Restrictions on linear heat capacities from Joule-Brayton maximum-work cycle efficiency

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This paper discusses the possibility of using the Joule-Brayton cycle to determine the accessible value range for the coefficients a and b of the heat capacity at constant pressure C_p, expressed as $C_p = a + bT$ (with T the absolute temperature) by using the Carnot theorem. This is made for several gases which operate as the working fluids. Moreover, the landmark role of the Curzon-Ahlborn efficiency for this type of cycle is established.

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I. INTRODUCTION

As is well known, the Carnot theorem establishes a superior bound for the efficiency of thermal cycles performing between two thermal baths at absolute temperatures T_h and $T_c < T_h$. This limiting efficiency is the Carnot efficiency, given by [1]

$$\eta_C = 1 - \tau, \tag{1}$$

where $\tau = T_c/T_h$. Any other thermal cycle with more than two thermal reservoirs, but with T_h and T_c as their extreme temperatures, has an efficiency lower than η_C (although fully regenerative cycles such as the Stirling and Ericsson can also reach η_C). For example, reversible cycles such as the Otto, Joule-Brayton (JB), Diesel, and Atkinson cycles, which have an infinite number of auxiliary reservoirs, necessarily have efficiencies below η_C. Otto and JB cycles operating at a maximum-work (MW) regime have efficiencies given by the so-called Curzon-Ahlborn efficiency

$$\eta_{CA} = 1 - \sqrt{\tau}, \tag{2}$$

when the working substance has a constant heat capacity [2]. On the other hand, Diesel and Atkinson cycles have MW efficiencies very close to η_{CA} [2,3]. Thus, any working substance operating this type of cycle must have thermal properties consistent with the Carnot theorem. Within this context, the consistency of JB cycle efficiencies with the Carnot theorem can be used as a discriminator of the thermal property models of working substances. A very important thermal property involved in thermal cycles is the heat capacity of working fluids. For example, Gilbert and Lewis have shown that the theoretical values for heat capacities at constant pressure C_p [4] for several gases can be represented within an error of 1% by a series of the form

$$C_p = a + bT + cT^2 + \cdots, \tag{3}$$

where T is the absolute temperature and the coefficients $a,b,c,\ldots$ are calculated by means of theoretical quantum methods, although series such as Eq. (3) can be also considered as empirical relations [4,5]. In general, the coefficient c is four orders of magnitude smaller than coefficient b, which is three magnitude orders smaller than coefficient a [4,5]. For this reason we shall treat a gas with a heat capacity $C_p = a + bT$. This gas will perform as a working fluid in a JB cycle.

This article shows that there exists a set of a and b values which lead to MW-JB efficiencies η_{MW} with negative values or above η_C. Evidently these values are forbidden by the Carnot theorem. Furthermore, there is another set of a and b values which lead to $0 \leqslant \eta_{MW} \leqslant \eta_C$, as it must be. By means of the definition of a parameter $\epsilon = b/a$, a ϵ-τ plane is constructed which can be split into well defined regions, some where $0 \leqslant \eta_{MW} \leqslant \eta_C$ (permitted regions) and some others where this is not satisfied (forbidden regions). Interestingly, the permitted regions correspond to experimentally reported a and b values [4,5]. The forbidden regions are associated with a and b values (through ϵ) that have not been reported, as is expected. Thus, this simple procedure can be used to test experimental or theoretical values of the aforementioned coefficients regarding their consistency with the second law of thermodynamics. Furthermore, when $\epsilon \to 0$ ($C_p \to$ const), the η_{MW} contained in the permitted regions tends to η_{CA}, assigning to η_{CA} a landmark role for cycle efficiencies depending on working substance properties. The present article is organized as follows: In Sec. II JB cycles are analyzed when the working fluids have a linear heat capacity; in Sec. III a discussion on permitted and forbidden regions is presented. Finally, some concluding remarks are given.

II. JOULE-BRAYTON CYCLE FOR A LINEAR HEAT CAPACITY

The efficiency of a JB cycle operating at MW will be calculated by using a gas with heat capacity at a constant pressure given by

$$C_p = a + bT, \tag{4}$$

with a and b being real constants. The JB cycle consists of two adiabatic processes and two processes at constant pressure (see Fig. 1). Following the cycle depicted in Fig. 1, the input and output heats are given by the equations

$$Q_{\text{in}} = \int_T^{T_h} C_p d\mathcal{T} = a\int_T^{T_h}(1+\epsilon\mathcal{T})d\mathcal{T} = a\left[(T_h - T) + \frac{\epsilon}{2}\left(T_h^2 - T^2\right)\right] \tag{5}$$

and

$$Q_{\text{out}} = \int_{T'}^{T_c} C_p d\mathcal{T} = a\int_{T'}^{T_c}(1+\epsilon\mathcal{T})d\mathcal{T} = a\left[(T_c - T') + \frac{\epsilon}{2}\left(T_c^2 - T'^2\right)\right]. \tag{6}$$

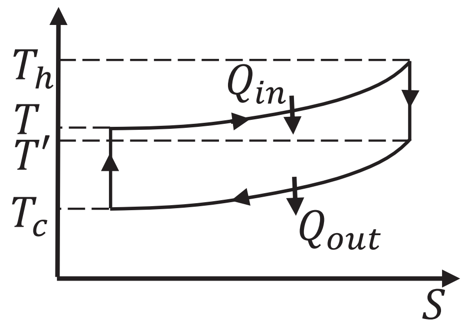

FIG. 1. T-S diagram of a reversible Joule-Brayton cycle, which is equivalent to an Otto cycle with isochores instead of isobars.

The temperatures T and T' are restricted by the conditions that the total entropy change is zero, and that the work is maximum. The total entropy change is given by

$$\Delta S = \int_{T}^{T_h} \frac{C_p}{\mathcal{T}} d\mathcal{T} + \int_{T'}^{T_c} \frac{C_p}{\mathcal{T}} d\mathcal{T} = a\left[\ln\left(\frac{T_h T_c}{T\,T'}\right) + \epsilon(T_h + T_c - T - T')\right] = 0, \quad (7)$$

which results in the condition,

$$T = \epsilon^{-1}\text{ProductLog}\left[\epsilon e^{\epsilon(T_h+T_c-T')}\frac{T_h T_c}{T'}\right], \quad (8)$$

where the ProductLog[z] is the principal value of the Lambert W-function which is the inverse function of $z = we^w$ (Ref. [6]). This condition [Eq. (8)] gives the MW for a cycle with given T_h, T_c, and T'. In addition, the maximum of all these works can be obtained by replacing Eq. (8) in the work $W = |Q_{\text{in}}| - |Q_{\text{out}}|$ and maximizing with respect to the temperature T', giving the following condition:

$$T e^{\epsilon T} = T' e^{\epsilon T'} = \sqrt{T_h T_c} e^{\epsilon(T_h+T_c)/2}. \quad (9)$$

The equality $T = T'$ is maintained as the MW condition, just as it occurs in the case of constant C_p [2,3] and when $C_p = \alpha T^n$, α and n being constant real numbers [7]. Note that Eq. (9) reduces to the known result for constant C_p when $\epsilon = 0$. Finally, the efficiency $\eta = 1 - |Q_{\text{out}}|/|Q_{\text{in}}|$ at the MW regime η_{MW} is given by

$$\eta_{\text{MW}} = \eta_{\text{MW}}(\epsilon,\tau,T_h) = 1 - \sqrt{\tau}\left(\frac{-\epsilon\sqrt{\tau T_h} - \frac{1}{2}\epsilon^2(\tau T_h)^{3/2} + \frac{2g+g^2}{2\sqrt{\tau T_h}}}{\epsilon\sqrt{T_h} + \frac{1}{2}\epsilon^2 T_h^{3/2} - \frac{2g+g^2}{2\sqrt{T_h}}}\right), \quad (10)$$

where g is defined as the solution of the equation $ge^g = \epsilon\sqrt{\tau}T_h e^{\epsilon T_h(1+\tau)/2}$. In Fig. 2 η_{MW} vs τ is depicted for several values of ϵ by using Eq. (10). In order to generate Fig. 2, numerical values for ϵ and T_h are proposed, and τ is taken from the interval (0,1). This figure shows that for $\epsilon > -0.003$ K^{-1} the depicted MW efficiencies fulfill the Carnot theorem, that is, $0 \leqslant \eta_{\text{MW}} \leqslant \eta_C$, and for $\epsilon < -0.003$ K^{-1} the MW efficiencies do not. In $\epsilon = -0.003$ K^{-1} the efficiency curve has two behaviors: one in agreement with the Carnot theorem for $\tau \in (0,0.15)$ and also for $\tau \in (0.33,0.35)$, and the other with nonphysical values for η_{MW} in the intervals $\tau \in (0.15,0.33)$

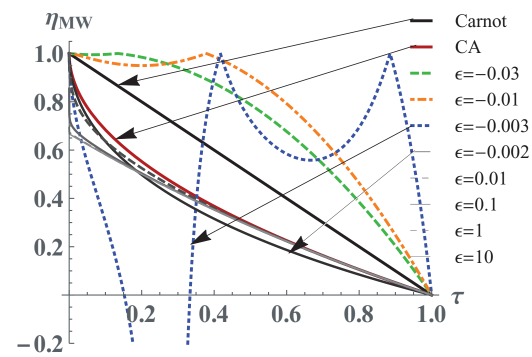

FIG. 2. (Color online) Efficiency at MW η_{MW} vs τ for several values of ϵ at fixed $T_h = 500$ K. A plot exists, such as the one depicted in this figure, for each value of $T_h > 0$ K.

(forbidden by the first law) and $\tau \in (0.35,1)$ (forbidden by the Carnot theorem). The only value that reproduces the CA efficiency is $\epsilon = 0$ K^{-1}, that is, the constant heat capacity case [2,3,7]. For the case discussed here, as can be seen in Fig. 2, η_{CA} works as a closer limit than η_C for cycles depending on the working fluid properties and performing between the same extreme temperatures.

The efficiencies with nonphysically acceptable values have to do with the unrealistic solutions for $T = T'$, as can be seen in Fig. 3. The MW condition for a range of values of ϵ leads to T,T' values outside the interval (T_c,T_h) which are not permitted for a valid JB cycle between these two extreme temperatures. By means of Eq. (9) the condition that $T = T' = T_c$ gives the threshold value of ϵ at which the efficiency starts to present anomalous behaviors for given T_c and T_h,

$$\epsilon_{\text{crit}} = \frac{\ln(\tau)}{T_h(1-\tau)}. \quad (11)$$

If in addition we demand that for any $0 < T_c < T_h$ the efficiency must be always well behaved, then the critical value of ϵ is found in the limit $\tau \to 1$,

$$\lim_{\tau\to 1}\epsilon_{\text{crit}} = \epsilon^*_{\text{crit}} = -\frac{1}{T_h}. \quad (12)$$

For $T_h = 500$ K, $\epsilon^*_{\text{crit}} = -0.002$ K^{-1}, that is, for $\epsilon < -0.002$ K^{-1}, the efficiency will present an anomalous behavior. The crossing point A between the calculated intermedi-

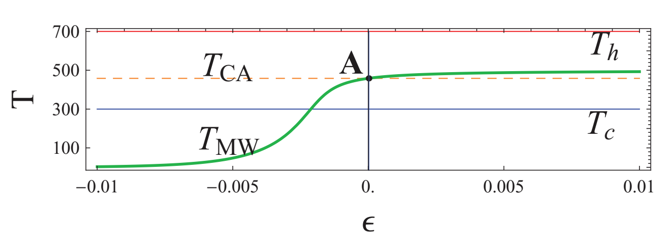

FIG. 3. (Color online) Intermediate temperatures T,T' for the MW-JB cycle operating between the extreme temperatures $T_h = 700$ K and $T_c = 300$ K. The dashed line represents $\sqrt{T_h T_c}$, which is the C_p constant case. The S-shaped curve is the solution of Eq. (9). The point A corresponds to the crossing point between T_{MW} and $\sqrt{T_h T_c}$ at $\epsilon = 0$ K^{-1}.

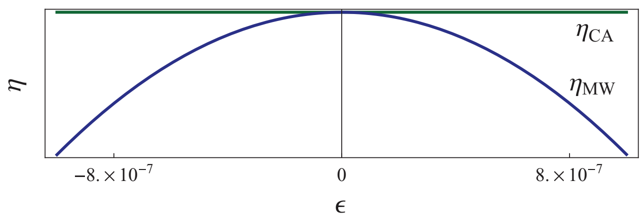

FIG. 4. (Color online) $\eta_{\rm MW}(\epsilon)$. The horizontal line corresponds to $\eta_{\rm CA}$ for $T_h = 700$ K and $T_c = 300$ K. $\eta_{\rm CA}$ is the maximum value of the permitted $\eta_{\rm MW}$ for this type of heat capacity, and corresponds to the case of $\epsilon = 0$ K^{-1}.

ate temperatures and the intermediate CA-type temperature ($\sqrt{T_c T_h}$) [2,3,7] is located only at $\epsilon = 0$ K^{-1} (see Fig. 3).

As previously mentioned, in the case under study, $\eta_{\rm CA}$ plays a very important role. As a matter of fact, as can be seen in Fig. 4, at $\epsilon = 0$, the values of $\eta_{\rm MW}$ within the permitted region reach their maximum value, which is $\eta_{\rm CA}$. That is, for all the possible values of the coefficients a and b, those where $b = 0$ give the maximum efficiency in the MW regime. Then the CA efficiency takes once more an outstanding role not only in maximum power engines [8–16], but also in reversible cycles operating at MW, as can be found in some other articles [2,3,7]. A possible explanation for this fact can be given by analyzing Fig. 2 from Ref. [7], for the so-called symmetric cases (equal heat capacity in the input and output heat exchange processes). In that figure a convex curve of $\eta_{\rm MW}$ vs n is depicted for the case $C_p = \alpha T^n$ mentioned before just after Eq. (9). The curve shows how for $C_p = \alpha$ ($\eta_{\rm MW} = \eta_{\rm CA}$) in $n = 0$, up to $n = 1$; that is, when $C_p = \alpha T$, $\eta_{\rm MW}$ is evidently a decreasing function lower than $\eta_{\rm CA}$. A heat capacity of the form $C_1 = \alpha$ always has a bigger efficiency than another with heat capacity $C_2 = \beta T$ regardless of the α and β constant values. Their respective efficiencies are $\eta_1 = \eta_{\rm CA}$ and $\eta_2 = \eta_{\rm MW}(C_p = \beta T)$. With this in mind, it is possible to construct a third heat capacity $C_3(t) = t\alpha + (1-t)\beta T$ in such a way that by varying t from 0 up to 1, $C_3(t)$ goes from C_2 to C_1. The corresponding efficiency at MW will be denoted as η_3. The net result for this definition of the heat capacity is that, now in Eq. (10), $\epsilon \to \frac{1-t}{t}\epsilon$. In this way a continuous transformation from η_1 to η_2 is obtained with the same considerations on the values of ϵ. When t goes from 0 to 1, also η_3 goes from η_2 to $\eta_1 > \eta_2$, but never exceeding this value, proving that η_3 is bounded by the value of $\eta_1 = \eta_{\rm CA}$. Three examples of JB cycles are depicted in Fig. 5 for different values of ϵ.

III. PERMITTED AND FORBIDDEN REGIONS

In Fig. 6, there are well defined separated regions, where in some the efficiencies have nonphysically accepted values (forbidden regions) and in others (in color) the efficiencies are consistent with the Carnot theorem (permitted regions), bounded by the curves corresponding to the conditions $\eta_{\rm MW} = \eta_C$ and $\eta_{\rm MW} = 0$. Since the MW efficiency is a function depending on ϵ, τ, and T_h, there are an infinite number of such boundaries in the ϵ-τ plane (for each value of $T_h > 0$). Three examples are depicted in Fig. 6 in which the condition $0 \leqslant \eta_{\rm MW} \leqslant \eta_C$ is fulfilled for a certain T_h. From left to right the colored areas correspond to the permitted regions

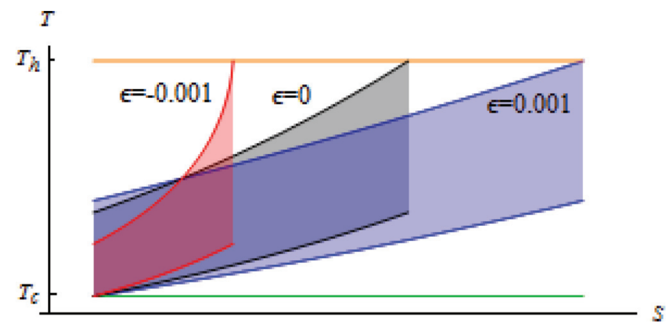

FIG. 5. (Color online) Three JB cycles for different values of ϵ in a T-S plane. As ϵ deviates from 0, the efficiency of the cycle diminishes. The temperatures considered are $T_h = 950$ K, $T_c = 290$ K, and $\epsilon = -0.001$ K^{-1} (small cycle), $\epsilon = 0$ K^{-1} (medium cycle), and $\epsilon = 0.001$ K^{-1} (large cycle). The small and large cycles have efficiencies below $\eta_{\rm CA}$.

at $T_h = \{300$ K,2000 K,25 000 K$\}$, respectively. Note that, according to Fig. 2, for each value of T_h there exists a value of ϵ with two behaviors (one permitted and another forbidden). This is reflected in Fig. 6 in the case $T = 300$ K, through the green "island" at the left side of the figure. When the temperature T_h grows, the corresponding boundaries tend to vertical lines located at $\epsilon = 0$ K^{-1}. According to the reported data in Refs. [4,5], the substance with the lowest value of ϵ is the molecule H_2, with $\epsilon = -2.88 \times 10^{-4}$ K^{-1}. This molecule has a binding energy around $T_b \sim 10^5$ K, and up to this temperature the experimental data reported do not violate the Carnot theorem. By taking experimental values for a and b for 14 gases in Ref. [4] and 22 from Ref. [5], all of them are located in the permitted areas in Fig. 6. From these 30 substances (excluding repeated cases), only two (H_2 and P_4) have an $\epsilon < 0$ K^{-1}, the H_2 with the value referred to above and the P_4 with an $\epsilon = -2.05 \times 10^{-4}$ K^{-1} and the other 28 substances have ϵ reported in the interval ($3.082\,19 \times 10^{-5}$ K^{-1},0.005 336 K^{-1}) [4,5]. The temperature interval where the data were obtained is typically between 290 and 1800 K [4]. In this way, by taking $T_h = 2000$ K as in Fig. 6, it is guaranteed that all data are contained in the

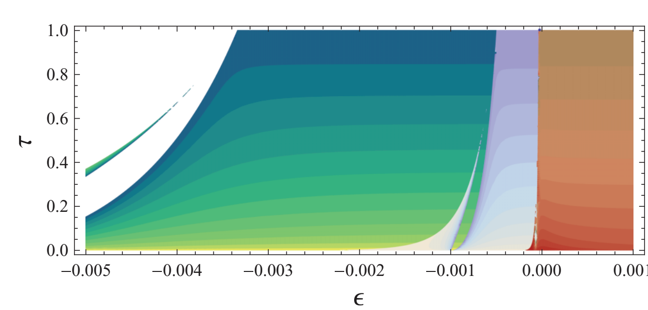

FIG. 6. (Color online) Three cases in which the condition $0 \leqslant \eta_{\rm MW} \leqslant \eta_C$ is fulfilled for a certain value of T_h. From left to right the colored regions correspond to $T_h = \{300$ K,2000 K,25 000 K$\}$, respectively. The reported ϵ values for several gases are located at the right side of the vertical line located at $\epsilon = -2.88 \times 10^{-4}$ K^{-1} (for H_2).

permitted region, including those with $\epsilon < 0\ \mathrm{K}^{-1}$. As stated before, for growing T_h the boundary between the permitted and forbidden regions tends to the vertical line at $\epsilon = 0\ \mathrm{K}^{-1}$. Thus, all $\epsilon > 0\ \mathrm{K}^{-1}$ are allowed. In order to exclude the $\epsilon < 0\ \mathrm{K}^{-1}$ cases, $T \sim 10^6$ K is needed. Therefore, in practice, all reported values belong to the physically accepted region. This simple thermodynamic procedure allows a first approach to the thermodynamical constraints of these kinds of experimental coefficients.

IV. CONCLUDING REMARKS

In summary, throughout the limits imposed by the Carnot theorem to the thermal efficiencies, in particular to the JB cycle, a simple procedure to bound the range of physically accessible values of the coefficients a,b has been proposed. Furthermore, the outstanding role of η_{CA} as a superior limit for MW-JB efficiencies, for the case of thermal efficiencies which depend on working fluid properties, has been clearly established. This procedure can be applied step by step to any cycle presenting a symmetry as the JB engine [7], such as the case of the Otto cycle using a linear C_V instead of C_p. Finally, it is notable that the MW condition for JB cycles performing with working fluids with both constant C_p or $C_p = \alpha T^n$, that is, equal intermediate temperatures, $T = T'$, is fulfilled by fluids with $C_p = a + bT$.

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