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Infinite time (reversible) versus finite time (irreversible) thermodynamics: a misconceived distinction

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1. Introduction

Over the past 25 years, a school of thought has promoted the idea of finite time (irreversible) thermodynamics (FTT) [1–4]. The basic argument of the school is twofold: (i) reversible processes require an infinite interval in time and, therefore, are the subject of infinite time or reversible thermodynamics; and (ii) in contrast, irreversible processes (defined exclusively as heat conduction through thermal resistances) require a finite interval in time and, therefore, are the subject of the special techniques of FTT.

The only process addressed by FTT is a power producing plant operating between two reservoirs at temperatures T_1 and T_2 . It consists of two thermal resistances, and a cyclic engine that is reversible and called endoreversible (Fig. 1). For such a plant a fascinating aura surrounds its attractiveness because, according to FTT, reversible thermodynamics yields a thermal efficiency at maximum power

$$\eta_{\rm C} = 1 - \frac{T_2}{T_1} \tag{1}$$

but the maximum power is zero, whereas the corresponding result of FTT is equally general and explicit, that is

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

but the maximum power is greater than zero. The subscript "C" of $\eta_{\rm C}$ stands for Carnot, and the

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Fig. 1. Schematic of an endoreversible engine.

subscript "CA" of η_{CA} for Curzon and Ahlborn [2], two authors that derived Eq. (2) independently of the first derivation by Novikov [1].

Another explicit result of FTT is the thermal efficiency [3]

$$\eta_{\rm E} = \frac{(\eta_{\rm C} + \eta_{\rm CA})}{2} > \eta_{\rm CA} \tag{3}$$

which is found by the maximization of what the authors call the ecological function

$$\dot{E} = \dot{W} - T_0 \dot{S}_{\rm irr} \tag{4}$$

where \dot{W} is the power of the plant, T_0 the environmental temperature (usually equal to T_2), and \dot{S}_{irr} the rate of entropy generation. The efficiency η_E is greater than η_{CA} because \dot{W} depends on \dot{S}_{irr} and, therefore, in the maximization of \dot{E} the entropy generation is assigned a greater weight than that required by its actual detrimental effects which are accounted for in the maximization of \dot{W} .

It is noteworthy that, whereas Eqs. (2) and (3) are derived for a specific model, Eq. (1) represents a truly fundamental result for at least two reasons: (1) $\eta_{\rm C}$ is valid for any engine (any type and any cycle) operating between the two reservoirs; and (2) it is a special illustration of a much broader concept, that is, under any conditions the best and only limiting process is the reversible, and all reversible processes of the same type are equivalent.

All the analytical results of FTT are correct, and their simplicity is very impressive. The rationale behind the results, however, misrepresents the foundations of thermodynamics, is internally inconsistent, and contradicts the overwhelming empirical evidence.

2. Foundations of thermodynamics

The laws and theorems of thermodynamics are valid for any system (both microscopic and macroscopic), for any state (both thermodynamic equilibrium and not thermodynamic equilibrium), and for any interval in time (both infinite and finite).

All FTT analyses are primarily, if not exclusively, based on two theorems, the energy balance

and the entropy balance. These theorems are valid in a time interval of any duration (lifetime of the compound nucleus in nuclear reactors, time constant of any energy exchange in nuclear and fossil fueled power plants, and times related to the age of the universe). Accordingly, no theoretical basis exists for the distinction between infinite time and finite time thermodynamics.

The apparent need for distinction arises from the arbitrary attribution of the (spontaneous) entropy generation to energy flowing only through non-power producing thermal resistances, and to the flow rate determining the temperature differences rather than the other way around. But plant designers make every effort to avoid such waste by inventing ingenious new devices that extract work from an energy stream while it is degraded to the environmental temperature, and by using working fluids with small heat of vaporization. Such inventions reduce the margin for spontaneous entropy generation, increase the performance of the plant, and are environmentally beneficial.

Examples of the new devices are high temperature gas turbines, magnetohydrodynamic generators, thermionic energy converters, and fuel cells used as topping engines of steam power plants. Examples of working fluids with small heat of vaporization are those used in organic Rankine units which in turn are attached as bottoming engines to power plants. Not all of these inventions are presently commercially viable but, as we will see shortly, some have made remarkable contributions to low-cost, high-efficiency, and low-pollution power plants.

The association of (spontaneous) entropy generation solely with thermal resistances leaves the uninitiated to the science of thermodynamics with the false impression that this is the only cause of irreversibility [5], an impression that contradicts many physical phenomena. For example, the fission fragments in a nuclear reactor have kinetic energy of 170 MeV and practically no entropy. Accordingly, their available energy is 170 MeV. Because they are fully ionized—stripped of all their electrons—they deposit all their energy almost at the location of their birth and thus the kinetic energy becomes energy at the temperature of the fuel rod $T_f \approx 1000$ K. As a result, in an environment at $T_0=300$ K, the available energy is reduced by 30% ($T_0/T_f=300/1000=0.3$), and yet this reduction involves no creation of a temperature difference by heat flow (see also Ref. 6). An almost identical result is obtained in the course of combustion of a solid, liquid, or gaseous fuel.

Again, as discussed in Ref. 7, a temperature difference across a thermal resistance is the effect and not the cause of a heat interaction at one end of the resistance.

3. Internal inconsistency

In FTT, a power plant is modeled as shown in Fig. 1. The power generator is an endoreversible cyclic engine. Whereas a basic premise of FTT is that no power can be produced by a reversible engine in a finite interval in time, the most intricate and most important parts of the plant are modeled by a reversible, cyclic process with a cycle period anywhere between about 50 μ s and 100 ms. This is an important inconsistency because power producing engines cannot be modeled as thermal resistances and yet can be very inefficient, that is, can spontaneously generate a relatively large amount of entropy.

A second inconsistency is discussed by Seculic [8].

A third inconsistency is that in nuclear power plants, many of which are used in comparisons of η_{CA} or η_{E} with reported plant efficiencies, the temperature of the coolant is not determined by

 T_1 and its associated thermal resistance. On the contrary, for important reasons related to the strength of the reactor vessel, the temperature, pressure, and flow rate of the coolant, and the thermal power rating of the plant determine the temperatures within the fuel elements.

4. Empirical evidence

The premise of FTT contradicts the overwhelming empirical evidence. One experiment is provided by two identical electricity storage batteries with an internal-discharge-time-constant of 100 days. We can discharge one battery very slowly, say over 10⁴ days, and the other very fast, say over 1 day, and ask "Which discharge process is closer to reversible?" [9]. As is very well-known from billions of experiments, the fast process is very close to reversible, whereas the slow process is totally irreversible because in the fast process practically all the stored adiabatic availability is transferred out, whereas in the slow process practically no adiabatic availability is transferred; it is all dissipated in the battery.

Another experiment involves two spark-ignition internal combustion engines, one with only one spark plug, and the other with 1000 spark plugs. It is well known that the combustion process in the first engine is about 1000 times slower than in the second engine, and so we can ask "Which of the two combustion processes is closer to reversible?" Of course, the answer is that both processes are equally irreversible because the spontaneous generation of entropy is determined by the end states, which in the two experiments under consideration are identical, and not by the rate of combustion.

A third experiment is provided by the recently marketed gas-turbine, combined-cycle power plants manufactured by General Electric and other international corporations. Such plants have a thermal efficiency of over 60%. If we represent this efficiency by η_{CA} (Eq. (2)), then we would conclude that $T_2/T_1 < 0.16$ and, therefore, that the available energy of the products of combustion is greater than 84% of the available energy of the fuel–air mixture for $T_2=T_0=300$ K, or equivalently that the loss of available energy upon combustion is less than 16%. But every calculation and every measurement yield a loss of about 30%.

Incidentally, the economics, resource conservation, and environmental impact of gas-turbine, combined-cycle power plants are very attractive and much better than anything we can achieve by thinking along the lines of FTT. The capital cost is about 400 \$/kW, much less than the few thousand dollars per kilowatt of nuclear and fossil-fueled plants. The fuel consumption is almost two times less than that of ordinary coal or oil fired plants. And last but not least, the environmental impact is much less than that of other fossil fueled plants both because of the high efficiency of gas-turbine, combined-cycle plants, and the reduced pollution characteristics of hydrocarbons versus coal.

In view of the preceding remarks, it seems to me that professional journals must exercise greater restraint in publicizing numerically correct but theoretically and experimentally faulty results of FTT.

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