Considerations About The Anomalous Efficiency Of Particular Thermodynamic Cycles

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Abstract: Some years ago Vignati (refs. 1, 2, 3) showed that, under some particular circumstances (*inter alia* : isobaric processes connected through internal heat exchangers), the efficiency of an Ericsson cycle involving a real gas can exceed the Carnot limit η_C , in contradiction with the second principle of thermodynamics. However, the convergence of Vignati's algorithm, giving the temperature difference between the intermediate heat exchangers, has not yet been proved. In particular, it isn't clear, if the number of intermediate heat exchangers infinitely increases, the condition of a total (perfect) heat recovery may be asymptotically approximated. This remark is relevant because the claimed anomalous efficiencies appear only in the limit of a perfect heat recovery. Considering a suitable counterexample, we prove that, in general, the residual heat discharged on the external sources does not vanish in that limit, even when the isobars exchange the same amount of heat. Therefore the violation of the second law inferred from Vignati's calculation is merely apparent, being referred to a situation which is not (in principle) physically realisable. The essentials of the Vignati's argument are then applied to an Ericsson cycle involving an ideal gas undergoing chemical reactions. Again, no contradiction arises with the second principle.

1. Introduction

Let's consider a closed system composed of N classical identical particles; denoting with n_i the number of particles having the total energy $\varepsilon_i (i = 1, 2, ...)$ and with U the internal

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energy, the following constraints hold :

$$U = \Sigma_i \varepsilon_i n_i \qquad (1)$$

$$N = \Sigma_i n_i = constant \qquad (2)$$

Differentiating the eq. (1) and assuming (ref. 4) :

$$dQ = \Sigma_i \varepsilon_i dn_i \qquad (3)$$

$$dL = -\Sigma_i n_i d\varepsilon_i \qquad (4)$$

we easily obtain the first principle of thermodynamics :

$$dU = dQ - dL \qquad (5)$$

where Q and L respectively represent the quantity of heat exchanged by the system and the work done by it.

The entropy is defined as (ref. 5) :

$$S = -k\Sigma_i n_i ln(n_i) \qquad (6)$$

The system is said to be in thermal equilibrium at the absolute temperature T if

$$n_i = n_0 exp(-\varepsilon_i/kT) \qquad (7)$$

During an infinitesimal equilibrium process, the entropy increase is :

$$dS = -k\Sigma_i dn_i ln(n_i) - k\Sigma_i n_i(dn_i/n_i) = -k\Sigma_i dn_i(ln(n_0) - \varepsilon_i/kT) - kdN =$$

$$-k(ln(n_0) + 1)dN + k\Sigma_i dn_i \varepsilon_i/kT = (1/T)\Sigma_i \varepsilon_i dn_i = dQ/T \qquad (8)$$

In other words, the Clausius equality can be derived from microphysics[1]. If the system is in thermal equilibrium with an external reservoir at the same temperature T :

$$T_{sys} = T_{res} = T \qquad (9)$$

the Clausius equality can be written as :

$$dS = dQ/T_{res} \qquad (10)$$

For "reservoir" we mean here a system in thermal equilibrium at a given temperature T_{res}, having so great heat capacity that it can assure the constancy of T_{res} during the

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[1] This reasoning holds for free particles but, using the canonical ensemble in a consistent way, the same conclusion is obtained for the general case of interacting particles. See, for example, ref. 11.

process. If a system which is initially in equilibrium at the temperature T_{sys} interacts with the reservoir at the temperature $T_{res} \neq T_{sys}$, they exchange an amount dQ of heat in an irreversible process. The system entropy increases by an amount dS which satisfies the well known Clausius inequality :

$$dS \geq dQ/T_{res} \tag{11}$$

in which ever the reservoir temperature appears. From eq. (2) follows :

$$dS = -k\Sigma_i dn_i ln(n_i)$$

and therefore, the eq. (11) becomes :

$$-k\Sigma_i dn_i ln(n_i) \geq (1/T_{res})\Sigma_i \varepsilon_i dn_i$$

that is :

$$\Sigma_i dn_i(ln(n_i) + \varepsilon_i/kT_{res}) \leq 0 \tag{12}$$

Of course, it is not possible to derive the inequality (12) from the statistics of the equilibrium states, because it involves the time evolution of the coefficients dn_i/dt which is likely to tend to the thermal equilibrium with the reservoir at the temperature T_{res}. When the thermal interaction begins, the relation (7) holds, with $T = T_{sys}$; as a consequence:

$$\Sigma_i dn_i(ln(n_0) - \varepsilon_i/kT_{sys} + \varepsilon_i/kT_{res}) \leq 0$$

that is :

$$dQ(1/T_{res} - 1/T_{sys}) \leq 0 \tag{13}$$

Defining the absolute temperature as positive, we have therefore:

$$T_{res} > T_{sys} \qquad \text{if} \qquad dQ > 0$$

$$T_{res} < T_{sys} \qquad \text{if} \qquad dQ < 0$$

In other words, the heat flows from the system into the reservoir, if the system is warmer than the reservoir, and *viceversa* if it is colder. Therefore, the essentials of the second principle of thermodynamics are given by relation (11). We arrive to the same conclusion by writing the entropy increase for the reservoir:

$$dS_{res} = (-dQ)/T_{res}$$

and for the system:

$$dS_{sys} = dQ/T_{sys}$$

According to relation (13), the total increase $dS_{tot} = dS_{res} + dS_{sys}$ is ≥ 0.

Let us consider now a thermodynamic cycle consisting of two reversible isotherms at temperatures T_{min}, T_{max}, alternated with two other processes A, B. From eq. (5) we

have, for the amount of heat Q exchanged with external reservoirs and the work L done by the cycle, the equation $L = Q$, because the internal energy U is a function of state. Therefore :

$$L = Q = Q(T = T_{max}) - Q(T = T_{min}) + Q_A - Q_B \tag{14}$$

Now we suppose that a heat exchange occurs between the sections A and B, in such a way that $Q_A = Q_B$; therefore, the condition of a perfect heat recovery (or compensation) holds :

$$L = Q = Q(T = T_{max}) - Q(T = T_{min}) \tag{15}$$

If the global process $A + B$ is reversible (which includes a perfectly reversible thermal exchange between them), then from the Clausius equality we obtain, for the associated entropy increase, $\Delta S = \int_{AB}$ *(net amount of heat exchanged with external reservoirs at the temperature T)/T = 0*. Therefore, the total increase of entropy along the cycle amounts to:

$$(\Delta S)_{cycle} = (\Delta S)_{T=Tmax} + (\Delta S)_{T=Tmin} = 0 \tag{16}$$

because S is a function of state. From the Clausius equality, eq. (10), we have:

$$Q(T = T_{max}) = T_{max}/(\Delta S)_{T=Tmax}/,$$

$$Q(T = T_{min}) = T_{min}/(\Delta S)_{T=Tmin}/.$$

We easily obtain the efficiency of the cycle :

$$\eta = 1 - Q(T = T_{min})/Q(T = T_{max}) = 1 - T_{min}/T_{max} = \eta_C \tag{17}$$

It is equal to the Carnot efficiency. The eq. (17) follows from the first principle [eq. (5)] and the Clausius equality [eq. (10)], which have been microphysically justified.

Assuming the thermal exchange is still compensated, but it is not reversible, then from the Clausius inequality we obtain, for the associated entropy increase, $\Delta S > \int_{AB}$ *(net amount of heat exchanged with external reservoirs at the temperature T)/T = 0*[2]. Therefore :

$$(\Delta S)_{cycle} = (\Delta S)_{T=Tmax} + (\Delta S)_{T=Tmin} + \Delta S = 0 \tag{18}$$

For an engine cycle,
$(\Delta S)_{T=T_{max}} > 0$, then $(\Delta S)_{T=T_{min}} < 0$ and $|(\Delta S)_{T=T_{min}}| > |(\Delta S)_{T=T_{max}}|$.
The equality (17) is then substituted by the inequality :

$$\eta = 1 - Q(T = T_{min})/Q(T = T_{max}) < 1 - T_{min}/T_{max} = \eta_C \tag{19}$$

In next section a particular cycle of this kind is considered in detail.

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[2] Hereinafter we take into account only engine cycles, wherein the processes A, B involve only spontaneous thermal irreversibility without absorption of external work.

2.   Heat recuperators and heat regenerators

Let us consider, on the PV plane, a thermodynamic cycle consisting of two reversible isotherms at temperatures T_{min} , T_{max} , alternated with two isobars at pressures P_{min}, P_{max} (Ericsson cycle). During the isobaric processes the gas does not exchange heat with external sources; instead, the expanding gas exchanges heat with the compressed gas. This is possible, if the cycle is accomplished by a stationary flow of gas instead of gas undergoing alternating phases.

The gas coming from the heater at temperature T_{max} (Fig. 1) is diverted in the ducting and is sent to the cooler at temperature T_{min}; the gas coming from the cooler is diverted in another ducting and is sent to the heater. Both ductings' cross-section is shaped in such a manner as to permit to keep constant the gas pressure.

The ductings are perfectly insulated from the outside and connected through N ideal heat exchangers; the i-th heat exchanger has its definite operating temperature T_i and :

$$T_{min} < T_1 < T_2 < ..... < T_N < T_{max}$$

Each heat exchanger is assumed to be thermally insulated from the outside. The thermal conductivity of each exchanger is hypothetically infinite, so a perfect heat exchange between the ductings is guaranteed. In such a manner, we have constructed an (ideal) "heat recuperator". Both the gas being heated and the gas being cooled simultaneously pass through the recuperator; it is in this feature that it differs from a regenerator. The regenerator, in fact, is applied to the thermodynamic cycles involving alternating phases. It absorbs heat from the fluid subjected to cooling during one phase and then releases it to the fluid subjected to heating in the next phase. Coming back to consider the setup, we remark that the volume of involved gas is necessarily finite; therefore, only in extremely particular conditions the temperature of each exchanger will be stationary. These conditions are largely discussed in the next section.

Let us consider now how the recuperator influences the efficiency. The quantity of heat exchanged between two isobars is:

$$\Delta = Q(P = P_{max}) - Q(P = P_{min}) + Q_{res} = R + Q_{res}$$

where [C_p = specific heat per mole of gas at pressure p]:

$$Q(P = P_{\max}) = \int_{T_{\min}}^{T_{\max}} C_{p_{\max}} \, dT \quad ,$$

$$Q(P = P_{\min}) = \int_{T_{\min}}^{T_{\max}} C_{p_{\min}} \, dT \quad ,$$

and Q_{res} is the residual heat depending on the recuperator construction.

According to the first principle, the amount of heat R must be transferred from the external sources : if $R > 0$ the gas absorbs it from the heater at the temperature T_{max},
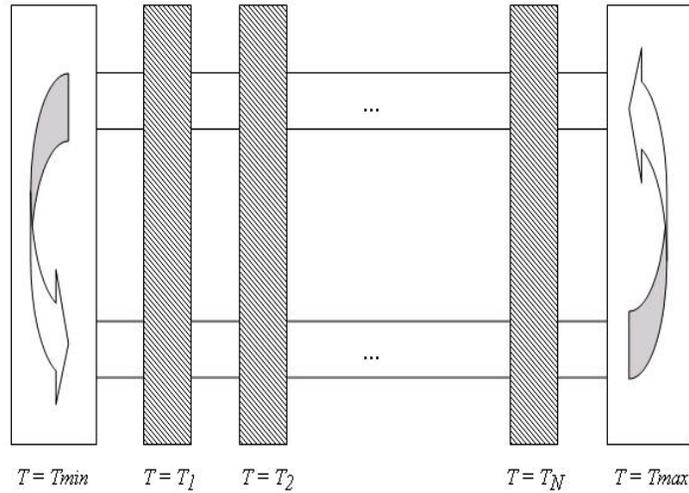
Fig. 1

if $R < 0$ the gas releases it to the cooler at the temperature T_{min}. As it is detailed in the next section, the gas absorbs the amount of heat Q_{res} from the heater and releases it to the cooler.

For example, if $R > 0$, the gas absorbs the quantity of heat :

$$Q_2 = \Delta + Q(T = T_{max})$$

from the heater at the temperature T_{max}, and it releases the quantity of heat:

$$Q_1 = Q_{res} + Q(T = T_{min})$$

to the cooler at the temperature T_{min}.

3.   Some considerations about the recuperator

The heat exchange between the isobaric processes may be compensated only if:

$$R = Q(P = P_{max}) - Q(P = P_{min}) = 0 \tag{20}$$

otherwise, no matter the recuperator construction, Δ will not vanish, because a residual heat, R, will be discharged on the heater at T_{max} (if $R > 0$) or on the cooler at T_{min} (if $R < 0$). The validity of the condition (20) may be secured by selecting in a proper manner the cycle on the PV plane.

Obviously, the recuperator not influences the isothermal work. As far as the isobaric work concern, it is still equal to $p\Delta V$ provided that $R = 0$. We can conclude that under these circumstances the work L done by the cycle is not influenced by the presence of the recuperator. Since L is fixed, the efficiency of cycle in the presence of recuperator :

$$\eta = L/[Q_{res} + Q(T = T_{max})]$$

is maximum, when $Q_{res} = 0$. In other words, the maximum of efficiency is obtained when the heat exchange between the isobaric processes is exactly compensated.

The eq. (20) surely holds if

$$Cp_{min}(T) = Cp_{max}(T) \qquad T_{min} \leq T \leq T_{max}$$

that is, *e.g.*, for cycles involving an ideal gas[3].

There is another possibility available only for a real gas with T/Tc slightly more than 1 (where Tc is the critical temperature of gas); it is illustrated in Fig. 2. Let us consider

Fig. 2
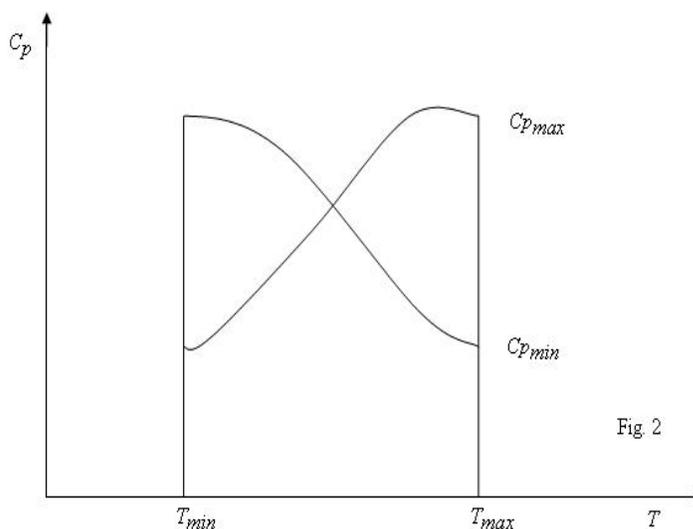
now the other term contributing to Δ, that is Q_{res}; it depends on the number N of heat exchangers and their temperatures. These two factors can't be selected arbitrarily, if one needs to have a stationary temperature distribution.

The i-th heat exchanger absorbs heat from the hotter gas $(T > T_i)$ entering it through one ducting , and release heat to the colder gas $(T < \quad T_i)$ entering it through another ducting. Only if these two amounts of heat are equal , the temperature, T_i, of the heat exchanger may remain constant.

Because we are considering an engine which performs a positive work, the point representing the state of a selected mass of gas must run clockwise along the cycle outline on the PV plane. So, the gas is cooled during the isobaric process at P_{min}, while it undergoes heating during the isobaric process at P_{max}.

Therefore, the i-th exchanger absorbs the amount of heat:

$$Q_{in}(i) \quad = \quad \int_{T_i}^{T_{i+1}} C_{p_{min}} \, dT \tag{21}$$

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[3] The cycle involving an ideal gas is a particular case of the situation presented in the last section, when $n = n'$; that is, when no dissociation/recombination occurs.

from the gas at temperature greater than T_i, flowing in it through the pipe at lower pressure. Instead, it releases the amount of heat :

$$Q_{out}(i) \quad = \quad \int\limits_{T_{i-1}}^{T_i} C_{p_{\max}} \, dT \tag{22}$$

to the gas at temperature lower than T_i , flowing in it through the pipe at higher pressure.

We may have a set of stationary temperatures $\{T_i \; ; \; i \; = \; 1,2, \; \ldots \; , \; N \; \}$ only if the condition :

$$Q_{in}(i) = Q_{out}(i) \tag{23}$$

holds for each value of i.

The temperature of each heat exchanger can be obtained, by recursively applying eqs. (21)-(23) following two distinct procedures.

According to the first procedure, $T_0 \; = \; T_{min}$ and T_1 are fixed; the eq. (22) gives Q_{out} (1), and Q_{in} (1) is then derived from (23). Substituting Q_{in} (1) in eq. (21) we obtain an equation for the unknown T_2; replacing the value of T_2 in eq. (22) we obtain $Q_{out}(2)$ and so on. This iterative procedure is stopped when a temperature $T_{i+1} > T_{max}$ is finally reached. The value of i is the number N of intermediate heat exchangers which is compatible with the selected value of T_1. The residual heat :

$$\int\limits_{T_{\max}}^{T_{N+1}} C_{p_{\min}} (T) \; dT \quad = \quad \alpha$$

is not compensated; in order to reduce α it is necessary to vary T_1. We can change T_1 continuously until we obtain $T_{N+1} = T_{max}$, so that $\alpha \; = \; 0$.

According to the second procedure, we fix $T_{N+1} = T_{max}$ and T_N ; the eq. (21) gives Q_{in} (N), and Q_{out} (N) is then derived from (23). Substituting Q_{out} (N) in eq. (22), we obtain an equation for the unknown T_{N-1}. Replacing the value of T_{N-1} in eq. (21) as the lower extreme of integration, we obtain $Q_{in}(N-1)$ and so on. This iterative procedure is stopped when a temperature $T_{i-1} < T_{min}$ is finally reached. The value of i is then redefined as 1 and the number of iterations is the number N of heat exchangers which is compatible with the selected value of T_N. The residual heat :

$$\int\limits_{T_0}^{T_{\min}} C_{p_{\max}} (T) \; dT \quad = \quad \beta$$

is not compensated; in order to reduce β it is necessary to vary T_N. We can change T_N continuously until we obtain $T_0 = T_{min}$, so that $\beta \; = \; 0$.

Anyhow, the same set of stationary temperatures $\{T_i \; ; \; i \; = \; 1,2, \; \ldots \; , \; N \; \}$ is obtained for the same value of N; it means that we have obtained a recuperator which is in thermal equilibrium, but not a perfect heat recovery between two isobaric processes. As we can

see in Fig. 1, the gas flowing through the pipe at lower pressure into the cooler at temperature $T = T_{min}$ releases to it an amount of heat :

$$\int_{T_{\min}}^{T_1} C_{p_{\min}}(T) \ dT \quad = \quad Q_{res} \quad , \tag{24}$$

which is not compensated; it is discharged on the cooler. Analogously, the gas flowing through the pipe at higher pressure into the heater at $T = T_{max}$ releases to it an amount of heat :

$$\int_{T_{\max}}^{T_N} C_{p_{\max}}(T) \ dT \quad ,$$

which is not compensated. This integral amounts to $-Qres$ as a consequence of eqs. (21)-(23). Therefore, the gas absorbs from the heater at $T = T_{max}$ an amount of heat :

$$Q_{res} \quad = \quad \int_{T_N}^{T_{\max}} C_{p_{\max}}(T) \ dT \quad ; \tag{25}$$

which contributes to Δ, as it has been exposed before.

If the eq. (20) holds, one has $\Delta = Q_{res}$; in such a case, the efficiency η is the highest when $Q_{res} = 0$. However, the condition $Q_{res} = 0$ (corresponding to a complete or "perfect" heat recovery) is unattainable, because N is a finite number. The question arises if

$$\lim_{N \to \infty} Q_{res} \quad = \quad 0 \quad , \tag{26}$$

that is, if it is possible to approximate indefinitely the condition of perfect (and reversible) heat recovery by increasing the number of intermediate heat exchangers.

It is easy to find a situation which violates the eq. (26). Let us consider a particular case of the situation represented in Fig. 2, for which an analytical calculation is possible. We represents it in Fig. 3. The specific heat per mole of gas along the isobars is expressed as ($C, A > 0$):

$$C_{P_{\max}}(T) \quad = \quad C + \frac{2A}{(T_{\max} - T_{\min})} (T_\chi - T)$$
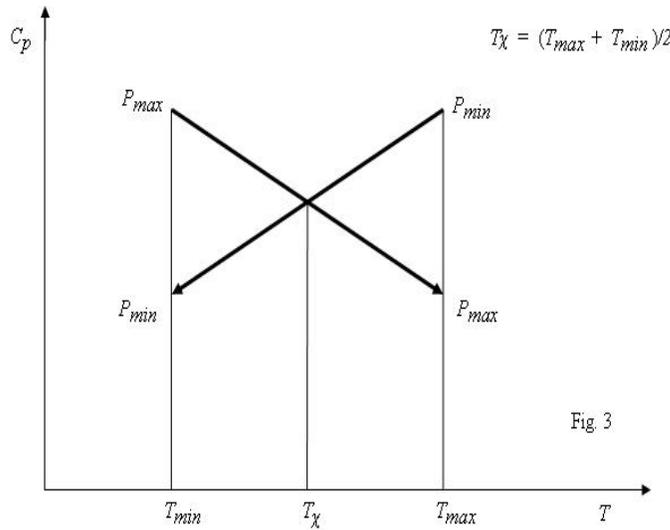
$$C_{P_{\max}}(T) \quad = \quad C - \frac{2A}{(T_{\max} - T_{\min})} (T_\chi - T) \quad .$$

Therefore: $Q(P = P_{max}) = Q(P = P_{min}) = C(T_{max} - T_{min})$

so that $\Delta = Q_{res}$.

Let us assume that $T_0 = T_{min}$ and $T_1 \quad < \quad T_\chi$. The integral (22), evaluated for $i = 1$, is the area under the curve $C_{Pmax}(T)$ in the interval (T_0, T_1), that is :

$$S \quad = \quad C(T_1 - T_0) + \frac{2A}{(T_{\max} - T_{\min})} \left[T_\chi (T_1 - T_0) - \frac{1}{2} (T_1^2 - T_0^2) \right] \quad .$$

Fig. 3

The integral (21), evaluated for $i = 1$, is the area under the curve C_{Pmin} in the interval (T_1, T_2); this area is:

$$S = C(T_2 - T_1) - \frac{2A}{(T_{\max} - T_{\min})} \left[T_\chi (T_2 - T_1) - \frac{1}{2} (T_2^2 - T_1^2) \right] \quad .$$

From the equality of these areas [eq. (23)] one obtains

$\frac{T_2 - T_1}{T_1 - T_0} = \frac{C + \alpha [T_\chi - ((T_1 + T_0)/2)]}{C - \alpha [T_\chi - ((T_1 + T_2)/2)]}$, where $\alpha = 2A/(T_{\max} - T_{\min})$.

And, in general :

$$\frac{T_{i+1} - T_i}{T_i - T_{i-1}} = \frac{C + \alpha [T_\chi - ((T_i + T_{i-1})/2)]}{C - \alpha [T_\chi - ((T_i + T_{i+1})/2)]} \quad .$$

Consider now the $i0$-th heat exchanger, with $T_{i0+1} > T_{i0} > T_{i0-1} \geq T_\chi$. For $i > i_0$ the expressions in brackets are negative, so that :

$$\frac{T_{i+1} - T_i}{T_i - T_{i-1}} \leq \frac{C}{C - \alpha [T_\chi - ((T_i + T_{i+1})/2)]} \leq \frac{C}{C - \alpha (T_\chi - T_{i0-1})} = q < 1 \quad .$$

That is :

$$T_{i+1} - T_i \leq q^{i-i0+1} (T_{i0} - T_{i0-1}) \quad .$$

Let's denote with T_{init} the temperature of $(i0 - 1)$-th heat exchanger; n is the number of heat exchangers between T_{init} and T_{max} and $\Delta T_i = T_i - T_{i-1}$ is the temperature difference between two adjacent heat exchangers. Summing up the $n + 1$ temperature differences (we assume that $T_{n+1} = T_{max}$) one has :

$$\sum_i \Delta T_i = T_{\max} - T_{init} \quad ,$$

so that :

$$\Delta T_{i0} \sum_{i \geq i0} q^{i-io} = \Delta T_{i0} \frac{1 - q^{n+1}}{1 - q} \geq T_{\max} - T_{init}.$$

For $n \to \infty$, this expression becomes :

$$\Delta T_{i_0} \ge (1 - q)(T_{\max} - T_{init}) \quad ,$$

where $q = C/[C - \alpha (T\chi - Tinit)]$. Therefore, the first segment (T_{i0-1}, T_{i0}) of the sequence does not tend to vanish in the limit $n \to \infty$, but it tends to a positive value dependent on the arbitrarily selected temperature T_{init}, except perhaps for $T\chi = Tinit$. As a consequence, the integrals (21), (22) in this interval, in general, do not vanish, and a finite residual heat is discharged on the external heater.

In each situation similar to one illustrated in Fig. 3 the curve at P_{min} is above the curve at P_{max} for $T > T\chi$. Since the area subtended by the lower curve on a given segment of temperatures must be equal to the area subtended by the upper curve on the subsequent segment [eq. (23)], this segment must be shorter than the previous one. The area subtended by the lower curve on the new segment will be less than the area subtended by the same curve on the previous segment. Therefore, the segment following this one will be shorter than preceding one and so on.

This result is reasonable, because (see Fig. 3) it is $C_{Pmin}(T) > C_{Pmax}(T)$ for $T > T\chi$; therefore from eq. (23) immediately follows that $\Delta T_i > \Delta T_{i+1}$, so we have an infinite sequence of shorter and shorter segments ΔT_i which forms the interval $(T\chi, T_{max})$. Just in this case, indeed, the temperature difference between the "last" heat exchanger and T_{max} is infinitesimal, so that no residual heat is discharged on the heater. But if the first segment was too short, the decrease of the following segments would be too sharp to guarantee the complete covering of the temperature axis until T_{max}. A finite temperature difference would remain with respect to the external source which would have to discharge a finite amount of heat. In general, if the first interval is too short, relation (26) is not satisfied and the proposed algorithm does not converge; the sequence converges towards a temperature $T_{limit} < T_{max}$; the integral of the specific heat on $[T_{limit}, T_{max}]$ is a residual heat discharged on the external heater. Referring to Fig. 3, this happens when :

$$\Delta T_{i_0} \le (1 - q)(T_{\max} - T_{init}) \quad .$$

On the other hand, the first interval must not be too long, otherwise it remains finite in the limit $n \to \infty$. According to our algorithm [eqs. (21),(22),(23)], a finite residual heat is discharged on the external heater so that, in conclusion, the eq.(26) can hold only for $T\chi = Tinit$ (that is, $q = 1$). In other words, a heat exchanger must operate at temperature $T\chi$.

A specular reasoning is valid for the segment $(Tmin, T\chi)$: starting from the heat exchanger, in which the reaction takes place, and approaching to $Tmin$, the temperature interval between two adjacent heat exchangers has to become shorter and shorter and the segment has to be completely covered, otherwise there is a finite temperature difference between the heat exchangers and the cold source and the latter has to discharge a finite amount of heat.

4.   The Vignati's argument

In his interesting work, Vignati studied the situation illustrated in Fig. 2. According to his heuristic argument, the eq. (26) was *ever* true and then was *ever* possible to approximate at least ideally, the condition $Q_{res} = 0$. Therefore, in order to have $\Delta = 0$ it was enough to individuate the Ericsson cycles on the PV plane in such a way that $Q(P = P_{max}) \approx Q(P = P_{min})$. The cycles, involving real gas, had to be near the critical temperature of gas ($T_{min}/Tc \approx 1$).

Vignati paid a particular attention to argon, because for this gas extensive tabulations and accurate modelizations were available from NBS-27 report (ref. 6). He was able to find several cycles, whose efficiency η, in the presence of a recuperator, (given that $Q_{res} = 0$) was, in fact, more than η_C .

The original ERICSSON code written by Vignati, in GWBASIC language, to perform the calculation of $\eta(Q_{res} = 0)$ according to NBS-27, is published in appendix to ref. 1. We have rechecked each line of this code, even making comparison with NBS-27 equations and tables, searching for a mistake, without results. We also reproduced the original Vignati's calculations and obtained the same results. For example, at

$$P_{max} = 62atm, \qquad P_{min} = 55atm \tag{27}$$

$$T_{max} = 180^0 K, \qquad T_{min} = 152^0 K$$

(we remark here that for argon $Tc = 150.86$ °K) we have $R = 5.68$ J/mol, a very small value. The cycle efficiency, without recuperator, is 0.025; the cycle efficiency with recuperator and $Q_{res} = 0$ is $\eta(Q_{res} = 0) = 0.270$. The Carnot efficiency between the temperatures $Tmax$ and $Tmin$ amounts to $\eta_C = 0.155$. Therefore, for this cycle: $\eta(Q_{res} = 0) > \eta_C$.

The report NBS-27 gives analytic expressions both for the internal energy of gas argon, U, as a function of P, T and its equation of state. In calculating the efficiency, the heat exchanged during each process is evaluated by applying the first principle in the form of $Q = \Delta U + \int pdV$.

Therefore, according to the Vignati judgement, the result $\eta(Q_{res} = 0) > \eta_C$ should reveal a contradiction between the first and the second principle, if it was possible to obtain the perfect (and reversible) heat compensation.

However, numerical computations performed independently by Vignati himself and by us shown, without any doubt, that even for a great number of intermediate heat exchangers ($N = 20$ or more), the effective residual heat Q_{res} is high enough to decrease the efficiency η to values below the Carnot limit η_C (ref. 7).

Of course, by numerical methods only, it is impossible to prove that for argon $Qres \to 0$ with $N \to \infty$, because starting from a certain value of N, the increase in temperature between the adjacent heat exchangers becomes less than the processor rounding error, as a consequence the computer program fails to enter a loop. In any case, the physical realization of a heat recuperator, having heat exchangers so finely graduated in

temperature, is not likely. The original Vignati's argument would be taken into account merely as a *gedanken*[4].

However, a critical re-examination of Vignati's analysis, based upon the results presented in previous sections, is now possible. At first we remark that, for $Q_{res} = 0$, the cycle is completely reversible, therefore [according to the eq. (17)] the efficiency must be equal to η_C. Otherwise we have a violation of eqs. (5) and (10) [which have been microphysically justified !] , rather than a violation of the second principle.

The key of the puzzle consists in the violation of eq. (26). In the limit $N \to \infty$ the condition $Q_{res} = 0$ is not reached, because at least one of the following conditions occurs :

(1) The temperature of some heat exchanger is not stationary and a heat exchange between the isobaric processes and external heat sources is requested in order to guarantee the thermal equilibrium.

(2) The heat recovery does not cover the whole range of temperature (T_{min}, T_{max}); in other words, the cycle does not close itself. So, the cycle really does not exist.

In the first case the efficiency calculated, according to Vignati's prescription, as

$$\eta(Q_{res} = 0) = 1 - Q(T = T_{min})/Q(T = T_{max}) \tag{28}$$

is not the correct efficiency; in the second case, it is not the efficiency of a physically possible cycle. Obviously, no contradiction arises if this fictitious efficiency exceeds the Carnot limit.

The argument can be restated as follows. Let us consider a particular cycle with a heat input $Q(T = T_{max})$ and a heat output $Q(T = T_{min})$; we assume these amounts of

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[4] A chapter of Vignati's book (1) is dedicated to the Xu Yelin experiment (8). We do not believe this interesting experiment, recently updated (9) and independently reproposed by other research workers [it coincides with the first setup investigated in ref. (12)], really violates the second principle. In fact, let us consider a closed circuit (electromagnetically and optically insulated) wherein a non biased diode, in thermal equilibrium with the environment, is inserted. It is possible to arrange the work function of cathode and anode and their surfaces in such a manner that a net current of thermoelectrons flows from the cathode towards the anode. Therefore an electric current, mantained by the thermal interaction between the diode and the environment, flows along the circuit. However, a single thermoelectron has the same energy when it leaves the cathode and when it comes back to it; so the amount of heat exchanged between the environment and the apparatus is really null. In absence of electric resistance, the work done by the circuit is also null. In the presence of a resistor, the current flowing in it generates a voltage between cathode and anode. The single thermoelectron gains an amount of energy when it interacts with the electric field generated by the presence of the resistor, and then, it releases that energy to the resistor (eq. 1e of ref. 8). As a consequence, we have here a mere transformation of electric work in heat or in other kynds of work. Thermal fluctuations serve here just to mantain the energy distribution of thermoelectrons, without any net transfer of energy to the apparatus; there is not a conversion of environmental heat in work. In other terms, the apparatus is not a heat engine. The rather interesting fact is that the spontaneous self-organization of a desordered motion (thermal fluctuations) leading to an ordered motion (the electric current) occurs *in thermal equilibrium*. Ideally, the environment may be substitued with an insulated thermostat operating at the same temperature, so obtaining self-organization in an insulated apparatus in thermal equilibrium !

heat to be independent on the number of heat exchangers N. The cycle efficiency is then :

$\eta =$[$Q(T = T_{max})$ - $Q(T = T_{min})$]/ [$Q(T = T_{max}) + Q_{res}(N)$] =
$\{$[$Q(T = T_{max})$ - $Q(T = T_{min})$]/ $Q(T = T_{max})\}$ $\{$ $Q(T = T_{max})$/ [$Q(T = T_{max}) + Q_{res}(N)$]$\}$ =
η_0 / [$1 + Q_{res}(N)$/ $Q(T = T_{max})$], (for $N > 0$)

where $\eta_0 =$[$Q(T = T_{max})$ - $Q(T = T_{min})$]/ $Q(T = T_{max})$. If $Q_{res}(N) \to 0$ for $N \to \infty$, then $\eta \to \eta_0$ in the same limit. But in this limit, due to the complete reversibility, the eq. (17) holds, so that $\eta_0 = \eta_C$. Then, in general, the following relation holds :

$$\eta = \eta_C/[1 + Q_{res}(N)/Q(T = T_{max})] < \eta_C$$

in agreement with the second principle. Therefore, no contradiction exists between the first and the second principle at this level.

Turning the argument on his head, we can say that a reversible cycle with an efficiency, calculated according to eq. (28), exceeding the Carnot limit, is not physically possible because the reversible limit $Q_{res}(N) \to 0$ for $N \to \infty$ does not exist for it.

For example, the cycle (27) may be realised only without recuperator or with a finite number N of heat exchangers. The numerical calculations performed with Vignati's code itself give an efficiency without recuperator which is less than η_C (in agreement with the first principle and the Clausius equality, see Appendix). For several finite values of N, the numerical calculations performed with Vignati's RECUPERF code or, in alternative, with our RECUPE code, give an efficiency below η_C (in agreement with the second principle and the Clausius inequality).

The reader is referred to Table n. 1 for a synopsis; the reported efficiency is estimated, following Vignati's procedure, as $\eta = \eta_0$ / [$1 + Q_{res}$/ $Q(T = T_{max})$], where η_0 is given by eq. (28). We have here $\eta_0 \neq \eta_C$, because the reversible limit does not exist for this cycle. No violation of the second principle [eq. (19)], even mathematically possible, is evidenced.

Table n. 1; The efficiency of the cycle (27), estimated with RECUPERF and RECUPE codes;

N	η/η_C
0	0.161
1	0.260
2	0.320
5	0.424
10	0.207
20	0.194

5.   A cycle with chemical reactions

In order to eliminate the difficulties related to numerical calculations, we consider in this section a modified setup for which an analytical treatment is possible. The system model is an Ericsson engine involving an ideal gas, a recuperator being situated between two isobaric processes. One of the recuperator's heat exchangers operates at temperature $T\chi$ between T_{min} and T_{max}.

   Let us introduce a modification in the original Vignati's setup, supposing that in this heat exchanger at temperature $T\chi$ (with $T_{min} \leq T\chi \leq T_{max}$), and only in it, due to a suitable catalyser installed there, the inflowing gas undergoes such chemical reactions as:

- a dissociation, when it moves from $Tmin$ towards $Tmax$;
- a recombination, when it moves from $Tmax$ towards $Tmin$.

   The reaction is assumed to occur at constant pressure, and the reaction heat generated at $T = T\chi$ during the dissociation process is assumed to be integrally absorbed during the recombination process occuring in the same heat exchanger at the same temperature.

   Since the number of freedom degrees of the gas molecule changes during the reaction, the gas specific heat $C_p(T)$ changes as well. Hereinafter we limit our attention to a given mass of gas small enough to keep uniform its temperature and pressure during the whole cycle. This mass will amounts to n and n' moles respectively before and after the reaction occuring in the pipe at higher pressure.

   We redefine $C_p(T)$ to be the heat capacity of this mass. The $C_p(T)$ curve, which is identical for both isobaric processes, is represented in Fig. 4. This curve is covered
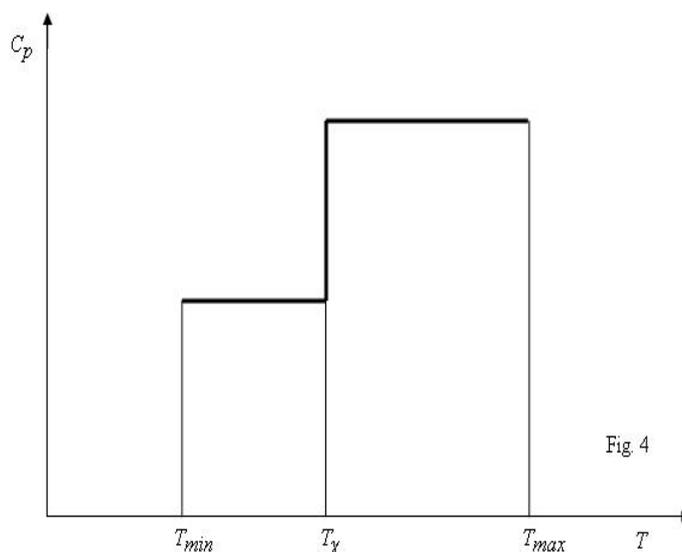

Fig. 4

from the left to the right during the isobaric process at higher pressure; while it is covered from the right to the left during the isobaric process at lower pressure. Therefore, $Q(P = P_{max}) = Q(P = P_{min})$, so that $\Delta = Q_{res}$.

   The work done by the isobaric process at P_{max} may be expressed as a sum of the work

done by expanding gas , at temperature range from T_{min} to $T\chi$ $[= P_{max} (V\chi^- - -V_1')]$, the work of expansion done by the reaction $[= P_{max} (V\chi^+ - -V\chi^-)]$ and the work done of expanding gas at temperature range from $T\chi$ to T_{max} $[= Pmax (V_1 - -V\chi^+)]$. Since :

$$P_{max}V_1 = n'RT_{max}, \qquad P_{max}V_1' = nRT_{min}$$

this work is $P_{max}(V_1 - V_1') = n'RT_{max} - nRT_{min}$.

The work done by the isobaric process at P_{min} may be express as a sum of the compression work at temperature range from T_{max} to $T\chi$ $[= P_{min} (V\chi^+ - -V_2)]$, the compression work done by the reaction $[= P_{min} (V\chi^- - V\chi^+)]$ and the compression work at temperature range from $T\chi$ to T_{min} $[= P_{min} (V_2' - V\chi^-)]$. Since :

$$P_{min}V_2' = nRT_{min}, \qquad P_{min}V_2 = n'RT_{max}$$

this work is $P_{min}(V_2' - V_2) = nRT_{min} - n'RT_{max}$.

The total work done by two isobaric processes of the cycle is then zero. The work produced by the cycle is expressed as the sum of the isothermal contributes only :

$L = n' RTmax \ ln \ (V_2/V_1) + n \ RTmin \ ln \ (V_1'/V_2')$.

The Vignati's efficiency $\eta(Qres= 0)$ can be expressed as[5] :

$$\frac{L}{Q_2} \ = \ 1 \ + \ \frac{n}{n'} \frac{T_{min}}{T_{max}} \frac{\ln\left(V_1'/V_2'\right)}{\ln\left(V_2/V_1\right)} = 1 + \frac{n}{n'}(\eta_C - 1).$$

Therefore $\eta(Q_{res} = 0) > \eta_C$ for

$$1 - \frac{n}{n'} + \frac{n}{n'}\eta_C \geq \eta_C$$

$$1 \ - \ \frac{n}{n'} \ \geq \ \eta_C \left(1 \ - \ \frac{n}{n'} \right) \ \ .$$

The condition $n' > n$ is satisfied for a dissociation; in such a case we have $0 < 1 - n/n'$ < 1, that is $\eta_C \leq 1$; this is an ever true statement. Therefore, if $n' \ > \ n$ is ever $\eta(Qres = 0) \ \ > \eta_C$.

Let us assume that $T_0 = T_{min}$ and let us fix a value of $T_1 \ \ \in (T_{min}, T\chi)$. The value of integral (22) is determined and equal to the value of integral (21). The equality between two integrals [eq. (23)] is expressed as:

$$(T_1 - T_0)Cp_{max} = (T_2 - T_1)Cp_{min}$$

For temperatures in the interval (T_{min}, T_χ) we have $Cp_{max} = Cp_{min}$, so that $T_1 - T_0 = T_2 - T_1$ and, in general :

$$T_{i+1} - T_i = T_i - T_{i-1} \quad \text{for} \quad T_{min} \leq \quad T \leq T_\chi$$

In others words, the temperature interval between two adjacent heat exchangers is constant on the segment (T_{min}, T_χ). Denoting with N_1 the number of exchangers operating at temperature intermediate between T_{min} and T_χ one has

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[5] We pose $Q_2 = Q(T = T_{max})$, $Q_1 = Q(T = T_{min})$, $P_2 = P_{max}$, $P_1 = P_{min}$.

$$\Delta T_1 = T_1 - T_0 = (T_\chi - T_{min})/(N_1 + 1)$$

a condition which assure that the amounts α and β of the residual heat on this segment are null.

At the temperature T_χ there is the $(N_1 + 1)$-th heat exchanger, that is $T_{N1+1} = T_\chi$. Applying the same line of reasoning to $T > T_\chi$, we can obtain :

$$T_{N_1+2} - T_{N_1+1} = T_{N_1+3} - T_{N_1+2}$$

and in general :

$$T_{i+1} - T_i = T_i - T_{i-1} \quad \text{for} \quad T_\chi \leq T \leq T_{max}$$

By denoting with N_2 the number of heat exchangers operating in the temperature interval (T_χ, T_{max}) one has

$$T_{N_1+2} - T_{N_1+1} = (T_{max} - T_\chi)/(N_2 + 1)$$

a condition which assure that the amounts α and β of the residual heat on this segment are null.

We have, therefore, N_1 heat exchangers operating in the interval (T_{min}, T_χ), one heat exchanger operates at $T = T_\chi = T_{N1+1}$ wherein the reactions occur and N_2 heat exchangers operate in the interval (T_χ, T_{max}) ; the total number of heat exchangers is

$$N = N_1 + N_2 + 1$$

The heat exchanger wherein the reactions occur absorbs a heat amount $(T_{N1+2} - T_{N1+1})C_p(T > T_\chi)$ from the cooling gas; it releases a heat amount $\Delta T_1 C_p(T < T_\chi)$ to the heating gas. In order to make T_χ value stationary, these amounts must be equal, so that :

$$T_{N_1+2} - T_{N_1+1} = T_{N_1+2} - T_\chi = \frac{C_p(T < T_\chi)}{C_p(T > T_\chi)}\Delta T_1$$

The uncompensated residual heat that the gas absorbs from the heater at T_{max} therefore is:

$$Q_{res} = C_p(T > T_\chi)(T_{N_1+2} - T_\chi) = C_p(T < T_\chi)\Delta T_1$$

It is easy to verify that $Qres \to 0$ for $\Delta T_1 \to 0$, that is for $N_1 \to \infty$ or $N_2 \to \infty$. The situation of perfect heat recovery may be indefinitely approximated. The eq. (26) is then ever satisfied.

Therefore, the condition $Qres \to 0$ involving a perfect (and reversible) heat recovery is ever, at least ideally, achievable. If it is actually achieved, we have a cycle with an efficiency $\eta = \eta(Qres = 0) > \eta_C$.

However, this efficiency takes in account only the pV work. The proposed cycle can not do mechanical pV work only; indeed, the total increase of entropy along it is :

$$Q_2/T_{max} - Q_1/T_{min} + (\Delta S)_{dissociation} + (\Delta S)_{recombination} = 0$$

where :

$$Q_2 = n'RT_{max}ln(P_1/P_2), \qquad Q_1 = nRT_{min}|ln(P_1/P_2)|$$

The isobaric sections do not contribute in the reversible limit, because their thermal exchange is compensated. Therefore :

$$Q_2/T_{max} - Q_1/T_{min} = (n' - n)R|ln(P_1/P_2)| > 0 \quad , \text{because} \quad n' > n$$

Of consequence :

$$(\Delta S)_{dissociation} + (\Delta S)_{recombination} < 0$$

But :

$$(\Delta G)_{dissociation} = (\Delta H)_{dissociation} - T_\chi(\Delta S)_{dissociation}$$

$$(\Delta G)_{recombination} = (\Delta H)_{recombination} - T_\chi(\Delta S)_{recombination}$$

$$(\Delta H)_{dissociation} = -(\Delta H)_{recombination}$$

so that :

$$(\Delta G)_{dissociation} + (\Delta G)_{recombination} = -T_\chi[(\Delta S)_{dissociation} + (\Delta S)_{recombination}] > 0$$

Therefore, the chemical processes of gas dissociation and recombination request an external (not pV) work. This work must be supplied from the cycle. The maximum work requested amounts to $T_\chi [(\Delta S)_{dissociation} + (\Delta S)_{recombination}]$.

The (minimum) useful work done by the cycle is then :

$$L' = L + T_\chi[(\Delta S)_{dissociation} + (\Delta S)_{recombination}] = L + T_\chi[Q_1/T_{min} - Q_2/T_{max}]$$

and the effective efficiency is :

$$\eta' = L'/Q_2 = (Q_2 - Q_1)/Q_2 + (T_\chi/Q_2)[Q_1/T_{min} - Q_2/T_{max}] =$$

$$1 - (T_\chi/T_{max}) + (Q_1/Q_2)(T_\chi/T_{min} - 1) =$$

$$1 - (T_\chi/T_{max}) - (1 - \eta)(1 - T_\chi/T_{min}) =$$

$$T_\chi[(1-\eta)/T_{min} - 1/T_{max}] + \eta = (T_\chi/T_{min})[1 - \eta - T_{min}/T_{max}] + \eta =$$

$$(T_\chi/T_{min})(\eta_C - \eta) + \eta = \eta - |\eta - \eta_C|/T_{min})T_\chi$$

We can see that η' decreases when T_χ increases. It is $\eta' > \eta_C$ when $T_\chi < T_{min}$, a condition which is never satisfied. Therefore, it is $\eta' < \eta_C$, a result which is still in agreement with the second principle of thermodynamics.

Conclusions

The efficiency of a perfectly reversible cycle can be inferred from the first principle and the Clausius equality, without relation with the second principle. The anomalous efficiencies, calculated by Vignati assuming the reversible limit $Q_{res} = 0$ for particular cycles with gas argon, may be explained as referred to actually forbidden cycles.

For finite values of N and $Q_{res} \neq 0$, the efficiencies calculated according to the Vignati's prescription (Table n. 1) give results in agreement with the second principle, so that no contradiction arises with the usual laws of thermodynamics. This conclusion is strengthened by an analytical calculation on cycles involving chemical reactions.

Appendix

Let us consider a cycle represented by a closed curve on the plane TS (Fig. 5). Each point of this curve represents a state in equilibrium with an external reservoir depending on the point, because the temperature $T = Tsys = Tres$ is a function of cycle point. Therefore, the system exchanges heat with a sequence of external sources which repeats by itself at each cycle.

Under these conditions, the eq. (10) holds and dQ is the infinitesimal element of area of the plane TS. So, if no internal heat recovery occurs, the area Σ enclosed in the cycle is the total amount of heat, Q, exchanged with the external reservoirs:

$Q = area \ \Sigma$, if no internal heat recovery occurs.

Therefore, referring to Fig.5, denote with Q_2, the area under the upper branch CD and with Q_1 the area under the lower branch AB, then the quantity of exchanged heat is $Q_2 - Q_1$. According to the first principle, this heat is equal to the work L done by the cycle; the efficiency $\eta = L/Q_2$ is then expressed as $(area \ \Sigma)/Q_2$. As one may verify from Fig. 5, abscissa and ordinate extremes, T_1, T_2, S_1, S_2, have once been fixed, Q_1 is minimum for $A \equiv A'$, $B \equiv B'$. In this case, Q_2 is maximum for $C \equiv A''$, $D \equiv B''$. The maximum of the efficiency $\eta = (Q_2 - Q_1)/Q_2 = 1 - Q_1/Q_2$ is then obtained, when the cycle coincides with the Carnot rectangle $A'B'B''A''$. Its value is :

$$\eta_{\max} = \frac{(S_2 - S_1)\,(T_2 - T_1)}{(S_2 - S_1)\,T_2} = 1 - \frac{T_1}{T_2} = \eta_C$$
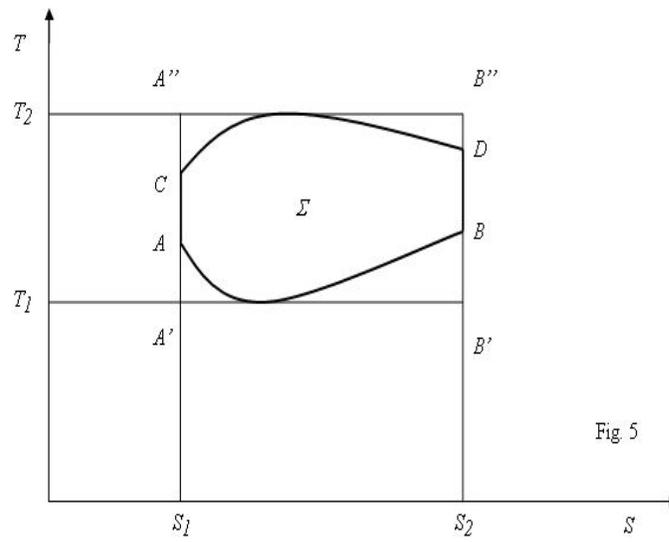
Fig. 5

Therefore, if no internal heat recovery occurs, the Carnot theorem may be inferred, for a perfectly reversible cycle, from eqs. (5), (10).

References

[1] M. Vignati; Riflessioni sulla potenza motrice del calore ambientale (e sulle macchine idonee a sviluppare questa potenza); Astrolabium , Civitavecchia, 1993 . *In italian.*

[2] M. Vignati; Transformation from heat of low temperature sources into work; fundamentals for a maximum of efficiency; International Conference on Cold Fusion 5; 9-13 April 1995, Monte Carlo – Monaco.

[3] M. Vignati; Notiziario Ordine degli Ingegneri di Verona; n. 74 (1) gennaio-marzo 2002; pag 35-43; *in italian.*

[4] G. Careri; Ordine e disordine nella materia; Laterza, Bari, 1982. *In italian.*

[5] J. C. Slater; Introduction to chemical physics; *italian transl.* ; Sansoni, Bologna, 1963.

[6] A. L. Gosman, R. D. McCarty, J. G. Hust; Thermodynamic properties of argon from the triple point to 300 ˚K at pressures to 1000 atmospheres; Report NSRDS-NBS 27, National Bureau of Standards 1969.

[7] Our own Fortran77 code RECUPE is available on request; the author wishes thank M. Vignati for the availability of his GWBasic code RECUPERF. These codes implement the algorithm based upon eqs. (21)-(22)-(23).

[8] Xu Yelin ; A Trial and Study on Obtaining Energy from a Single Heat Reservoir at Ambient Temperature; Science Press, Beijing (1988).

[9] Xu Yelin ; Missiles and Space Vehicles 3, 53-60 (2000).

[10] E. Fermi; Thermodynamics; *it. transl*; Boringhieri, Torino (1972)

[11] P.W. Atkins; Physical Chemistry, III˚ ed., chapter 21.2(b).

[12] D.P. Sheehan; Journal of Scientific Exploration 12 (2), 303-314 (1998) and there quoted references