A universal Carnot theorem for the efficient use of energy by any kind of thermodynamical device

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Sadi Carnot, in his seminal work of 1824 *Reflections on the Motive Power of Fire* (Dover, 1988) developed the theory of the thermal motors, showing that the most efficient use of heat energy is achieved by a motor functioning reversibly between a hot furnace at temperature T_1 and a condenser at temperature T_2 with efficiency $\eta_{\max} = 1 - (T_2/T_1)$. In his book Carnot sets the basis for the second law of thermodynamics, but also opens the way to study the maximum efficiency of other thermal devices like heat pumps, refrigerators, etc. Based on a previous work [4] here it is shown that Carnot's results for thermal devices can be extended to all other sorts of thermodynamical apparatuses like air pumps and wind generators, as well as to any other functioning device between a "furnace" at high Y_1 and a "condenser" at low T_2, where Y is any intensive thermodynamical variable. Then $\eta_{\max} = 1 - Y_2/Y_1$ sets the norm for the achievement of an efficient use of energy by these generalized means.

Keywords: Thermal motors, thermodynamic efficiency, Carnot theorem.

Sadi Carnot, en su libro fundamental de 1824 "Sobre la potencia motriz del fuego" (IPN, 1963), desarrolla la teoría de los motores térmicos y demuestra que el uso de energía por calor más eficiente es el de un motor que funciona reversiblemente entre una caldera a temperatura T_1 y un condensador a temperatura menor T_2, con la eficiencia máxima $\eta_{\max} = 1 - (T_2/T_1)$. En su libro, Carnot sienta las bases de la segunda ley de la termodinámica, pero también abre el camino al estudio de la eficiencia máxima de otros dispositivos térmicos como refrigeradores, bombas de calor, etc. Basado en un trabajo anterior [4], aquí se muestra que los resultados térmicos de Carnot pueden ser extendidos a otros aparatos termodinámicos, por ejemplo bombas de aire y aerogeneradores, así como a cualquier otro aparato que funcione reversiblemente entre una "caldera" a alta Y_1 y un "condensador" a baja Y_2, siendo Yuna variable termodinámica intensiva cualquiera. Entonces $\eta_{\max} = 1 - (Y_2/Y_1)$ fija la norma para el uso eficiente de la energía por estos medios.

Descriptores: Motores térmicos, eficiencia termodinámica, teorema de Carnot.

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1. Introduction

If sustainable development is ever achievable it would necessarily require, among other conditions, the satisfaction of the social energy needs by means of all sorts of renewable sources of energy. It is crucial, then, to make the transition from the present widespread use of non renewable sources of energy (coal, oil and to a lesser extent uranium) to the renewable ones (direct and indirect solar energy) plus geothermal energy.

Two factors, in particular, make evident the need of present civilization to depend on renewable sources of energy. First, the exhaustion on non renewable sources of energy can lead to severe disruptions of the social order between countries and within them, if the alternative energy options are not ready on time for substitution. War is one of these possible social disorders. In fact, we are at present witnessing wars in the Middle East, that similarly happened during the last several decades, all around the control of oil reserves for the thirsty and highly industrialized countries, even if these oils reserves are far from exhaustion.

Second, the continued consumption of coal, oil and uranium has been threatening the ecological stability of the environment, together with a generalized pollution that seems to affect it irreversibly. It is a fact that the temperature of the biosphere has increased by measurable amounts that could eventually lead to severe climatic changes.

However even the use of only renewable sources of energy do not constitute by itself an integral solution for the sustainability of our societies and the environment. It is also required a different mode of utilization, one that makes compatible both the non centralized incidence and the social processing of solar energy. Consequently the big dams should be avoided, as an example of the present use of highly concentrated use of renewable sources of energy, which irreversibly breaks down by clogging the stable circulation of soil, among other negative environmental and social problems.

On the other hand the efficient use of energy is required whatever is the mode of utilization prevailing at a certain moment, be it highly or low centralized. The efficient use of energy plays an essential role in the energy transition because it contributes to extend the time of exhaustion of the non renewable sources of energy, therefore contributing to "buy" time for the transition. In the decentralized mode of renewable energy utilization its efficient use contributes to the matching between energy needs and the end uses of energy .

An episode of important oil and coal savings in the history of mankind, due to increases in the efficient use of energy, occurred as a consequence of the 1973 oil embargo by the oil country producers against the highly industrialized countries that supported Israel against Syria and Egypt during the Yom Kippur war. The oil savings by increase of efficiency in thermal devices and tasks was one of the measures that contributed to decrease the subsequent oil prices; another measure taken by the highly industrialized countries was the access to the oil of other country producers, like Mexico.

It was in 1975 when the book *Efficient Use of Energy* was published by the American Institute of Physics (a society of societies which among others include the American Physical Society), co-authored by the physicists R. H. Socolow, K. Ford, G. Rochin and M. Ross, as a thermodynamical study response to the oil embargo. In this book the old questions of Sadi Carnot formulated in 1824 [1] were extended to the efficiencies of other thermal devices like refrigerators and heat pumps, and the concept of thermodynamical task efficiency was developed. By this it was understood the quotient between the minimum exergy needed and the exergy actually consumed to perform the task. Exergy was the name given to the concept of available work originally discovered by Clausius in the XIX century. Both efficiencies, also called *first law efficiency* (for devices) and *second law efficiency* (for tasks) were extremely useful for the saving of fossil fuels, as they set the benchmark for further improvements in he actual use of energy.

As an example of the importance of the previous ideas for the saving of oil consider the following hypothetical but realistic example. If in a country like the United States of America 11% of her total oil equivalent consumption was dedicated in 1973 to space heating using solely electric resistance heaters (about 1.98 million barrels of oil per day), she could have saved 1.65 million barrels of oil equivalent by completely employing heat pumps instead, with a COP of 6. In barrels of oil saved the amount corresponded to more than the total Mexican oil production, which was about 1.5 million barrels of oil the following years.

It then could be understood from the foregoing the relevance it could have the extension of the ideas of Carnot and the physicists of the AIP, to the first law efficiencies of another than thermal devices like the ones functioning under pressure, chemical or any other kind of intensive variable gradient. A similar extension of second law efficiencies for tasks another than thermal would not be necessary, as long as the expression for exergy includes gradients on all sorts of intensive variables.

In the following a short review is made of the Carnot theorem for thermal devices, which sets the stage for the pressure or baric case and for the further extension to any kind of thermodynamical device.

2. The thermal theorem of Carnot

Based on the work of his father Lazare Carnot about the maximum vertical water wheels efficiency, Sadi Carnot derived a similar theorem stating that the maximum efficiency of a thermal motor working between two fixed thermal reservoirs corresponds to a reversible one.

$$\eta_{R,T} > \eta_{I,T} \tag{1}$$

Here R means reversible, I irreversible and T refers to thermal motors.

Carnot's theorem (1) is deduced nowadays in textbooks [3] from the thermal Second Law of thermodynamics, either formulated in the Planck or Clausius version of it:

Planck's thermal statement of Second Law of thermodynamics: It is impossible to build a thermal motor working in a cycle whose only effect is to completely convert heat from a hot energy reservoir into work. (2)

Clausius thermal statement of the Second Law of thermodynamics: It is impossible to build a thermal refrigerator working in a cycle whose only effect is to pass energy as heat from a cold to a hot reservoir. (3)

From (2) or (3) it is also deduced the corollary of Carnot's theorem, which says that the efficiency of all the reversible motors working between the same fixed hot and cold reservoirs have the same efficiency.

$$\eta_{R_i,T} = \eta_{R_j,T}, \ \forall i\&j \tag{4}$$

From (4) two related results can be derived; first the existence of the absolute temperature T, and the equation

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{5}$$

Q_1 and Q_2 here denotes the heats processed from the hot (at T_1 temperature) and cold (at T_2temperature) reservoirs, respectively. Then, the maximum efficiency and work of any reversible thermal motor operating in the specified conditions are

$$\eta_{R,T} = 1 - \frac{T_2}{T_1} \tag{6}$$

$$W_{M,T} = \eta_{M,T} Q_1 = Q_1 \left(1 - \frac{T_2}{T_1}\right) = \frac{Q_1}{T_1}(T_1 - T_2) \tag{7}$$

These two expressions are the corresponding answers to two of the basic questions formulated by Carnot in 1824. One question dealt with the possibility of increasing η without limit, for example by changing either the design or the working substance of the motor. Carnot observed that the efficiencies of the motors that he studied normally increased according with the modernity of their date of construction, but he also noted the astounding fact that the values of the efficiencies tended not to surpass a certain upper bound. He then wondered if that apparent upper limit was the consequence of an undiscovered law of nature. The other question was more specific: "We do not know whether the fall of caloric from 100 to 50 degrees furnishes more or less motive power than the fall of this same caloric from 50 to zero ([1], p. 15)."

Carnot also showed that the reversible cycle of maximum efficiency should consist of two adiabats and two isotherms. On the isotherms at T_1, T_2 the hot, cold reservoir interchanges energy by heat Q_1, $Q_2$with the working substance, respectively. On one of the adiabats the substance lowers its temperature from T_1 to T_2, doing the reverse on the other adiabat.

Later on Clausius, elaborating on Carnot's ideas and basically using Eq. (5) showed that there exists another internal variable of any system, which he called entropy and denoted by the letter S, such that for any reversible infinitesimal change of the state of the system by a heat q_R

$$q_R = TdS \tag{8}$$

On the T, S space the Carnot cycle results in a rectangle composed of two straight lines for the isotherms, intersecting the other two straight lines for the adiabats. The area of the rectangle is the maximum work W_M as given by (7).

The physicists of the AIP went forward from Carnot and formulated similar questions for the most used thermal devices and showed that their maximum coefficients of performance are

$$\begin{aligned}
&\text{Thermal motor (result already obtained by Carnot):}\\
&\qquad \eta_{M,T} = 1 - \frac{T_2}{T_1}\\
&\text{Thermal refrigerator: } COP_{M,T} = \frac{1}{\frac{T_0}{T_3} - 1}\\
&\text{Heat pump: } COP_{M,T} = \frac{1}{1 - \frac{T_0}{T_2}}\\
&\text{Heater using heat: } COP_{M,T} = \frac{1 - T_0/T_1}{1 - T_0/T_2}\\
&\text{Refrigerator using heat: } COP_{M,T} = \frac{1 - T_0/T_1}{T_0/T_3 - 1}\\
&\text{Here } T_1(\text{hot furnace}) > T_2(\text{residential})\\
&\qquad > T_0(\text{environment}) > T_3(\text{refrigerator}).
\end{aligned} \tag{9}$$

These values set the norm for the optimal operation of the actual devices operating in society, and therefore for an estimation of the saving potential of energy use by these means. As an example think that the best actual thermal power plants operates with an efficiency a bit higher than 40%, while in the fifties their efficiencies were close to only 30%. However, (9) indicates that η_T could be as high as 50%, depending of the values of T_1 and T_2.

3. The baric theorem of Carnot

The ideas developed in this section are based on a previous work by the author [4]. The central point is based on the observation of the symmetrical role played by heat and work in the expression for the first law of thermodynamics.

$$\Delta U = Q + W \tag{10}$$

ΔU means the change of internal energy of the system due to interactions by heat and work with the exterior. The symmetrical role of Q and W in (10) allows one to separately characterize the net work developed in a cycle by the working substance by "ins" and "outs" of work and heat. For instance in the case of the thermal motor the First Law of thermodynamics tell us that

$$W = Q_1 - Q_2, \tag{11}$$

while in the case of a fluid working in cycles between two energy reservoirs, one at high pressure and another at low pressure

$$W = W_1 - W_2 \tag{12}$$

Here W_1 and W_2 denotes the energies processed as work between the working substance and the high and low pressure energy reservoirs, respectively. A baric motor could be materialized by the functioning of a wind generator, where air plays the role of the working substance. The corresponding refrigerator for a baric motor is an air compressor, which can be utilized to move air from a low pressure to a high pressure reservoir.

It is in terms of baric motors and "refrigerators" that corresponding expressions for the Second Law of thermodynamics and its deductions, like Carnot theorem and its corollary, could be stated.

Baric motor statement of the Second Law of thermodynamics: It is impossible to build a baric motor working in a cycle whose only effect is to completely convert work from a high pressure energy reservoir into work. (13)

Baric "refrigerator" statement of the Second Law of thermodynamics: It is impossible to build a fluid pump working in a cycle whose only effect is to pass fluid from a low pressure energy reservoir to a high pressure energy reservoir. (14)

From (13) and (14) a baric Carnot theorem and its corollary can be deduced, similar to (1) and (4), where T is changed by p. From

$$\eta_{R_i,p} = \eta_{R_j,p}, \quad \forall \ i\&j \tag{15}$$

it could be deduced that

$$\frac{W_1}{W_2} = \frac{p_1}{p_2} \tag{16}$$

Also the maximum efficiency and work of any reversible baric motor operating in the specified conditions are

$$\eta_{R,p} = 1 - \frac{p_2}{p_1} \tag{17}$$

$$W_{M,p} = \eta_{M,p} W_1 = W_1 \left(1 - \frac{p_2}{p_1}\right) = \frac{W_1}{p_1}(p_1 - p_2) \tag{18}$$

One could make a similar construction like Clausius did for any reversible thermal cycle to show that for the baric case there exists, like the entropy S, an internal state variable, now the volume V, such that for an infinitesimal process it should be valid that

$$w_{R,p} = pdV \tag{19}$$

Of course this result could have been established directly from the standard definition of infinitesimal work, buy here we have derived it again from a Clausius' integral theorem just to show the symmetric role played by heat and work, temperature and pressure in thermodynamics.

The Carnot baric cycle on the p,V space is now a rectangle composed of two isobars at pressures p_1 and $p_2$and two intersecting isochors at volumes V_1 and V_2. Using (19) one can deduce that $W_1 = p_1 (V_1 - V_2)$ and $W_2 = p_2 (V_1 - V_2)$, so that one regains (16), (17) and (18) immediately.

Betz' law [5] and other laws for wind generators predicts maximum efficiencies of 59% or about half of this last value, considering more realistic assumptions. But whatever the hypothesis about the working substance or the design of the wind generators is, the maximum efficiency could not surpass (17).

Besides baric motors, another devices operating between several energy reservoirs at different pressures could be conceived. Their maximum efficiencies and COP's could lead to a set of values similar to those given in (9), offering thus a complete set of technical predictions. There are thus expected big energy savings if the efficiency conclusions reached for the thermal devices could be extended to the case of the baric ones.

4. Universal Carnot theorem

A chemical motor functioning between two energy reservoirs at high μ_1 and low μ_2 chemical potentials could be imagined [6], so that results for the thermal and baric cases could be similarly reproduced. In particular, the maximum chemical efficiency would be

$$\eta_{M,\mu} = 1 - \frac{\mu_2}{\mu_1} \tag{20}$$

This result is expected to be applicable to any kind of chemical motors, like for instance fuel cells. The corresponding "chemical refrigerator" would be a chemical concentrator, for which a maximum COP would have a similar expression to the one appearing in (9).

The chemical Carnot theorem given by (20) was anticipated from the second law differential expression

$$dU = TdS - pdV + \mu dN, \tag{21}$$

where the infinitesimal reversible chemical work $w_\mu$is given by

$$w_\mu = \mu dN \tag{22}$$

N is the number of molecular components with chemical potential μ.

Consequently, one could straightforwardly generalize all the previous results if one could define some high Y_1 and low Y_2 energy reservoirs between which a Y-motor functions performing an infinitesimal work

$$w_Y = YdX, \tag{23}$$

Then a kind of Carnot Y-theorem would show that the maximum efficiency would be

$$\eta_{M,Y} = 1 - \frac{Y_2}{Y_1} \tag{24}$$

Similar expressions for (9) could also be formulated in terms of the variable Y.

In conclusion, what the present generalization of the Carnot theorem reveals is an ample opportunity for savings in energy resources that could be essential for the energy transition, compatible with a sustainable development scenario.

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