

On endoreversible thermodynamic potentials

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ABSTRACT. We discuss the method to construct finite-time thermodynamic potentials proposed by Salamon, Andresen and Berry. We find that this method does not lead to suitable potentials for endoreversible thermal cycles. We propose an alternative manner to define an endoreversible thermodynamic potential that permits to recover the appropriate endoreversible (finite-time) efficiency for a Curzon and Ahlborn cycle. The proposed endoreversible potential also allows us to obtain a generalized Clausius-Clapeyron equation for a finite time liquid-vapor transition. This procedure is equivalent to those consisting in getting a finite-time Clausius-Clapeyron equation by means of a generalized thermodynamic graphic method.

RESUMEN. Discutimos el método propuesto por Salamon, Andresen y Berry para construir potenciales termodinámicos a tiempo finito. Encontramos que este método no conduce a potenciales adecuados para ciclos térmicos endorreversibles. Proponemos una manera alternativa para definir un potencial termodinámico endorreversible que permite recuperar apropiadamente la eficiencia endorreversible (a tiempo finito) de un ciclo de Curzon y Ahlborn. El potencial endorreversible propuesto permite obtener una ecuación generalizada de Clausius-Clapeyron para una transición líquido-vapor a tiempo finito. Este procedimiento es equivalente a aquel que consiste en la obtención de una ecuación de Clausius-Clapeyron mediante un método gráfico generalizado.

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1. INTRODUCTION

In the last two decades a finite-time thermodynamics (FTT) has been developed [1,7]. FTT has been conceived as an extension of classical equilibrium thermodynamics (CET) for processes which occur endoreversibly; *i.e.*, processes where the system undergoes internally reversible transformations, but it is irreversibly coupled with its surroundings. One example of this situation is attained by thermal engines exchanging heat with suitable heat reservoirs [1-5]. The use of the endoreversibility condition requires that the internal relaxation times of the working substance be negligibly short compared to the time scale of the process to be considered. The FTT formalism has been very useful for modeling thermal engines in a more realistic context than those models obtained from

CET [6–10]. The FTT models have also permitted to obtain optimized configurations of several macroscopic systems by considering finite irreversible rate processes in the couplings between the system and its surroundings [11–15]. One of the main goals of the FTT formalism namely to construct a theoretical framework for macroscopic processes which occur in finite-time, producing entropy due at least to certain kind of irreversibilities has been achieved only in part. In the spirit of this objective, Salamon, Andresen and Berry (SAB) published an interesting paper [16] where they present a generalization of the thermodynamic potential concept for finite-time processes. They illustrated the proposed method by the construction of the finite-time potential for a process consisting in the expansion of a gas in a piston while it is receiving heat from a thermal reservoir according to the Newton's law of heat conduction. The considered system undergoes a quasi-static process with entropy production due to two irreversible phenomena: finite heat exchange and irreversible expansion with friction. According to SAB, the potential function, P , obtained for this process, has the property that $W_{\text{irr}} = \Delta P = P_f - P_i$ *i.e.*, ΔP gives the value of the useful work delivered in that irreversible quasi-static process. SAB use the word "potential" to mean a function of state whose changes give (or bound) the value of a process variable such as heat or work.

In this paper, in Sect. 2, we present a brief review of the SAB-method for constructing finite-time potentials. In Sect. 3 we analyze the properties of the finite-time potential, P , constructed by SAB for the quasi-static irreversible expansion of an ideal gas. We show that the function P , reproduces well the maximum work obtained in the reversible limit, but it has not the ability to lead to the endoreversible efficiency of a typical finite-time thermal cycle like the Curzon and Ahlborn cycle. In Sect. 4, we propose an alternative way for defining endoreversible finite-time potentials and we show that these functions have the same properties of equilibrium potentials as the Gibbs free energy. We use the endoreversible Gibbs potentials to obtain a Clausius-Clapeyron equation compatible with those obtained recently by a generalized method of the Carnot cycles [17].

2. SAB-POTENTIALS FOR FINITE-TIME PROCESSES

Within the context of conventional time-independent thermodynamics, SAB [16] developed an algorithm to construct potentials P that define the extremal values of work for processes with arbitrary constraints. That algorithm is based in two theorems extending the capability of thermodynamics from reversible processes to one class of time-dependent processes. They also show how such potentials can be constructed for a system whose time-dependence is of first order. As is well known [18], the change of a conventional thermodynamic potential, (as the Gibbs function G or the Helmholtz potential F), between two extreme states i and f , is linked with the work delivered W_{if} , during the process, by inequalities such as $W_{if} \leq -\Delta G_{if}$ for isobaric-isothermic processes; and $W_{if} \leq -\Delta F_{if}$ for isochoric-isothermic processes. The equal sign is held only for the reversible case and it represents the maximum work obtainable from the corresponding process. When irreversible dissipation in the process is considered, then $W_{\text{irr}} < W_{\text{max}}$ is obtained, for the same extreme states. Within the FTT context the problem was stated of how to get new functions of state whose changes between extreme states have the capability of giving

the irreversible work, *i.e.*, functions that replace the CET inequalities by FTT equalities. This was precisely the proposal of Salamon *et al.* and in this way, they contributed to the construction of a FTT theory of processes. We now present the SAB-method.

In a reversible process, heat and work can be expressed as differential forms on the space of functions of state,

$$dQ = T dS, \quad dW = p dV. \quad (1)$$

Now, given an integral of motion (*e.g.*, constant pressure) one can make these differential forms exact by adding a zero. In the constant pressure case, this “zero” is the differential form $V dp$. If we add this form to dW and dQ we get

$$dW = p dV = p dV + V dp = d(pV) = dP_1$$

and

$$dQ = T dS = dU + p dV = dU + p dV + V dp = d(U + pV) = dP_2,$$

where p , V , T , S , and U follow the standard thermodynamic nomenclature [20]. The functions $P_1 = pV$ and $P_2 = U + pV$ give us a work potential and a heat potential respectively (for $p = \text{const.}$). The simple construction as described above can be generalized for less common cases. SAB [16] find potentials P for a spherical system with constant surface tension, $P_3 = \frac{1}{2}V(3p - e_{\text{ex}})$ and for a cylinder with a spring loaded piston, $P_4 = A^2 p^2 / 2k$, where k is the force constant and A is the surface area of the piston. These examples consist of complex reversible systems, *i.e.*, in internal equilibrium. The potential function is obtained by using the condition that equilibrium is maintained to find an integral of motion of one of the coupled systems. This integral of motion can then be used to integrate the inexact differential forms dW and dQ to give suitable potentials. Thus, one gets the work extracted from a coupled system, expressed as a change in a function of state of one of the coupled systems. The general problem implicit in the above examples is as follows: given the integral of motion $g(p, V) = \text{const.}$, we look for a function $f(p, V)$ such that $p dV + f dg$ is an exact differential. That differential form can be written as

$$\begin{aligned} p dV + f dg &= p dV + f \left[\left(\frac{\partial g}{\partial p} \right)_V dp + \left(\frac{\partial g}{\partial V} \right)_p dV \right] \\ p dV + f dg &= \left[p + \left(\frac{\partial g}{\partial V} \right)_p \right] dV + \left[f \left(\frac{\partial g}{\partial p} \right)_V \right] dp. \end{aligned} \quad (2)$$

By the application of the exactness condition (equal cross derivatives) and rearrangement terms, we obtain

$$\left(\frac{\partial f}{\partial V} \right)_p \left(\frac{\partial g}{\partial p} \right)_V - \left(\frac{\partial f}{\partial p} \right)_V \left(\frac{\partial g}{\partial V} \right)_p = \{f, g\}_{p,V} = 1, \quad (3)$$

where $\{...\}$ denotes the Poisson bracket. Given a solution f , the exact differential $p dV + f dg = dP$ is formed. This technique is a Legendre construction. Salamon *et al.* [16] formalize this results through the next theorem: “suppose we are giving a function $g(p, V)$, continuously differentiable on an open set D in p, V space. If the vector $\vec{\nabla}g$ is zero on at most a finite number of points in D , then there exist continuously differentiable functions $f(p, V)$ and $P(p, V)$ such that $dP = p dV + f dg$. Furthermore if f, P and f', P' are any two pairs of functions with the above property, then $f - f'$ and $P - P'$ can be expressed as functions of g ”. Salamon *et al.* proved this theorem in Ref. [16]. As can be seen this theorem is formulated only in the context of reversible processes. These authors generalize the above theorem for a class of quasi-static processes which produce entropy by the consideration that such a process can be seen as a time-parametrized sequence of equilibrium states. The generalized theorem is: “suppose given a system Σ , and a quasi-static noncyclic process π of Σ . (For cyclic processes, each branch must be treated separately). The process π is given by the time-parametrized curve $\sigma(t)$ of states of Σ and a function $W(t)$ of time that specifies (say) the work output of the system during the process. Then, there exists a function of state $P[\sigma]$, such that $\Delta P[\sigma(t)] = W(t)$ for all t along the process π . P is unique up to an integral of motion”. The proof of this theorem is also given in Ref. [16]. In order to illustrate how this theorem works, Salamon *et al.* constructed the function P for an ideal gas which undergoes an expansion in a cylinder exchanging heat with the environment according to the Newton’s cooling law. Then, the system obeys two irreversible equations:

$$\frac{dS}{dt} = \frac{k(T_{\text{ex}} - T)}{T} \quad (4a)$$

and

$$\frac{dV}{dt} = aV, \quad (4b)$$

where T_{ex} is the temperature of the environment, k is the heat conductance, a is a constant and t is time. Eq. (4b) is typical of many engines [16]. The following step is to find a “zero”. By coupling Eqs. (4a) and (4b), we obtain

$$(TV) dS - \frac{k(T_{\text{ex}} - T)}{a} dV = 0 = dg. \quad (5)$$

The useful work is given by

$$dW = p dV - \alpha \left(\frac{dV}{dt} \right) dV = (p - a\alpha V) dV, \quad (6)$$

where α is the coefficient of friction against the walls. Now, we look for a function f such that the differential form

$$(p - a\alpha V) dV + f \left[(TV) dS - \frac{k(T_{\text{ex}} - T)}{a} dV \right] = dP \quad (7)$$

is exact. By the condition that cross-partial derivatives be equal and solving the resulting differential equation, Salamon *et al.* obtain

$$f = \frac{nR}{V(\frac{k}{a} - nR)}. \quad (8)$$

When Eq. (8) is substituted into Eq. (7), and using the ideal gas law, the exact differential becomes [16]

$$dP = A dT - 2BV dV + C \frac{dV}{V}, \quad (9)$$

where

$$A = \frac{n^2 RC_V}{\frac{k}{a} - nR}, \quad B = \frac{\alpha a}{2}, \quad \text{and} \quad C = \frac{T_{\text{ex}} k A}{anC_V},$$

with C_V the molar heat capacity at constant volume, n the number of moles of gas and R the universal gas constant. By integrating Eq. (9), Salamon *et al.* finally, obtain

$$P = AT - BV^2 + C \ln V$$

or

$$P = A \left(\frac{T_{\text{ex}} k}{anC_V} \ln V + T \right) - BV^2. \quad (10)$$

This potential P must have the property that ΔP is the value of the useful work delivered in a quasi-static process which proceeds according to Eqs. (4).

3. SOME SAB-POTENTIAL PROPERTIES

In this section we discuss the behavior of the potential P given by Eq. (10). We shall consider that the gas expansion proceeds without friction, in order to be in the most typical case of finite-time engines [1]. Under this assumption, Eq. (10) becomes

$$P = A \left(\frac{T_{\text{ex}} k}{anC_v} \ln V + T \right). \quad (11)$$

By substituting the constant A in Eq. (11) we obtain

$$P = \frac{nRT_{\text{ex}}}{1 - \frac{nRa}{k}} \ln V - \frac{n^2 RC_V}{\frac{k}{a} - nR} T. \quad (12)$$

Now, we calculate the work delivered by an isothermic process between the endstates 1 and 2, which proceeds according to the irreversible Eqs. (4):

$$W_{12} = \Delta P_{12} = P_2 - P_1 = \frac{nRT_{ex}}{1 - \frac{nRa}{k}} \ln \frac{V_2}{V_1}. \quad (13)$$

If we take the reversible limit of Eq. (13), *i.e.*, when the conductance $k \rightarrow \infty$, we obtain immediately

$$W_{12} = nRT_{ex} \ln \frac{V_2}{V_1}, \quad (14)$$

which is the expected result in the context of the classical equilibrium thermodynamics for an ideal gas isothermic expansion. Thus, the SAB-potential reproduces well the reversible limit for the treated case.

One of the first problems discussed for the FTT formalism was the so called Curzon and Ahlborn cycle [1]. It consists in a Carnot-type cycle with heat transfer in the isothermal branches given by the Newton's Law of cooling [Eq.(4a)]. This cycle is depicted in an entropy-temperature diagram in the figure. The two isothermal branches ($1 \rightarrow 2$ and $3 \rightarrow 4$ in the figure) fulfill the conditions given in the gas expansion which satisfy Eq. (12). Then, one would expect that using Eq. (13) for the works W_{12} and W_{34} , respectively, one would obtain the endoreversible efficiency [1],

$$\eta_{CA} = 1 - \frac{T_{2\omega}}{T_{1\omega}} = 1 - \sqrt{\frac{T_2}{T_1}}, \quad (15)$$

where $T_{1\omega}$ and $T_{2\omega}$ are the internal temperatures of the working substance in the isothermic expansion and compression respectively; and T_1 and T_2 are the hot and cold reservoirs temperatures respectively. Nevertheless, that is not the case. If we use Eq. (13) for the processes $1 \rightarrow 2$ and $3 \rightarrow 4$, we obtain

$$\eta = 1 - \frac{|Q_2|}{|Q_1|} = 1 - \frac{|W_{34}|}{|W_{12}|} = 1 - \frac{T_2}{T_1}, \quad (16)$$

which is the Carnot reversible efficiency, where T_1 and T_2 are the external temperatures, *i.e.*, the temperatures of hot and cold reservoirs, respectively. Thus, the function given by Eq. (12) seems to be no suitable to calculate efficiencies of finite-time engines like the CA-cycle. A possible reason for such a discrepancy must be the fact that the time-parametrized quasi-static internal process used by Salamon *et al.* [16] can not be considered as equivalent to an endoreversible process, since in an endoreversible machine all irreversibilities take place in the coupling between system and reservoirs and not in the system at work [21].

4. ON POSSIBLE ENDOREVERSIBLE POTENTIALS

It is well known [18] that starting from the internal energy U , one can construct diverse thermodynamic potentials such as the Gibbs potential G ; the Helmholtz potential F

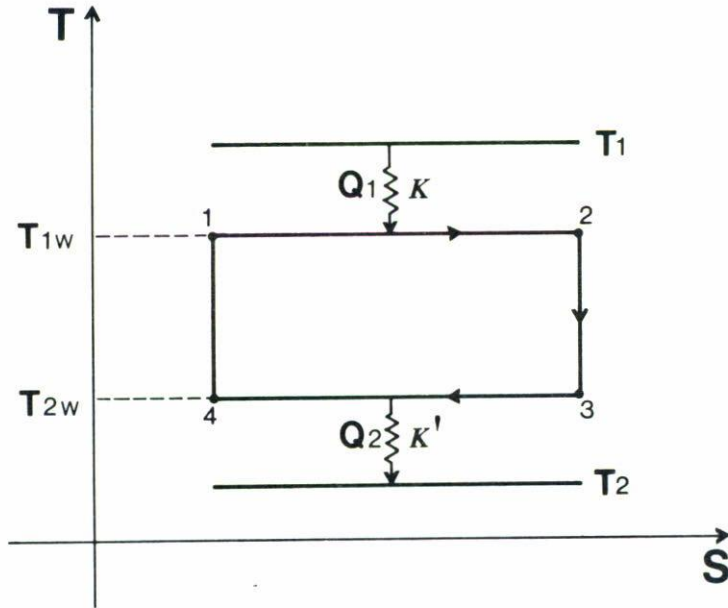


FIGURE. Temperature-entropy diagram of the CA-cycle. $x = T_1 - T_{1w}$ and $y = T_{2w} - T_2$.

and the enthalpy H . That construction is obtained by using Legendre transforms. These functions have similar properties to the mechanical potentials in the sense that they provide us equilibrium and stability criteria and they have the capability to generate thermodynamic forces by their first derivatives. Without mentioning that the thermodynamic potential U , S , F , G , and H being themselves thermodynamic variables, lead of course to Maxwell relations via the equalities between second cross derivatives. The functions of state P , obtained from inexact differentials by adding a suitable zero, like $P_1 = pV$ for isobaric processes or that given by Eq. (10), lack some of the mentioned properties of U , S , F , G and H . For example, the functions P can not generate either Maxwell relations, or stability criteria. In that sense, they are not true thermodynamic potentials.

As it was showed in Sect. 3, the function of state P given by Eq. (12) applied to the calculation of the efficiency of an endoreversible cycle leads us to the Carnot efficiency. This result constitutes a contradiction, because of a suitable finite-time potential would lead us to an efficiency expression different to the reversible case.

In this section we propose a manner to carry out endoreversible potentials construction that solves the previous contradiction and permits to obtain additional results. Several authors [22,25] have established that for Carnot-type thermal cycles with irreversibilities in the heat reservoirs or at the couplings between the working substance and surroundings, the following expression is held:

$$W = W_{rev} - T_2 \Delta S_u, \tag{17}$$

where W_{rev} is the maximum reversible work, W is the irreversible (finite-time) work, T_2 is the cold reservoir temperature and ΔS_u is the change of entropy in the thermody-

dynamic universe (system plus surroundings). Recently, Marcella [22] pointed out that for a noncyclic process,

$$Q = Q_{\text{rev}} - W_{\text{lost}}, \quad (18)$$

where $Q_{\text{rev}} = \Delta U_{\text{sys}} + W_{\text{rev}}$ is the maximum amount of heat that can be absorbed for a given change of state, Q is the heat flowing into the system during the irreversible change of state and W_{lost} is an additional amount of heat that could have been extracted from the reservoir had the process been reversible. In the CA-cycle depicted in the figure, $x = T_1 - T_{1\omega}$ and $y = T_{2\omega} - T_2$. When $x = 0$ and $y = 0$, we have the reversible Carnot limit, and for the isothermic expansion $1 \rightarrow 2$, we obtain (ideal gas as working substance)

$$Q_{\text{rev}} = nRT_1 \ln \frac{V_2}{V_1}. \quad (19)$$

When $x \neq 0$, the heat flowing into the system is

$$Q = nRT_{1\omega} \ln \frac{V_2}{V_1}. \quad (20)$$

It is clear, that in this case W_{lost} can be expressed by

$$W_{\text{lost}} = nR(T_1 - T_{1\omega}) \ln \frac{V_2}{V_1} = nRx \ln \frac{V_2}{V_1}. \quad (21)$$

From classical equilibrium thermodynamics we know that, for an isothermic expansion,

$$W_{\text{rev}} = -\Delta G_{12} = \int_1^2 V dp = nRT_1 \ln \frac{V_2}{V_1}. \quad (22)$$

In the case of Eq. (21), we observe that

$$W_{\text{lost}} = \Delta\varphi_{12}, \quad (23)$$

with

$$\varphi = nRx \ln V, \quad (24)$$

consequently, by using Eq. (18), we can write (since $\Delta U_{12} = 0$ for ideal gas)

$$Q = W_{12} = -\Delta G_{12} - \Delta\varphi_{12} \quad (25)$$

or

$$W_{\text{ER}} = -\Delta(G + \varphi) = -\Delta G_{\text{ER}}, \quad (26)$$

where W_{ER} is the finite-time (endoreversible) work and G_{ER} is an endoreversible Gibbs potential. From the definition of φ we see that

$$W_{\text{ER}} = -\Delta(G + \varphi) = nRT_{1\omega} \ln \frac{V_2}{V_1} = \int_{1\text{ER}}^2 V dp. \quad (27)$$

By using Eq. (27) and the equivalent equation for the compression $3 \rightarrow 4$ (Fig. 1), we obtain immediately

$$\eta_{\text{CA}} = 1 - \frac{|Q_2|}{|Q_1|} = 1 - \frac{|W_{34}|}{|W_{12}|} = 1 - \frac{T_{2\omega}}{T_{1\omega}}, \quad (28)$$

i.e., the endoreversible efficiency. Eq. (28) in the maximum power regime becomes $\eta_{\text{CA}} = 1 - \sqrt{T_2/T_1}$ [1].

In a recent paper [17] a generalization was proposed of the so called method of Carnot cycles (also known as the graphic method). This generalization consisted in extending the graphic method to endoreversible cycles. One of the results of such an extension was getting a Clausius-Clapeyron equation for a finite-time liquid-vapor transition given by

$$\left(\frac{dp}{dT} \right)_{\text{ER}} = \frac{Q_{\text{rev}}}{\lambda T_1 \Delta V}, \quad (29)$$

where λ is a quantity larger than unity and it provides us a measurement of the departure of the finite-time process from an ideal reversible process, and ER means endoreversible. The reversible Clausius-Clapeyron equation can be obtained by two approaches [18]: the graphic method and the equality of the Gibbs potential in the phase coexistence region [19]. Now, we shall obtain Eq. (29) by using the endoreversible Gibbs potential. In the endoreversible approach, the internal equilibrium is assumed and the irreversibility is considered only in the external coupling of the working substance. Consequently, we propose

$$dG_{\text{l}}^{\text{ER}} = dG_{\text{g}}^{\text{ER}}, \quad (30)$$

where l means liquid and g gas. Eq. (30) can be written as

$$-S_{\text{l}}^{\text{ER}} dT + V_{\text{l}}^{\text{ER}} dp = -S_{\text{g}}^{\text{ER}} dT + V_{\text{g}}^{\text{ER}} dp. \quad (31)$$

From this equation, it follows that

$$\left(\frac{dp}{dT} \right)_{\text{ER}} = \left(\frac{\Delta S}{\Delta V} \right)_{\text{ER}} = \frac{Q_{\text{ER}}}{T_{1\omega} \Delta V}, \quad (32)$$

where T_{ω} is the internal temperature and $\Delta V = \Delta V_{\text{ER}}$. From the figure, we see that

$$(T_1 - T_2) > (T_{1\omega} - T_{2\omega})$$

or

$$nR(T_1 - T_2) \ln \frac{V_2}{V_1} > nR(T_{1\omega} - T_{2\omega}) \ln \frac{V_2}{V_1}. \quad (33)$$

This inequality means (for the complete cycle)

$$Q_{\text{TOT}}^{\text{rev}} > Q_{\text{TOT}}^{\text{ER}}. \quad (34)$$

Now, we look for a coefficient β that convert the above inequality in an equality. The quantity λ in Eq. (29) is [17]

$$\lambda = \frac{\eta_c}{\eta_{\text{ER}}} = \frac{T_{1\omega}}{T_{2\omega}} \frac{(T_1 - T_2)}{(T_{1\omega} - T_{2\omega})} = \frac{T_{1\omega} Q_{\text{rev}}}{T_{2\omega} Q_{\text{ER}}}; \quad (35)$$

consequently

$$Q_{\text{ER}} = \frac{T_{1\omega} Q_{\text{rev}}}{T_1 \lambda}, \quad (36)$$

by substituting Eq. (36) in Eq. (32) we obtain

$$\left(\frac{dp}{dT} \right)_{\text{ER}} = \frac{Q_{\text{rev}}}{\lambda T_1 \Delta V}, \quad (37)$$

which is identical with Eq. (29) and it means that

$$\left(\frac{dp}{dT} \right)_{\text{ER}} = \frac{1}{\lambda} \left(\frac{dp}{dT} \right)_{\text{rev}}, \quad (38)$$

with $\lambda > 1$. Eq. (38) signifies that the slope of the liquid-vapor coexistence curve in a p - T space is larger in the reversible case than in the endoreversible (finite-time) case. In this way, we show that Eq. (29) can be obtained by means of two equivalent approaches: the generalized graphic method and the equalization of endoreversible Gibbs potentials in the coexistence region. That is, in the endoreversible case the same two equivalent approaches can be used as in the reversible case.

5. CONCLUSIONS

Finite-time thermodynamics is an extension of classical equilibrium thermodynamics and is relevant in principle across the entire structure of the subject, from the most abstract level to the most applied. Nowadays, the set of useful applications of FTT to thermodynamic practical problems is very extensive. Nevertheless, there exists a lack of respect for a theoretical apparatus giving support to FTT based in general principles. This is due in part to the great diversity of irreversible phenomena to be considered if a complete description of a real process is desired. It is pertinent to clear up that in the FTT approach the quantities of interest are global process variables as power, work and efficiency, in contrast

to the local variables approach of irreversible thermodynamics. Salamon, Andresen and Berry proposed a method to construct finite-time potentials for quasi-static processes with entropy production. This method is an extension of that consisting in adding a suitable zero to an inexact differential form to construct an exact differential form in the case of reversible processes. The potential constructed by that technique has not the capability to lead to an endoreversible efficiency expression for finite-time thermal cycles such as the CA-cycle. Based in the concept of lost work we propose that it is possible to define a kind of endoreversible thermodynamic potential that leads to the endoreversible efficiency and permits to obtain an endoreversible Clausius-Clapeyron equation, for the case of a finite-time liquid-vapor transition. That is, the proposed endoreversible potential allows us to have two equivalent procedures for obtaining the Clausius-Clapeyron equation: the method of endoreversible Carnot cycles (generalized graphic method) and the equalization of endoreversible Gibbs potentials in the coexistence region. This property is similar to those of the reversible thermodynamics consisting in the use of equivalent reversible approaches for getting the Clausius-Clapeyron equation.

REFERENCES

1. F.L. Curzon and B. Ahlborn, *Am. J. Phys.* **43** (1975) 22.
2. B. Andresen, P. Salamon and R.S. Berry, *Phys. Today* **37** (1984) 62.
3. P. Salamon, A. Nitzan, B.A. Andresen and R.S. Berry, *Phys. Rev.* **A21** (1980) 2115.
4. M.H. Rubin, *Phys. Rev.* **A22** (1980) 174.
5. M.H. Rubin and B. Andresen, *J. Appl. Phys.* **53** (1982) 1.
6. H.S. Leff, *Am. J. Phys.* **55** (1987) 602.
7. M. Mozurkewich and R.S. Berry, *Proc. Natl. Acad. Sci. USA* **78** (1981) 1986.
8. Y.B. Band, O. Kafri and P. Salamon, *Chem. Phys. Lett.* **72** (1980) 127.
9. V.N. Orlov and R.S. Berry, *Phys. Rev.* **A42** (1990) 7230.
10. Z. Yan and J. Chen, *J. Appl. Phys.* **65** (1989) 1.
11. M. Jo Ondrechen, B. Andresen and R.S. Berry, *J. Chem. Phys.* **73** (1980) 5838.
12. G.R. Brown, S. Snow, B. Andresen and P. Salamon, *Phys. Rev.* **A34** (1986) 4370.
13. P.H. Richter and J. Ross, *J. Chem. Phys.* **69** (1978) 5521.
14. J.L. Torres, *Il Nuovo Cimento* **13D** (1991) 177.
15. M.H. Rubin, *Am. J. Phys.* **46** (1978) 637.
16. P. Salamon, B. Andresen and R.S. Berry, *Phys. Rev.* **A15** (1977) 2094.
17. F. Angulo Brown, *Rev. Mex. Fís.* **39** (1993) 153.
18. L. García-Colín, *Introducción a la Termodinámica Clásica*, Trillas, México (1986) (in Spanish).
19. E. Piña G., *Termodinámica*, Ed. Limusa, México (1978) (in Spanish).
20. M.W. Zemansky y R.H. Dittman, *Calor y Termodinámica*, McGraw-Hill, México (1984) (in Spanish).
21. D. Jou and J. Casas-Vázquez, *J. Phys. A: Math. Gen.* **20** (1987) 5371.
22. T.V. Marcella, *Am. J. Phys.* **60** (1992) 888.
23. F. Angulo Brown, *J. Appl. Phys.* **69** (1991) 7465.
24. H.S. Leff and G.L. Jones, *Am. J. Phys.* **43** (1975) 973.
25. R.C. Tolman and P.C. Fine *Rev. Mod. Phys.* **20** (1948) 51. These authors established Eq. (17) in a more general context.