TOOLS OF FINITE-TIME THERMODYNAMICS

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1. Introduction

Finite-time thermodynamics was ‘invented’ in 1975 by R. S. Berry, P. Salamon, and myself as a consequence of the first world oil crisis. It simply dawned on us that all the existing criteria of merit were based on reversible processes and therefore were totally unrealistic for most real processes. That made an evaluation of the potential for improvement, of minimizing the losses, for a given process quite difficult [1].

Finite-time thermodynamics is developed from a macroscopic point of view with heat conductances, friction coefficients, overall reaction rates, etc. rather than based on a microscopic knowledge of the processes involved. Consequently most of the ideas of traditional thermodynamics have been assimilated, e.g. the notions of thermodynamic potential (Sect. 2.1) and availability (Sect. 2.2). At the same time we have seen new concepts emerge, e.g. the non-equivalence of well-honored criteria of merit (Sect. 3.2), the importance of power as the objective, the generality of the endoreversible engine, and in particular thermodynamic length (Sects. 2.3 and 3.3). Several of these abstract concepts have been successfully applied to practical optimizations [2–9]. We will present some of these tools below, roughly in order of increasing complexity.

The model of Curzon and Ahlborn [10] has evolved into almost a classic paradigm of systems operating in finite time. This is a Carnot engine with the simple constraint that it be linked to its surroundings through *finite* heat conductances. Figure 1 illustrates the slightly more general endoreversible system with the triangle signifying any reversible engine. (The term endoreversible means ‘internally reversible’, i.e. all irreversibilities reside in the coupling of flows to the surroundings. In this case that means resistance to heat transfer and possibly friction.) It turns out that the results derived by Curzon and Ahlborn (and by Novikov [11] and Chambadal [12] for simpler systems) explicitly for an interior Carnot engine are equally valid for a general endoreversible system. The maximum efficiency of their engine is of course $\eta_C = 1 - T_L/T_H$, obtained at zero rate so that losses across the resistors vanish, but these authors showed that, when the system operates to produce *maximum power*, the efficiency of the engine is only

$$\eta_w = 1 - \sqrt{\frac{T_L}{T_H}} \ . \tag{1}$$

Besides the simplicity of the expression it is remarkable that it does not contain the value of the heat conductances.

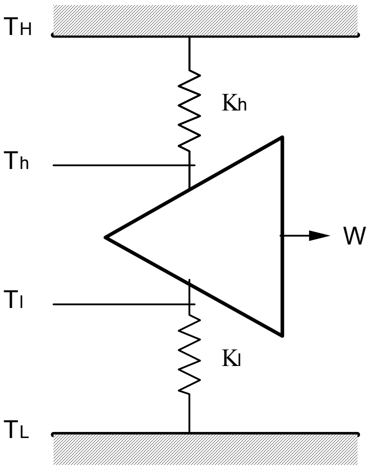

Figure 1. An endoreversible engine has all its losses associated with its coupling to the environment, there are no internal irreversibilities. This is illustrated here as resistances in the flows of heat to and from the working device indicated by a triangle. These unavoidable resistances cause the engine proper to work across a smaller temperature interval, $[T_h;T_l]$ than that between the reservoirs, $[T_H;T_L]$, one which depends on the rate of operation.

2. Performance bound without path

The smallest amount of information one can ask for concerning the performance of a system is a single number, e.g. the work or heat exchanged during the process, its efficiency, or any other figure of merit. In most cases this can be calculated without knowledge of the detailed path followed and is then computationally much simpler to obtain.

2.1 GENERALIZED POTENTIALS

In traditional thermodynamics potentials are used to describe the ability of a system to perform some kind of work under given constraints. These constraints are usually the constancy of some state variables like pressure, volume, temperature, entropy, chemical potential, particle number, etc. Under such conditions the decrease in thermodynamic potential $\mathcal{P}$ from state i to state f is equal to the amount of work that is produced when a reversible process carries out the transition, and hence is the upper bound to the amount of work produced by any other process,

$$W \leq W_{rev} = \mathcal{P}_i - \mathcal{P}_f. \tag{2}$$

In this section we will show that the constraints need not simply be the constancy of some state variable, and that the potentials may be generalized to contain constraints involving time [13]. The procedure will be a straight forward extension of the Legendre transformations [14] used in traditional thermodynamics [15, 16], and we will start with such an example.

In a reversible process heat and work can be expressed as inexact differentials,

$$dQ = TdS, \qquad dW = PdV, \tag{3}$$

i.e. they cannot by themselves be integrated, further constraints defining the integration path are required. Such a constraint could be that the process is isobaric, $dP = 0$. One can then add a suitable integrating zero-term, xdP to make dW an exact differential. The obvious choice is $x = V$,

$$dW = PdV = PdV + VdP = d(PV), \tag{4}$$

such that the isobaric work potential becomes $\mathcal{P} = PV$.

Now, the constraints need not be the constancy of one of the state variables. Consider a balloon with constant surface tension α. In equilibrium with an external pressure P_{ex} such a sphere of radius r has an internal pressure

$$P = P_{ex} + \frac{2\alpha}{r}, \tag{5}$$

which can be rearranged into

$$(P - P_{ex})V^{1/3} = 2\alpha \left(\frac{4\pi}{3}\right) 1/3. \tag{6}$$

Since the right hand side of this equation is a constant, this means that $(P - P_{ex})V^{1/3}$ is an integral of motion for the fluid inside the balloon. We can then add a suitable amount of $d[(P - P_{ex})V^{1/3}]$ (equal to zero) to dW to make it exact,

$$dW = PdV = PdV + \frac{3}{2}\ V^{2/3}\ d[(P - P_{ex})V^{1/3}]$$

$$= d[\frac{1}{2}\ V(3V - P_{ex})]. \tag{7}$$

Thus the work done by the coupled system, surface plus fluid, is given by the decrease in the potential $\mathcal{P} = \frac{1}{2}\ V(3V - P_{ex})$, regardless of path followed.

This procedure of adding a suitable amount of a ‘zero-quantity’ can be generalized to any differential constraint, even including time explicitly [13].

2.2 FINITE-TIME AVAILABILITY

One of the more powerful results in finite-time thermodynamics is the definition of a finite-time availability [17]. The traditional availability A of a system in contact with given surroundings is a state function with the quality that the decrease in its value in going from state i to state f is the maximum (and hence reversible) work that can be extracted during that process. The finite-time availability *A* retains this property and simply adds that the process is restricted to operate (go to completion) during time $\tau = t_f - t_i$. Then

$$\mathcal{A} = W_{max}(\tau) = \max\left[A(t_i) - A(t_f) - T_0 \int_{t_i}^{t_f} \dot{S}_{tot}\, dt \right], \tag{8}$$

where the last equality uses the Tolman-Fine form of the Second Law of thermodynamics [18].

The maximum search in eq. (8) can either be constrained to exactly reach a given final state at time t_f (the initial state is always considered known), in which case ΔA is fixed, and the optimization becomes one of minimizing the entropy production, or also the final state may be included in the optimization, in which case *A* must be evaluated by optimal control. If the final state is specified, a solution may not exist if τ is too short, since only a certain set of states can be reached from a given initial state in time τ. In addition, the finite-time availability does not necessarily have ΔA as its limit for very long times, because the system may contain internal relaxation processes which remain irreversible even for very slow operation. If there is a direct heat leak from the system reservoir to the surroundings, then a long process time may even reduce *A* to zero. On the other hand, losses are not always detrimental to the performance of a system if they open up new pathways — actually some processes depend on irreversibilities for their very existence (e.g. [19]).

2.3 THERMODYNAMIC LENGTH

For static purposes Weinhold [20, 21] defined a metric on the abstract space of equilibrium states of a system represented by all its extensive variables X_i as

$$\mathbf{M}_U = \left\{ \frac{\partial^2 U}{\partial X_i \partial X_j} \right\}, \tag{9}$$

where U is the internal energy.

Based on this metric Salamon and Berry [22] found a connection between the thermodynamic length along a process path and the (reversible) availability lost in the process. Specifically, if the system moves via states of local thermodynamic equilibrium from an initial equilibrium state i to a final equilibrium state f in time τ, then the dissipated availability $-\Delta A$ is bounded from below by the square of the distance (i.e. length of the shortest path) from i to f times ε/τ, where ε is a mean relaxation time of the system. If the process is endoreversible, the bound can be strengthened to

$$-\Delta A \geq \frac{L^2 \varepsilon}{\tau}, \tag{10}$$

where L is the length of the *traversed* path from i to f. Equality is achieved at constant thermodynamic speed $v = dL/dt$ corresponding to a temperature evolution given by [23]

$$\frac{dT}{dt} = -\frac{vT}{\varepsilon\sqrt{C}}, \tag{11}$$

where C is the heat capacity of the system. For comparison, the bound from traditional thermodynamics is only $-\Delta A \geq 0$.

An analogous expression exists for the total entropy production during the process:

$$\Delta S^{u} \geq \frac{L^{2}\varepsilon}{\tau} . \tag{12}$$

The length L is then calculated relative to the entropy metric

$$\mathbf{M}_{S} = -\left\{\frac{\partial^{2} S}{\partial X_{i} \partial X_{j}}\right\} . \tag{13}$$

In statistical mechanics, where entropy takes the form

$$S(\{p_i\}) = -\sum_{i} p_i \ln p_i , \tag{14}$$

the metric $\mathbf{M}_S$ is particularly simple, being the diagonal matrix [24]

$$\mathbf{M}_{S} = -\left\{\frac{1}{p_i}\right\} . \tag{15}$$

The same procedure of calculating metric bounds for dynamic systems has been applied to coding of messages [25] and to economics [26].

More recently [27] we have relaxed a number of the assumptions in the original work, primarily those restricting the system to be close to equilibrium at all times and the average form of the relaxation time ε. The more general bound replacing eq. (12) then becomes

$$\Delta S^{u} \geq \frac{1}{X}\left(\int_{x_i}^{x_f} \frac{1}{T\sqrt{C}}\left|\frac{dU}{dx}\right| \sqrt{1+\frac{q}{CT}\frac{dU}{dx}+\ldots}\, dx\right)^{2} \tag{16}$$

with $\Xi = \xi_f - \xi_i$ being the total duration of the process in natural dimensionless time units,

$$d\xi = dt/\varepsilon(T), \tag{17}$$

and where we have defined

$$\theta(T) = 1 + \frac{T}{2\,C}\frac{\partial C}{\partial T} . \tag{18}$$

The equality (lower bound) in eq. (16) is achieved when the integrand is a constant, i.e. when

$$\frac{dS^{u}}{d\xi} = \text{constant} . \tag{19}$$

Consequently, constant rate of entropy production, when expressed in terms of natural time, is the path or operating strategy which produces the least overall entropy.

One can express the optimal path in a form similar to eq. (11):

$$\frac{dT}{dt}\sqrt{1 + \frac{\theta(T)\,\varepsilon\,(dT/dt)}{T} + \ldots} = \text{constant} \times \frac{T}{\varepsilon\sqrt{C}} . \tag{20}$$

The constant thermodynamic speed algorithm, eq. (11), is thus the leading term of the general solution in an expansion about equilibrium behavior.

3. Optimal path

3.1 OPTIMAL PATH CALCULATIONS

A knowledge of the maximum work that can be extracted during a given process, e.g. calculated by one of the procedures described in the previous section, may not by itself be sufficient. One may also want to know *how* this maximum work can be achieved, i.e. the time path of the thermodynamic variables of the system. The primary tool for obtaining this path is optimal control theory.

This is not the place to repeat the mechanics of optimal control calculations (see e.g. [28 – 30]). Let it suffice to point out that in order to set up the optimal control problem one must specify

- the controls, i.e. the variables that can be manipulated by the operator (they may be a volume, rate, voltage, heat conductance, etc.);
- limits on the controls and on the state variables, if any (in order to avoid unphysical situations such as negative temperatures and infinite speeds);
- the equations that govern the time evolution of the system (they will usually be differential equations describing heat transfer rates, chemical reaction rates, friction, and other loss mechanisms);
- the constraints that are imposed on the system (e.g. conserved quantities, the quantities held constant, or any requirements on reversibility. The constraints may either be differential, instantaneous i.e. algebraic, or integral i.e. not obeyed at each point but over the entire interval);
- the desired quantity to be maximized, called the objective function (usually expressed as an integral); and finally
- whether the duration of the process is fixed or part of the optimization.

Typical manipulation usually leads to a set of coupled, non-linear differential equations for which a qualitative analysis and a numerical solution are the only hope. Thus answering the more demanding question about the optimal time path rather than the standard question about maximum performance requires a considerably larger computational effort. On the other hand, once the time path is calculated, all other thermodynamic quantities may be calculated from it, much like the wave function is the basis of all information in quantum mechanics.

3.2 CRITERIA OF PERFORMANCE

Efficiency, the earliest criterion of performance for engines, measured how much water could be pumped out of a mine by burning a ton of coal. Other familiar criteria include effectiveness (efficiency relative to the Carnot efficiency), change of thermodynamic potential, and loss of availability, all of which are measures of work. Potentials for heat can also be defined but are less common. In addition total of entropy production is indicative of inefficient operation [31]. The Curzon-Ahlborn analysis and many of our own analyses use a quite different criterion, that of *power.* This quantity is of course zero for any reversible system, and maximizing power forces us to deal with systems operating at finite rates. Other criteria of performance are the rate of entropy production and the rate of loss of availability. Under some circumstances, optimizing one of these quantities is equivalent to optimizing another. For example, minimizing the entropy production is equivalent to minimizing the loss of availability.

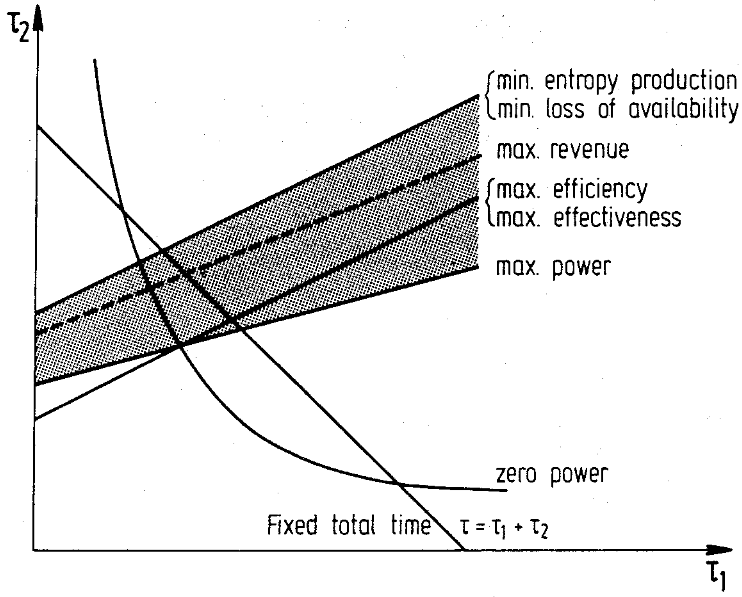

Figure 2. If an endoreversible engine (Fig. 1) spends time τ_1 in contact with the hot reservoir and τ_2 in contact with the cold reservoir, the optimal proportioning between τ_1 and τ_2 depends on what one chooses to optimize, as indicated. The locus of maximum revenue for a power producing system falls in the shaded area for any choice of prices, as described in the text. Only contact times above the hyperbola marked 'zero power' actually correspond to positive power production.

Salamon and Nitzan [32] have optimized the Curzon-Ahlborn engine for a number of these objective functions. Assuming the working fluid to be in contact with the hot reservoir for the period τ_1 and the cold reservoir for the period τ_2, the optimal time distributions are shown in Fig. 2. The diagonal $\tau = \tau_1 + \tau_2$ indicates fixed total cycle time, and only processes above the curve labeled 'zero power' produce positive power. It is quite obvious that different criteria of merit dictate different operating conditions for the process. Even when not knowing the precise objective function but only that it belongs to a specified class, one can sometimes say a good deal about the possible optimal behavior of the system. If one considers the Curzon-Ahlborn engine to be a model of a power plant which buys heat q (coal) at the unit price α and sells work w (electricity) at the unit price β, its net revenue is $\prod = \beta w - \alpha q$. All solutions to the problem of maximizing this revenue are bounded on one side by the solutions to the maximum power problem (when α is significant compared to β) and on the other side by the solutions corresponding to minimum loss of availability (when coal and electricity are priced according to their availability contents). While this is a very simple example, this approach has far reaching possibilities for describing biological, ecological, and economic systems.

3.3 DESIGN OF DISTILLATION COLUMN BY EQUAL THERMODYNAMIC DISTANCE

In Sect. 2.3 we saw that the concept of thermodynamic length not only provided a lower bound on dissipation (eqs. (10), (12), and (16)), it also predicted which path would achieve that bound, namely operation at constant thermodynamic speed. We will use that line of thought to improve the performance of a conventional distillation column.

The internal distribution of temperature and mole fractions of light and heavy components in a conventional distillation column where heat is added and withdrawn only in the reboiler and the condenser, respectively, is fixed exclusively by the laws of energy and mass conservation. In most columns that leads to an S-shaped curve of temperature versus plate number with most of the variation occurring near the end points of the column, connected with a flat stretch around the feed point (see Fig. 3). A qualitatively similar picture emerges for the mole fractions. This temperature profile implies that the major part of the entropy production in the distillation process occurs near the ends of the column and is thus not uniformly distributed. Even more importantly, if the number of plates is increased, essentially only the middle flat section is extended while the segments of rapid variation are unchanged. This means that dissipation does not approach zero as the number of plates goes to infinity.

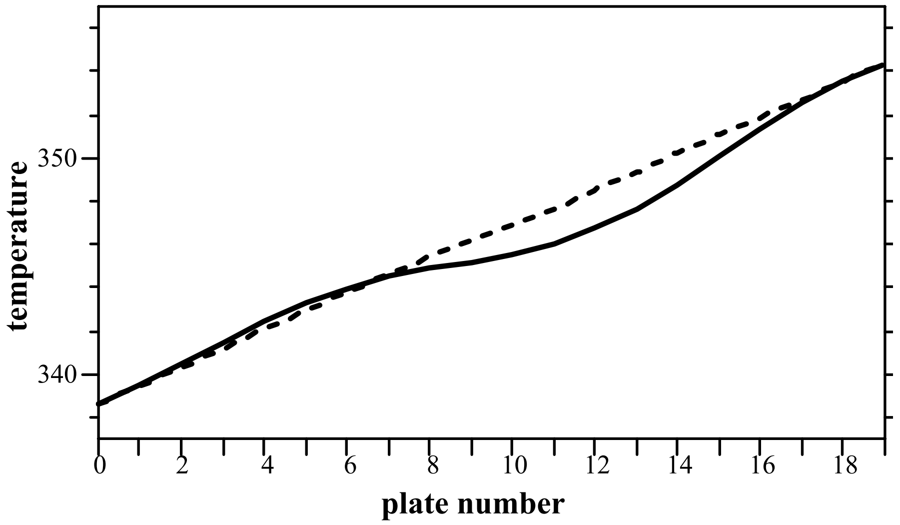

Figure 3. The temperature profile as a function of plate number, counted from the condenser, for conventional (solid) and equal-thermodynamic-distance (dashed) separation of methanol and isopropanol.

The principle of constant thermodynamic speed for continuous systems, or equivalently equal thermodynamic distance for discrete systems, aims at minimizing total dissipation in the column by distributing it evenly among the plates whatever their number [33, 34]. In [35] a general quasistatic step process was optimized, i.e. a process composed of N discrete steps where the system equilibrates fully after each step. The standard description of a distillation column is exactly such a process where it is assumed that gas and liquid come to equilibrium at a particular temperature on each plate. Entropy is produced when the up- and down-moving flows encounter liquid on the next plate at slightly different temperature and composition.

The result of the optimization [35], for processes not too far from equilibrium, was that the minimum of the entropy production

$$\Delta S^u \geq L^2/2N \tag{21}$$

is achieved when the thermodynamic distance between each pair of plates is kept constant, i.e. they are equidistant in that measure. L is the total thermodynamic distance from one end of the column to the other. For any other distribution of the total length along the column dissipation is larger.

Using the metric eq. (13), the thermodynamic distance $D_S{}^k$ from plate k–1 to plate k is equal to

$$D_S{}^k = \sqrt{\Delta\mathbf{X}^k\, \mathbf{M}_S{}^k\, \Delta\mathbf{X}^k} \tag{22}$$

where $\Delta\mathbf{X}^k = \mathbf{X}^k - \mathbf{X}^{k-1}$ is the difference in extensities from plate k–1 to plate k. The total thermodynamic length of the column is thus

$$L_S = \sum_{k=1}^{N} D_S{}^k\,. \tag{23}$$

Two consequences of this general result are immediate: dissipation (here entropy production) must be equally distributed along the column; and the total dissipation approaches zero as N, the number of plates, goes to infinity (eq. (21)), i.e. the separation becomes reversible.

In binary distillation 8 extensive quantities are involved on each plate, besides the objective function entropy, namely enthalpy, volume, mole number of light component, and mole number of heavy component, each one for both gas and liquid, leading to an 8×8 metric matrix. Fortunately a number of relations allows to reduce the dimensionality of the problem dramatically. First of all, the two components are usually considered non-interacting, at once making $\mathbf{M}_S$ block-diagonal. Next, constant pressure in the column, energy and mass conservation, and the gas-liquid equilibrium equation reduce the problem to just one free variable which may conveniently be taken to be temperature. After a lot of algebra the plate-to-plate distance then becomes simply

$$D_S{}^k = \frac{\sqrt{C_r{}^k}}{T^k}\,\Delta T \qquad (24)$$

where C_r is an effective heat capacity involving all the constraints mentioned above in a complicated expression.

The computational procedure is to integrate eq. (24) from the distillate temperature T_D to the reboiler temperature T_B (both of course given by the required product purities) to obtain the total thermodynamic column length L_S. The distance from one plate to the next must then be fixed at $D_S = L_S/N$ for optimal performance by adjusting the plate temperatures appropriately according to eq. (24).

Obviously such freedom of adjustment does not exist in a conventional adiabatic column. Rather, it is necessary to allow individual heat exchange with each plate to maintain it at the desired temperature. This heat addition/removal is of course part of the energy balance used above. The result of the whole calculation is either a graph like Fig. 3 specifying the temperature of each plate in the column or a graph of the amount of heat added/removed at each plate, Fig. 4. It should be emphasized that the total amount of heat used to perform a certain equal-thermodynamic-distance separation is only marginally different from that required by a conventional column, but a large part of it is used over a much smaller temperature difference than T_B to T_D leading to a correspondingly smaller entropy production.

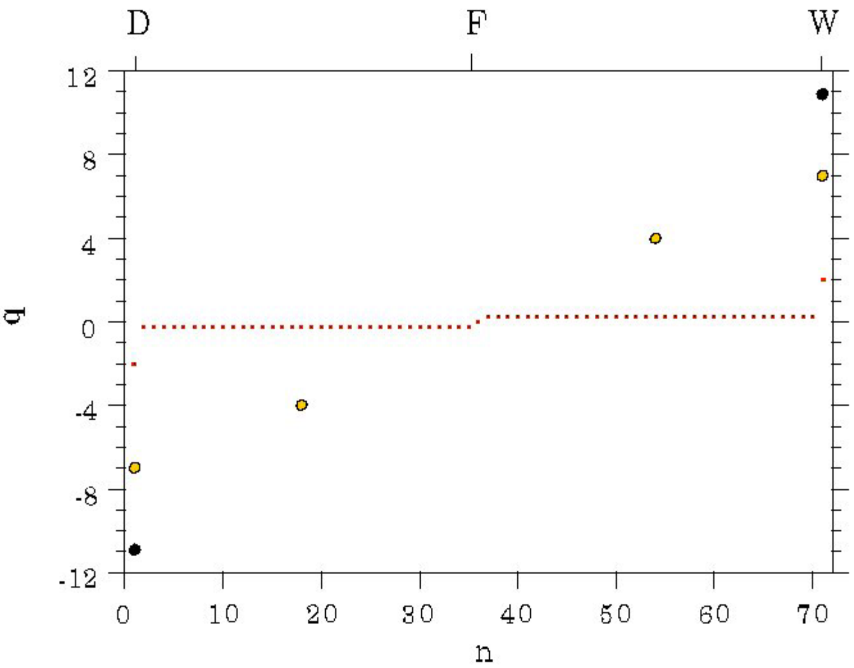

Figure 4. Amount of heat q added and removed per mole of benzene-toluene feed on the individual plates of a 71-plate column operated in the traditional fashion with heat added only in the reboiler and withdrawn only in the condenser (•); operated according to equal thermodynamic separation specifications with heat added or removed on each plate (·); and operated with just 2 additional heat exchange points, optimally located (◦).

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