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ON THE EVOLUTION OF THE DEFINITION OF ENTROPY FROM CLAUSIUS TO TODAY

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ABSTRACT

Carnot analyzed an engine operating between two reservoirs. Through a peculiar mode of reasoning, he found the correct optimum shaft work performed during a cyclic change of state of the engine. Clausius justified Carnot's result by enunciating two laws of thermodynamics, and introducing the concept of entropy as a ratio of heat and temperature of a thermodynamic equilibrium state.

By appropriate algebraic manipulations, in this paper we express Carnot's optimum shaft work in terms of available energies or exergies of the end states of the reservoirs, and Clausius' entropy in terms of energy and available energy.

Next, we consider the optimum shaft work performed during a cyclic change of state of an engine operating between a reservoir, and a system with fixed-amounts of constituents, and fixed-volume but variable temperature. We express the optimum shaft work in terms of the available energies of the end states, and Clausius' entropy in terms of energy and available energy. Formally, the entropy expression is identical to that found for the Carnot engine except for the difference in end states.

Finally, we consider the optimum shaft work performed during a cyclic change of state of an engine operating between system A initially in any state A_1 (thermodynamic equilibrium or not) and reservoir R. We call this optimum generalized available energy with respect to R, and use it together with energy to define an entropy of any state A_1. Again we observe that the expression for entropy is formally identical to the two given earlier except for the difference in end states.

NOMENCLATURE

A	system
B	system
c_R	positive constant of reservoir R
E	energy
E^Y	energy of system Y
E_i^Y	energy of system Y in state Y_i
$\mathbf{n}$	vector of types and amounts of constituents
$\mathbf{n}^Y$	vector of types and amounts of constituents of system Y
$\mathbf{n}_i^Y$	vector of types and amounts of constituents of system Y in state Y_i
S	Clausius entropy
S^Y	Clausius entropy of system Y
S_i^Y	Clausius entropy of system Y in state Y_i
S_{irr}	entropy generated spontaneously
T	temperature
T_i	temperature of system A in state A_i
T_Y	temperature of system Y
V	volume
V_i^Y	volume of system Y in state Y_i
$W_{ij}^{YZ\rightarrow}$	shaft work performed by composite system YZ as its state changes from state $(YZ)_i$ to state $(YZ)_j$
$\left(W_{ij}^{YZ\rightarrow}\right)_{rev}$	shaft work performed by composite system YZ as its state changes reversibly from state $(YZ)_i$ to state $(YZ)_j$
X	engine
Σ^Y	entropy of any system Y in any state
Σ_i^Y	entropy of any system Y in any state Y_i
Ω^Y	available energy or exergy of a system with respect to reservoir Y
Ω_i^Y	available energy or exergy of system A in state A_i with respect to reservoir Y; also generalized available energy of system A in state A_i with values $\mathbf{n}_i^A$ and V_i^A with respect to reservoir Y and a final state of A with values $\mathbf{n}_0^A$ and V_0^A and such that A and Y are in mutual stable equilibrium.

INTRODUCTION

Over the past few decades, we have adopted the viewpoint that the laws of thermodynamics are not either statistical or restricted only to macroscopic systems in thermodynamic equilibrium. In support of this viewpoint, we have presented both the quantum-theoretic foundations (Hatsopoulos and Gyftopoulos, 1976; Beretta et al., 1984; Beretta et al., 1985), and a nonquantal exposition of foundations and applications (Gyftopoulos and Beretta, 1991a).

Among the many novel results of the new viewpoint is the recognition that entropy is a nonstatistical property of matter, in the same sense that energy and momentum are nonstatistical properties of matter, and that it is well-defined for all systems, large and small, and all states, thermodynamic equilibrium and not thermodynamic equilibrium (Çubukçu and Gyftopoulos, 1994).

Most physicists and engineers find the new viewpoint, in general, and the extension of entropy to states that are not thermodynamic equilibrium, in particular, unacceptable and oppose them vehemently. To the best of our knowledge, their opposition is based solely and exclusively on the argument that the new ideas differ from the accepted dogma, and not on any experimental results or on any reasoned arguments either against our statements of the laws of thermodynamics and quantum theory, or against the faultlessly, noncircularly, and completely proven theorems, such as the theorems that result in the definition of entropy.

In this brief paper, continuing the efforts to elucidate the new point of view, I present the general definition of entropy as an outgrowth of the seminal ideas of Clausius. The paper is organized as follows.

The Clausius definition of entropy of a reservoir is discussed in the second section, the extension of this definition to a system with variable temperature in the third section, the definition of entropy of any system in any state in the fourth section, and a concluding remark in the last section.

CARNOT ENGINE

Carnot (1824) analyzed an engine X which interacts with two reservoirs A and B, and through a peculiar mode of reasoning found the correct optimum shaft work performed in the course of a cyclic change of state of the engine (Figure 1).

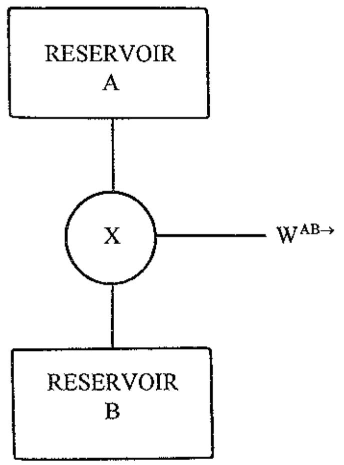

Figure 1. Schematic of a Carnot Engine

Using Clausius' pathfinding ideas about energy and entropy (1867), denoting energy by E, Clausius' entropy by S, temperature by T, volume by V, amounts of constituents by **n**, the values of these quantities for each reservoir at the beginning and the end of the cyclic change of state of the engine by the symbols listed on Figures 2a and 2b, respectively, we can reproduce Carnot's seminal result by beginning with the energy and entropy balances of the composite system AXB.

Energy balance of composite system AXB

$$E_2^A - E_1^A + E_2^B - E_1^B = - W_{12}^{AB\rightarrow} \tag{1}$$

Entropy balance of composite system AXB

$$S_2^A - S_1^A + S_2^B - S_1^B = S_{irr} \tag{2}$$

where $W_{12}^{AB\rightarrow}$ is the shaft work (energy transfer only) in the course of the cyclic change of state of the engine, and S_{irr} the amount of entropy generated spontaneously during the same time. The value of $W_{12}^{AB\rightarrow}$ is positive if work is done by the engine, and negative if work is done on the engine.

For each of the reservoirs A and B, the changes of energy and Clausius entropy are proportional to each other so that

$$S_2^A - S_1^A = \left(E_2^A - E_1^A\right) / T_A \tag{3}$$

$$S_2^B - S_1^B = \left(E_2^B - E_1^B\right) / T_B \tag{4}$$

So, using equations (2) to (4), we can eliminate the energy of reservoir B from equation (1) and find

$$W_{12}^{AB\rightarrow} = - \left(E_2^A - E_1^A\right) \left[1 - \frac{T_B}{T_A}\right] - T_B S_{irr} \tag{5}$$

Because the optimum is the reversible process and then $S_{irr} = 0$, equation (5) yields

$$\left(W_{12}^{AB\rightarrow}\right)_{rev} = - \left(E_2^A - E_1^A\right) \left[1 - \frac{T_B}{T_A}\right] \tag{6}$$

that is, Carnot's seminal result in terms of absolute temperatures, where $\left(W_{12}^{AB\rightarrow}\right)_{rev}$ denotes the shaft work if the process of the composite system AXB is reversible.

For the purposes of this paper, we rewrite equation (6) in several equivalent forms, such as

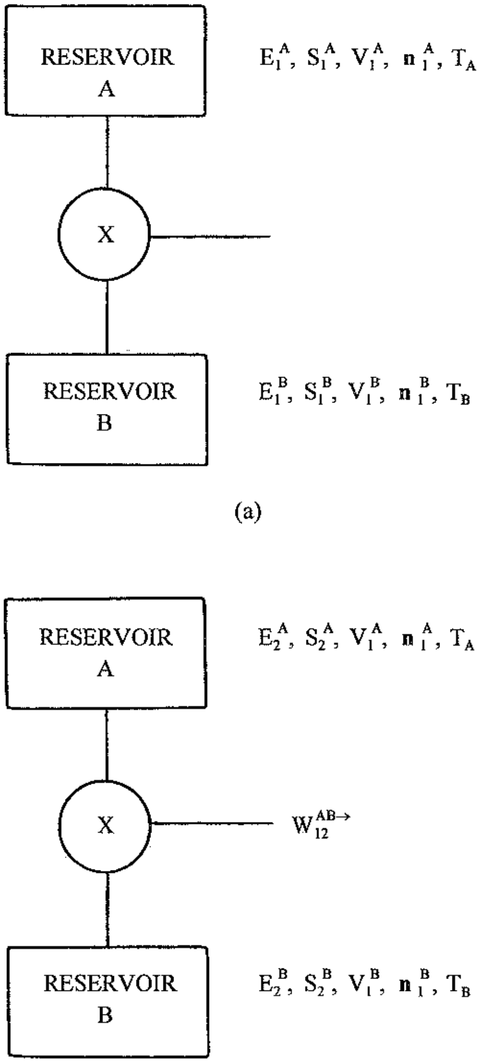

Figure 2. Schematic of a cyclic change of state of a Carnot engine: (a) initial states of the reservoirs; and (b) final states of the reservoirs

$$\left(W_{12}^{AB\to}\right)_{rev} = -\left(E_2^A - E_1^A\right) + T_B\left(E_2^A - E_1^A\right)/T_A$$
$$= -\left(E_2^A - E_1^A\right) + T_B\left(S_2^A - S_1^A\right) \qquad (7)$$

$$S_2^A - S_1^A = \left[\left(E_2^A - E_1^A\right) + \left(W_{12}^{AB\to}\right)_{rev}\right]/T_B$$
$$= \left[\left(E_2^A - E_1^A\right) - \left(\Omega_2^B - \Omega_1^B\right)\right]/T_B \qquad (8)$$

where in writing the second of equations (7) we use equation (3), the first of equations (8) is a rearrangement of the second equation (6), and the second equation (8) results from the definition of Ω_i^B as the available energy or exergy of an amount of energy E_i^A of system A in state A_i at fixed temperature T_A with respect to reservoir B at temperature T_B, that is,

$$\Omega_i^B = E_i^A\left[1 - \frac{T_B}{T_A}\right] \qquad (9)$$

As is very well known, the available energy or exergy Ω_i^B is a property of both system A and reservoir B. It is noteworthy, however, that the entropy S_i^A and the energy E_i^A are each independent of reservoir B. We can express this important result in another way. We consider the same changes of energy and entropy of system A from state A_1 to state A_2 but in a process of a composite system AXR consisting of system A, engine X, and reservoir R at temperature T_R. In the course of a cycle of X, we can readily verify that

$$S_2^A - S_1^A = \left[\left(E_2^A - E_1^A\right) - \left(\Omega_2^R - \Omega_1^R\right)\right]/T_R \qquad (10)$$

where Ω_i^R is the available energy or exergy of E_i^A at fixed temperature T_A with respect to a reservoir at temperature T_R, that is,

$$\Omega_i^R = E_i^A\left[1 - \frac{T_R}{T_A}\right] \qquad (11)$$

Though Ω^R and T_R depend on the reservoir, we see from equation (10) that neither E^A nor S^A has this dependence.

ENGINE OPERATING BETWEEN A SYSTEM THAT CAN ASSUME DIFFERENT TEMPERATURES AND A RESERVOIR

Next, we consider a cyclic change of state of an engine X while it interacts with system A and reservoir R so that the values of E, Clausius' entropy S, T, V, and n of the end states of A and R are as listed on Figures 3a and 3b. In contrast to the process depicted in Figure 2, here the initial temperature of A is T_1, and the final temperature $T_0 = T_R$, that is, at the end of the process, system A is in mutual stable equilibrium with reservoir R.

If the process of the composite system AXR is reversible, the energy transferred through the shaft $\left(W_{10}^{AR\to}\right)_{rev}$ is optimum, the energy and Clausius' entropy that flow out of system A are $E_0^A - E_1^A$ and $S_0^A - S_1^A$, respectively, and transfer of the entropy $S_0^A - S_1^A$ into reservoir R at the end of the cyclic change of state of X requires the concurrent transfer of energy $T_R\left(S_0^A - S_1^A\right)$ (equation [4]). So the energy balance for the composite system AXR yields

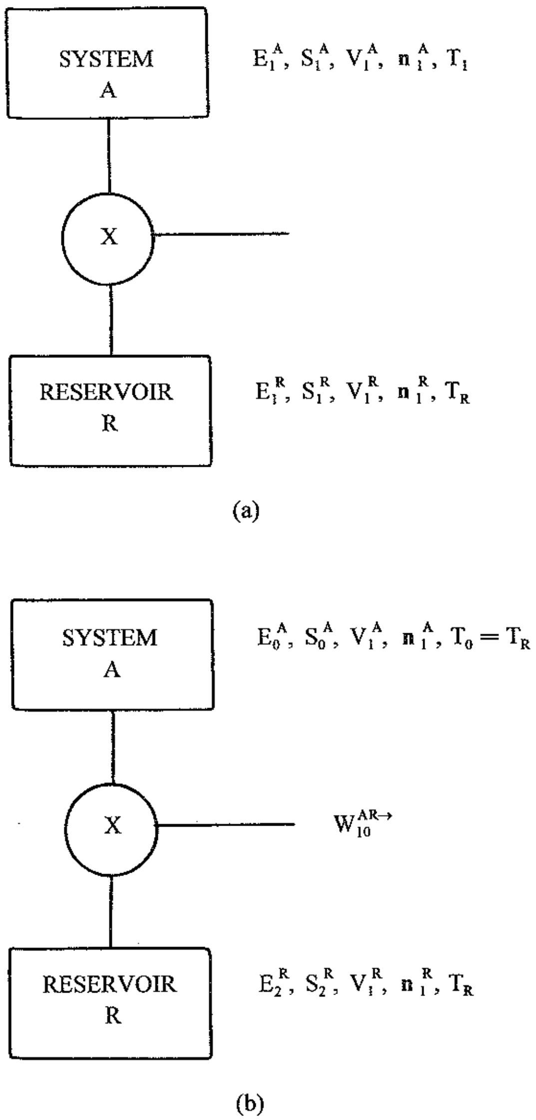

Figure 3. Schematic of a cyclic change of state of an engine: (a) initial state of A at temperature T_1; and (b) final state of A at temperature $T_0 = T_R$.

$$\left(W_{10}^{AR\rightarrow}\right)_{rev} = -\left[\left(E_0^A - E_1^A\right) - T_R\left(S_0^A - S_1^A\right)\right] \qquad (12)$$

or, equivalently,

$$\begin{aligned} S_1^A - S_0^A &= \left[\left(E_1^A - E_0^A\right) - \left(W_{10}^{AR\rightarrow}\right)_{rev}\right] / T_R \\ &= \left[\left(E_1^A - E_0^A\right) - \Omega_1^R\right] / T_R \qquad (13) \end{aligned}$$

where $\Omega_1^R = \left(W_{10}^{AR}\right)_{rev}$. It is clear that Ω_1^R is a property of both system A and reservoir R, and represents the largest work that can be done by the composite system AXR as A starts from an initial thermodynamic equilibrium state A_1 and ends in a thermodynamic equilibrium state A_0 such that A and R are in mutual stable equilibrium, and X undergoes a cyclic change of state. By definition, this work is the available energy or exergy of state A_1 with respect to reservoir R.

If during the cyclic change of state of X, the reversible process of the composite system AXR starts with system A in thermodynamic equilibrium state A_1 and ends with A in thermodynamic equilibrium state A_2 different from A_0, then repeated application of equation (13) yields

$$S_2^A - S_1^A = \left[\left(E_2^A - E_1^A\right) - \left(\Omega_2^R - \Omega_1^R\right)\right] / T_R \qquad (14)$$

Though in equations (13) and (14), both Ω^R and T_R depend on R, it is noteworthy that neither energy E^A nor Clausius entropy S^A exhibit such dependence.

The Clausius entropy appearing in equations (10) and (14) can be shown to satisfy the following conditions (Callen, 1985).

1. It applies to thermodynamic equilibrium states only.
2. It is independent of the reservoir.
3. It is nondecreasing in adiabatic processes.
4. It is additive.
5. It can be assigned nonnegative values only (third law of thermodynamics or Nernst's theorem).
6. For given values of energy, amounts of constituents, and volume, it assumes a maximum.
7. For given values of amounts of constituents and volume, the graph of S versus E is concave.
8. For mutual stable equilibrium between two systems, it yields the conditions of temperature equality, total potential equalities, and pressure equality.

In addition to these conditions, a scarcely appreciated fact is that the Clausius entropy applies to all systems, large and small, and is not statistical because neither Clausius nor other scientists that worked on the foundations and theorems of the theory of classical thermodynamics made any restrictive assumptions either about the size of the system or about the phenomena explained by this theory being statistical, or both.

A GENERAL ENGINE

Next, we consider an engine X that interacts with system A and reservoir R, and performs shaft work under the conditions listed on Figure 4. Initially, A is in state A_1 that is not necessarily thermodynamic equilibrium. In this state, the values of the amounts of constituents are $\mathbf{n}_1^A$, and the value of the volume is V_1^A (Figure 4a). At the end of the interactions, engine X has undergone a cyclic change of state and has performed shaft work $W_{10}^{AR\rightarrow}$, and the state of A has changed from A_1 to a thermodynamic equilibrium state A_0. The latter state corresponds to prespecified values $\mathbf{n}_0^A$ of the constituents and V_0^A of the volume, and is such that A and R are in mutual stable equilibrium (Figure 4b).

Using their statements of the laws of thermodynamics[1] (see Appendix), Gyftopoulos and Beretta (1991b) prove that if the process of AXR just cited is reversible, then the shaft work performed by the engine is optimum — the largest if done by the cyclic engine or the smallest if done on the cyclic engine. They call this optimum shaft work generalized available energy of state A_1 with respect to reservoir R and the values $\mathbf{n}_0^A$ and V_0^A, and for the sake of simplicity of nomenclature denote it by the same symbol Ω_1^R as that for available energy. It is noteworthy that, under the proper conditions, generalized available energy reduces to the available energy or exergy concept represented by either equation (11) or the definition in equation (13).

Next, Gyftopoulos and Beretta establish several characteristic features of generalized available energy. For example, they consider two arbitrary states A_1 and A_2 of system A, and a common state A_0 with prespecified values $\mathbf{n}_0^A$ and V_0^A. For an adiabatic process from A_1 to A_2 of system A only, they show that the energy difference $E_1^A - E_2^A$ of A and the generalized available energy difference $\Omega_1^R - \Omega_2^R$ of the composite of A and R satisfy the relations

If the adiabatic process of A *is reversible:*

$$E_1^A - E_2^A = \Omega_1^R - \Omega_2^R \qquad (15)$$

If the adiabatic process of A *is irreversible:*

$$E_1^A - E_2^A < \Omega_1^R - \Omega_2^R \qquad (16)$$

It is noteworthy that energy and generalized available energy are defined for any state of any system, regardless of whether the state is steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether the size of the system is large or small.

Now, we define the following linear combination of energy and generalized available energy

$$\Sigma_2^A - \Sigma_1^A = \left[\left(E_2^A - E_1^A\right) - \left(\Omega_2^R - \Omega_1^R\right)\right] / c_R \qquad (17)$$

where c_R is a positive constant which can be chosen so as to make Σ independent of R. The proof that such a choice of c_R is possible is given by Gyftopoulos and Beretta (1991c). It turns out that the value of c_R is also equal to the temperature T_R of the reservoir.

[1]All correct statements of the laws of thermodynamics that appear in the literature are proven to be special cases of the statements given by Gyftopoulos and Beretta (1991a).

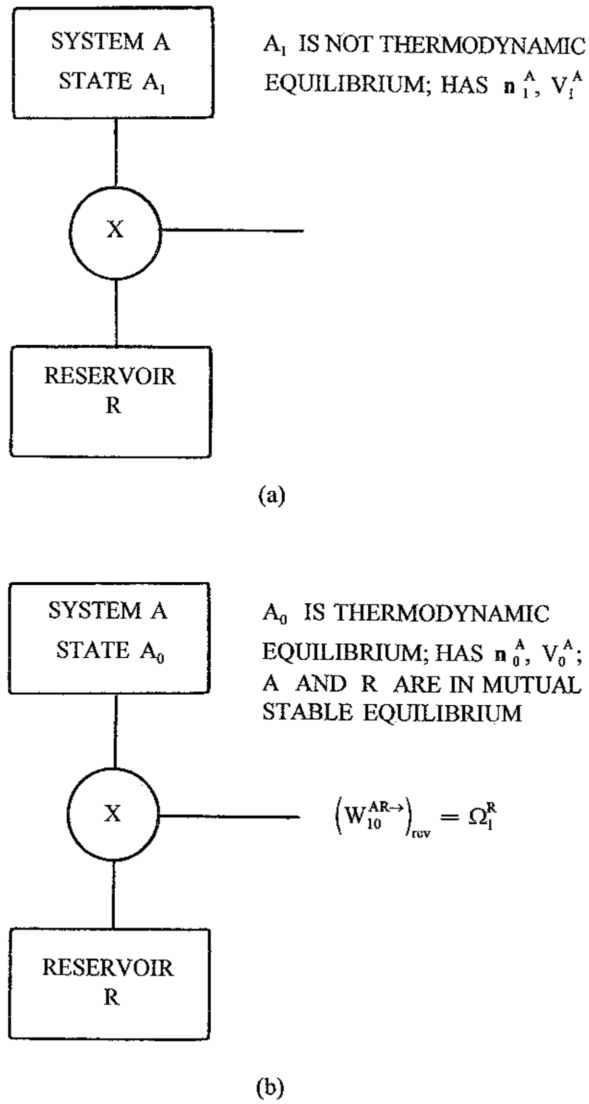

Figure 4. Schematic of a cyclic change of state of an engine: (a) initial state of A is not thermodynamic equilibrium; and (b) final state of A is thermodynamic equilibrium so that A and R are in mutual stable equilibrium

Based on the proven characteristic features of E and Ω^R, we find that Σ satisfies the following conditions.

1. For the specifications of either the Carnot engine or the engine operating between a system that can assume different temperatures and a reservoir, it reduces to either equation (10) or equation (14), respectively.
2. It is well defined for all systems and all states.
3. It is independent of R.
4. It is nondecreasing in adiabatic processes.

5. It is additive.
6. It can be assigned nonnegative values.
7. Among all the states of a system having given values of energy, amounts of constituents, and volume, there exists only one which has the largest Σ^A.
8. For given values of amounts of constituents and volume, the graph of Σ versus E of the thermodynamic equilibrium states (largest-Σ^A states) is concave.
9. For mutual stable equilibrium between two systems, Σ^A yields the conditions of temperature equality, total potential equalities, and pressure equality.

Comparison of this list with the list of characteristic features of Clausius' entropy for thermodynamic equilibrium states indicates that Σ behaves exactly like the Clausius entropy, and maintains the appropriate and expected behavior for states that are not thermodynamic equilibrium. So we can say that Σ is the entropy of any system in any state, and denote it by $\Sigma^A = S^A$.

CONCLUDING REMARK

It is alleged that the late Cardinal Cushing of Boston said: "When I see a bird that walks like a duck, swims like a duck, and quacks like a duck, I call that bird a duck." Though a non-Catholic, but a Bostonian over the past 43 years, I believe that the comparison of the characteristics of Clausius' entropy and Σ allows us to paraphrase the late Cardinal's statement and aver with a great degree of certainty that both states which are not thermodynamic equilibrium, and states which are thermodynamic equilibrium can be assigned entropy, and that this entropy is defined by equation (17) for $\Sigma^A = S^A$.

APPENDIX — THE LAWS OF THERMODYNAMICS

Gyftopoulos and Beretta state the laws of thermodynamics as follows.

First law: Any two states of a system may always be the end states of a weight process, that is, the initial and final states of a change of state that involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight. Moreover, for a given weight, the value of the quantity $Mg(z_1 - z_2)$ is fixed by the end states of the system, and independent of the details of the weight process, where M is the mass of the weight and g the gravitational acceleration.

Second law (simplified version): Among all the states of a system with a given value of the energy, and given values of the amounts of constituents and volume, there exists one and only one stable equilibrium state.

Third law (simplified version): For each given set of values of the amounts of constituents and the volume of a system, there exists one stable equilibrium state with zero temperature.

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