycle with arbitrary gas equation of state. 2006;27;719-726.

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