Enseñanza *Revista Mexicana de Física* **39**, *No. 1 (1993) 153–160*

The method of endoreversible Carnot cycles

FERNANDO ANGULO BROWN
Departamento de Física, Escuela Superior de Física y Matemáticas
Instituto Politécnico Nacional
Edificio 9, Unidad Profesional Zacatenco, 07738, México, D.F., México

Recibido el 18 de junio de 1992; aceptado el 24 de septiembre de 1992

ABSTRACT. The so called Method of Carnot Cycles, developed by Richard Becker within the framework of the classical equilibrium thermodynamics (CET), is extended for cycles working endoreversibly at finite time. We illustrate the extended method for two phase transitions.

RESUMEN. El llamado método de los ciclos de carnot, desarrollado por Richard Becker en el contexto de la termodinámica clásica de equilibrio, es extendido para ciclos que operan endorreversiblemente a tiempo finito. Ilustramos el método extendido para dos transiciones de fase.

PACS: 44.60.+k; 44.90.+c

1. INTRODUCTION

By means of Legendre transforms of the internal energy U of a thermodynamic system, it is possible to construct diverse thermodynamic potentials, like the Helmholtz potential F, the Gibbs function G, the enthalpy H and others [1]. The use of these state functions in the classical equilibrium thermodynamics (CET) formalism leads to a great number of important thermodynamic relations. For example, in phase transitions like the liquid-vapor and the superconducting transition, the properties of the function G leads to the Clausius-Clapeyron and Rutgers relations, respectively [2,3,4]. These equations in particular, and all equations of CET in general, are obtained by using the conditions of equilibrium and reversibility in the processes to be considered. Within the equilibrium formalism, as Becker [4] asserts, very often it is possible to use the second law of thermodynamics in its original form (à la Clausius), that is, taking into account the restrictions of equilibrium and reversibility through the attributes of the Carnot cycle. Essentially, this is the basis of the Method of Carnot Cycles (MCC), also known as the Graphic Method [2-4]. The MCC considers that the system of interest undergoes an infinitesimal Carnot cycle between two neighbor isotherms at temperatures T and $T-dT$ respectively (Fig. 1). If dA is the cycle's area and Q is the absorbed heat in the isothermic process at temperature T, then by the reversible-Carnot-efficiency formula it follows that,

$$\eta_C = 1 - \frac{T-dT}{T} = \frac{dT}{T} = \frac{dA}{Q}. \tag{1}$$

Next, the area dA (Cycle's work) is expressed in terms of the considered thermodynamic-space variables, resulting in a relationship between the variables defining dA, the heat

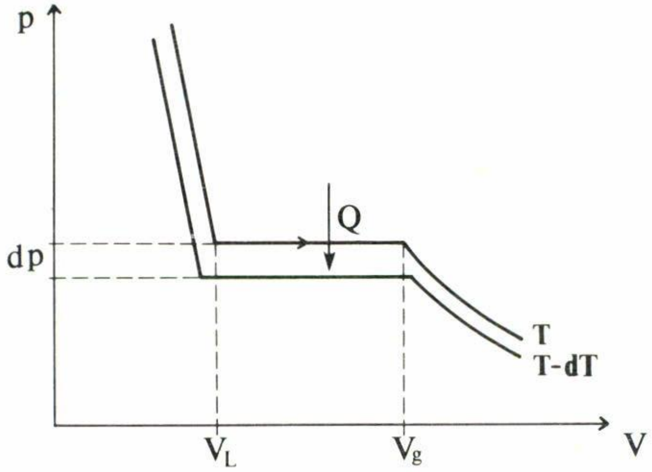

FIGURE 1. Pressure-volume diagram of an infinitesimal Carnot cycle.

involved in the process and the temperature. Hence, Eq. (1) represents a reversible process at maximum efficiency regime (Carnot theorem). Eq. (1) gives a very simple way to obtain equilibrium equations for diverse processes [4]. Some cases are: The Clausius-Clapeyron equation for liquid-vapor coexistence [2,3]; Rutgers' relation for superconducting transition [4]; Stefan-Botzmann formula for cavity radiation [2] and the law of mass action for chemical gaseous reactions [4]. It is well known that rigorously reversible processes represent an idealization of natural processes which are irreversible, dissipative and hence, with entropy production. If we want to approach a real process to the reversible regime by a succession of equilibrium states (quasiestaticity), it would be necessary to employ a time so large, that practically results infinite. Nevertheless, the quasiestaticity concept can be used, say in a weak version, for processes whose duration is very large with respect to the internal relaxation times of the system. This is the case, for instance, for adiabatic processes [5], but it is not for isothermic processes which make a quantity of work while receiving heat from certain heat reservoir. This flux of heat represents a remarkable cause of irreversibility. In 1975, Curzon and Ahlborn (CA) [6], proposed a model for the Carnot cycle in which, the working fluid at the isothermic branches is not in thermal equilibrium with their corresponding heat reservoirs, but there exists a finite heat transfer between working fluid and reservoirs, given by the so called Newton's cooling Law [7]. This model with one irreversible process coupling the working fluid with its surroundings, is a non-null power model, in contrast with all reversible models which are zero-power models. The CA cycle is endoreversible in the sense that permits the working fluid to be in internal equilibrium [8]. The expression for the power output associated with this cycle corresponds to a convex function with only a maximum point, such that, the efficiency of this cycle at maximum power regime is [6]

$$\eta_{\mathrm{CA}} = 1 - \sqrt{\frac{T_2}{T_1}}, \tag{2}$$

where T_2 and T_1 are the temperatures of cold and hot reservoirs respectively. The success of Eq. (2) consisted in reasonable predictions for the reported experimental values of efficiency for a certain number of power plants (See Table I of Ref. [6]). This result opened a new line in thermodynamics, which is known as finite-time thermodynamics (FTT) [9]. Diverse CET problems have been reformulated in the FTT framework, involving the duration of the processes, fundamentally through temporal equations which describe some irreversibilities present in the coupling between the system and its surroundings. The thermal cycles considered by FTT are endoreversible cycles, that is, the working substance undergoes reversible transformations without entropy production and the global irreversibility of the thermodynamic universe (working fluid plus surroundings) is only due to the coupling contributions.

In this paper we consider the Method of Carnot Cycles developed by Becker [4] for processes which occur reversibly at maximum efficiency regime (Carnot efficiency) and we extend it for processes which occur endoreversibly at finite time by means of several optimization criteria taken from FTT. The extended method is illustrated for two cases: liquid-vapor and superconducting transitions.

2. SOME FTT CRITERIA

In the CA paper it was shown that an endoreversible Carnot cycle working at the maximum power regime has an efficiency given by Eq. (2). Since the publication of that paper, diverse criteria of merit for endoreversible thermal cycles have been proposed. Some criteria use the formalism of differential and variational calculus [8,10] and other use the formalism of the optimal control theory [11]. In Ref. [12] it was proposed an optimization criterion for the CA cycle which consists in the maximization of the function,

$$E = P - T_2\sigma, \tag{3}$$

where P is the cycle's power output, σ is the total entropy production of the cycle plus heat reservoirs, and T_2 is the temperature of the cold reservoir. E is a convex function with a single maximum and it represents the CA-cycle configuration in which the best compromise between high power output and low entropy production (times T_2) is reached [12]. This function has the property that in its maximum point gives the 80 per cent of the maximum power of the cycle (CA point) and only the 30 per cent of the entropy produced in the maximum power regime. Another very interesting property of function E, is that the cycle-efficiency at maximum-E regime is given by [12]

$$\eta_E \approx \tfrac{1}{2}(\eta_{\mathrm{C}} + \eta_{\mathrm{CA}}), \tag{4}$$

with η_{C} the Carnot efficiency and η_{CA} the CA efficiency [Eq.(2)]. The convex functions P and E are written in terms of $x = T_1 - T_{1w}$ and $y = T_{2w} - T_2$ [6,12], where T_1 and T_2 are the temperatures of the hot and cold reservoirs respectively; and T_{1w} and T_{2w} are the temperatures of the high and low isotherm branches respectively (Fig. 2).

From Fig. 2 we see that the cycle's configuration with $x = y = 0$ corresponds to the reversible Carnot cycle. In the X–Y plane (see Fig. 3), the origin represents the Carnot

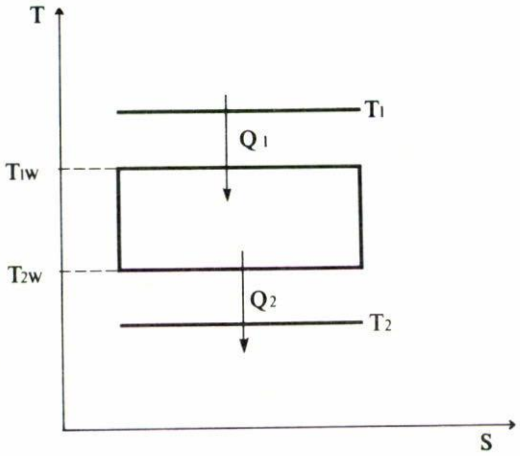

FIGURE 2. Temperature-entropy diagram of an endoreversible Carnot cycle.

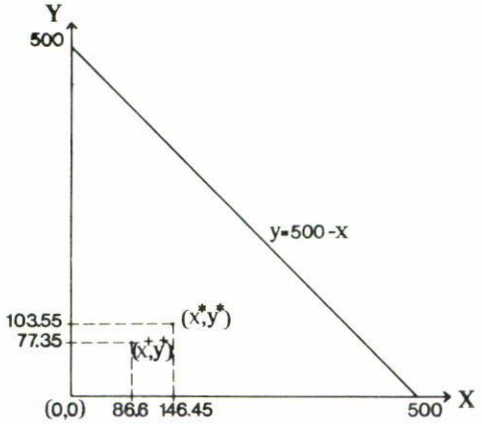

FIGURE 3. X–Y diagram including the maximum power (X^*, Y^*); the maximum-E (X^+, Y^+); and the maximum efficiency $(0, 0)$ configurations for $T_1 = 1000$ K and $T_2 = 500$ K with $\alpha = \beta = 100$J/k.s.

cycle (maximum efficiency and zero power); the point (x^*, y^*) corresponds to the CA configuration with maximum power and efficiency given by Eq. (2) [6]; and the point (x^+, y^+) corresponds to maximum E, with $\eta_E \approx 1/2(\eta_C + \eta_{CA})$ [12]. From the expression for $P = P(x, y)$ given in Ref. [6] we see that the domain where $P \geq 0$ is the represented in Fig. 3. It is clear that there exist (x, y) pairs (cycle's configurations) which do not correspond to any particular optimization criterion: maximum efficiency, maximum power or maximum E. Nevertheless, these (x, y) points also correspond to possible configurations of the CA cycle, and can be considered as a measurement of the deviations of finite-time cycles from the ideal Carnot regime.

3. METHOD OF ENDOREVERSIBLE CARNOT CYCLES

If in Fig. 1 we consider that the infinitesimal cycle works in the maximum power regime, we have

$$\eta_{\mathrm{CA}} = \frac{dA}{Q} = 1 - \sqrt{\frac{T - dT}{T}} \approx \frac{dT}{2T}, \tag{5}$$

where we have used a Taylor series expansion for $dT \ll T$. Now, if we consider that the CA cycle maximizes the function E, we have

$$\eta_E \approx \frac{dA}{Q} \approx \frac{1}{2}\left[1 - \frac{T - dT}{T} + 1 - \sqrt{\frac{T - dT}{T}}\right] \approx \frac{dT}{\frac{4}{3}T}. \tag{6}$$

The Eqs. (5) and (6) have the form

$$\frac{dA}{Q} = \frac{dT}{\lambda T}, \tag{7}$$

with $\lambda = 1$ for maximum efficiency; $\lambda = 4/3$ for maximum E and $\lambda = 2$ for maximum power; λ can take also values in the interval [1,2], which do not correspond to conspicuous criteria of merit. By using Eq. (7) with $\lambda = 1$ we obtain immediately the usual Clausius-Clapeyron (CC) equation [2,3]. Fig. 1 being a pressure-volume diagram, Eq. (7) takes the form,

$$\frac{(V_g - V_l)\, dp}{Q} = \frac{dT}{T}, \tag{8}$$

with V_g the molar gas volume and V_l the molar liquid volume. Eq. (8) immediately leads to,

$$\frac{dp}{dT} = \frac{Q}{T\Delta V}, \tag{9}$$

which is the well known CC-equation, where Q is the so-called heat of vaporization. If we consider that liquid-vapor transition evolves endoreversibly at finite time, then we can use Eq. (7) for different evolution criteria. Eq. (7), in a P–T diagram leads to

$$\frac{dp}{dT} = \frac{Q}{\lambda T\Delta V}. \tag{10}$$

For instance, if the considered process occurs at maximum power regime, then

$$\frac{dp}{dT} = \frac{Q}{2T\Delta V} \tag{11}$$

and if the process evolves maximizing the function E given by Eq. (3), then

$$\frac{dp}{dT} = \frac{Q}{\frac{4}{3}T\Delta V}. \tag{12}$$

From Eq. (10), we have

$$Q = \lambda T \Delta V (\frac{dp}{dT}). \tag{13}$$

This way, the heat of vaporization at finite time is different from Q for the corresponding equilibrium process. The "measurement" of entalphies of vaporization ($Q = \Delta H$) in general is realized by means of fitting vapor pressure experimental data, $P_{\mathrm{v}} = P_{\mathrm{v}}(T)$ [13,14], and then using Eq. (13) with $\lambda = 1$. These experiments are made slowly to reach equilibria conditions. For this reason, the entalphies data ($\Delta H = Q$) found in tables of experimental physical chemistry data [14] are satisfactorily close to those of ΔH calculated with equilibrium formalism. Nevertheless, as Majer and Svoboda [13] assert, the above procedure to measure entalphies of vaporization must be called pseudoexperimental method in contrast with those which by direct calorimetric techniques determine ΔH. This last kind of direct measurements are scarcely reported in the literature [13,14]. According to Majer and Svoboda the availability and confidence of ΔH data is not satisfactory, and in fact a great spreading of ΔH data are reported in literature. For example, for nitrogen, the reported experimental ΔH is in the interval 195–210 J/g [15]. Majer and Svoboda recognize that although ΔH is an equilibrium quantity, the vaporization experiment has a more or less non-equilibrium character. We expect that if a vaporization experiment is realized without sufficient slowness to maintain it near equilibrium conditions, then the parameter λ of Eq. (10) can be necessary to explain experimental results. In the case of superconducting transition apparently there are intrinsic irreversibilities associated to magnetic degrees of freedom [16] which relax so slowly toward equilibrium that its relaxation times are of the order of the process times. This fact permits a FTT approach of superconducting transition [17]. The CET applied to the superconducting transition gives the so called Rutgers' relation for the specific heat jump [2-4],

$$\Delta C|_{T_C} = C_n - C_s = -v\frac{T_C}{4\pi}\left(\frac{dH_C}{dT}\right)^2_{T_C}, \tag{14}$$

in which, C_{n} and C_{s} are the molar specific heats in the normal and superconducting states respectively, v is the molar volume, H_{c} is the critical field, and T is the absolute temperature. The agreement between the predictions of Eq. (14) and the experimentally determined values of ΔC for type I superconductors has been taken, along with the Meissner effect, as the evidence of the reversible character of the superconducting transition [18]. Nevertheless, important deviations from the predictions of Eq. (14) have been reported in many cases [18]. In the case of the Meissner effect, as London [19] asserts, Meissner original experiments did not show an "ideal Meissner effect". Even for the best spectroscopically pure metals there is still a locked-in induction of the order of one or two per cent of the threshold field, and alloys in general show a very poor Meissner effect. In practice, there are always deviations from a complete Meissner effect and from Eq. (14). In Ref. [17], under a FTT approach, Eq. (14) was extended applying the MCC for endoreversible cycles in the normal-superconducting interface. The generalized Rutgers' relation resulting is

$$\Delta C|_{T_C} = -\frac{VT_C}{n\pi}\left(\frac{dH_c}{dT}\right)^2_{T_C}, \tag{15}$$

with $n = 4$ for the maximum efficiency criterion (Carnot reversible case) and for the endoreversible cases: $n = 3$ for maximum-E criterion and $n = 2$ for maximum power criterion. By using Eq. (15) with $n = 2$, it is possible to obtain a better agreement with experimental ΔC data, as in the case reported by Shaviv *et al.* [20] for the $Y_1Ba_2Cu_3O_{8-\delta}$ system. These authors reported an experimental value $\Delta C = 5.9 \pm 1.0$ mJ K^{-1}g^{-1} and $\Delta C = 2.4$ mJ K^{-1}g^{-1} calculated by means of reversible Rutgers' relation ($n = 4$). For the so called strong coupling superconductors [21] the operative optimization criterion seems to be the maximum-E criterion [17]. In Ref. [17] several examples are shown which suggest that a FTT approach to the superconducting transition is adequate to take into account the irreversibilities always present in the experimental manipulation of that transition.

4. CONCLUSIONS

The old method of so called Carnot cycles has been very useful to obtain equilibrium thermostatic relations. The verification with experimental data suffers from the restriction that those data must be obtained from real static experiments, a condition rarely met. In this work we obtain new predictions that apply to experimental situations of non-equilibrium processes. We obtain this new results by using the old Carnot cycles logical construction in a novel fashion with endoreversible cycles. The resulting equations of the extended method would lead to results closer to real experimental data than the well known classical equilibrium relations, as it is suggested by the case of superconducting transition. In the case of the extended CC-equation presented in this paper the comparison with experimental ΔH data is not transparent because the heat of vaporization reported in experimental tables correspond to very slow close-to-equilibrium experiments. The versatility and applicability of the extended method is as wide as the MCC.

REFERENCES

1. H.B. Callen, *Thermodynamics and an Introduction to Thermostatics*, Wiley, N.Y. (1985).
2. L. García-Colín, *Introducción a la Termodinámica Clásica*, Ed. Trillas, México (1985).
3. A.B. Pippard, *Elementos de Termodinámica Clásica*, Ed. EASO, México (1989).
4. R. Becker, *Theory of Heat*, Springer-Verlag, N.Y. (1967).
5. P. Salamon, A. Nitzan, B. Andresen and R.S. Berry, *Phys. Rev.* **A21** (1980) 2115.
6. F.L. Curzon and B. Ahlborn, *Am. J. Phys.* **43** (1975) 22.
7. C.T. O'Sullivan, *Am. J. Phys.* **58** (1991) 956.

8. M.H. Rubin, *Phys. Rev.* **A19** (1979) 1277.
9. B. Andresen, P. Salamon and R.S. Berry, *Phys. Today* **37** (1984) 62.
10. J.L. Torres, *Rev. Mex. Fís.* **34** (1988) 18; F. Angulo Brown y G. Ramos Madrigal, *Rev. Mex. Fís.* **36** (1990) 363; F. Angulo Brown, *Rev. Mex. Fís.* **37** (1991) 87.
11. M. Rubin and B. Andresen, *J. Appl. Phys.* **53** (1982) 1.
12. F. Angulo Brown, *J. Appl. Phys.* **69** (1991) 7465.
13. V. Majer and S. Svoboda, "Entalphies of Vaporization of Organic Compounds", I.U.P.A.C., *Chemical Data Series* No. 32, Blackwell Sc. Pub. Oxford (1986).
14. R. Ried, J. M.Prausnitz, and T.K. Sherwood, *The properties of Gases and Liquids*, McGraw-Hill, N.Y. (1975).
15. A.W. Burgstabler and P. Hamlet, *The Phys. Teach.* (nov. 1990) 544.
16. Yowen Xu and M. Svenaya, *Phys. Rev.* **B43** (1991) 5516; Y. Yeshurun and A. P. Malozemoff, *Phys. Rev. Lett.* **60** (1988) 2202.
17. F. Angulo-Brown, E. Yépez and R. Zamorano-Ulloa, Submitted for publication.
18. D.E. Maphoter, *Phys. Rev.* **126** (1962) 2021.
19. F. London, *Superfluids*, Vol. I, Dover, N.Y. (1961).
20. R. Shaviv, E.F. Werstrum Jr., M. Sayer, X. Yu, R.J.C. Brown, R.D. Heyding and R.D. Weir, *J. Chem. Phys.* **87** (1987) 5040.
21. F. Marsiglio, R.A. Kis and J. P.Carbotte, *Phys. Rev.* **B36** (1987) 5245.