



HAL
open science

Thermodynamics a probability interpretation of the Carnot Theorem

Fausto Galetto

► **To cite this version:**

| Fausto Galetto. Thermodynamics a probability interpretation of the Carnot Theorem. 2023. <hal-04005853>

HAL Id: hal-04005853

<https://hal.science/hal-04005853v1>

Preprint submitted on 27 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Thermodynamics a probability interpretation of the Carnot Theorem

Fausto Galetto
Independent Researcher, fausto.galetto@gmail.com
(*past Lecturer of Quality Management at
Politecnico di Torino, Dipartimento Sistemi di Produzione ed Economia
dell'Azienda*)

Abstract

After the presentation of the paper "*The Mathematics of Thermodynamics*", based on ideas of B. Finzi [one of the professors at Milan Politecnico] to be found in a paper published in the "*Periodico di Matematiche, serie IV, vol. XIV, 1935*", related to a Caratheodory publication in "*Mat. Ann., 67, 355, 1909, Berl. Ber. 39, 1935*", the author now expands his ideas by including the Carnot way of thinking. He will use the ideas of the great scholars Fermi, Feynman and Finzi.

1. Introduction

This document tries to develop the Theory of *Thermodynamics* by using *Mathematics* about some known facts related to the *temperature*, the *thermal equilibrium*, the *transformation of energy* (mechanical, kinetic, gravitational, electromagnetic, nuclear, ..., heat), the *state variables*, the 0th, the 1st, the 2nd and the 3rd *Principles of Thermodynamics*.

The word *Thermodynamics* is derived from two Greek words "thermo" (meaning "hotness") and "dynamis" (meaning "force/power"); *Thermodynamics* is the "study" of getting work/power from heat.

All the Principles are shown in the figure 1, "*The Thermodynamics Tetralogy*" (showing the four, above mentioned, Principles).

We name them *Principles* because they are *assumptions induced* into our mind by known facts we see in Nature. From them we can derive Theorems able to predict, using *Mathematics*, the results of "real cases" happening in Nature. The same was done by Galileo, Newton, Maxwell, ..., Einstein, ..., Bohr, Schrödinger, Heisenberg, Born, ... about Mechanics, Electrodynamics, Relativity, Quantum Mechanics, ...

We start with some Feynman statements (notice that Feynman also consider ideas not known at Carnot days).

Some documents call "*Laws*" our *Principles*. See Feynman statements:

The results of thermodynamics are all contained implicitly in certain apparently simple statements called the *laws of thermodynamics*. At the time when Carnot lived, the first law of thermodynamics, the conservation of energy, was not known. Carnot's arguments were so carefully drawn, however, that they are valid even though the first *law* was not known in his time! Sometime afterwards, Clapeyron made a simpler derivation that could be understood more easily than Carnot's very subtle reasoning. But it turned out that Clapeyron assumed, not the conservation of energy in general, but that *heat* was conserved according to the caloric theory, which was later shown to be false. So it has often been said that Carnot's logic was wrong. But his logic was quite correct. Only Clapeyron's simplified version, that everybody read, was incorrect.

The so-called second *law* of thermodynamics was thus discovered by Carnot before the first *law*! It would be interesting to give Carnot's argument that did not use the first law, but we shall not do so because we want to learn physics, not history. We shall use the first law from the start, in spite of the fact that a great deal can be done without it.

Excerpt 1. Feynman statements

Now, what about the second law of thermodynamics? We know that if we do work against friction, say, the work lost to us is equal to the heat produced. If we do work in a

room at temperature T , and we do the work slowly enough, the room temperature does not change much, and we have converted work into heat at a given temperature. What about the reverse possibility? Is it possible to convert the heat back into work at a given temperature? The second law of thermodynamics asserts that it is not. It would be very convenient to be able to convert heat into work merely by reversing a process like friction. If we consider only the conservation of energy, we might think that heat energy, such as that in the vibrational motions of molecules, might provide a goodly supply of useful energy.

But Carnot assumed that it is impossible to extract the energy of heat at a single temperature. In other words, if the whole world were at the same temperature, one could not convert any of its heat energy into work: while the process of making work go into heat can take place at a given temperature, one cannot reverse it to get the work back again. Specifically, Carnot assumed that heat cannot be taken in at a certain temperature and converted into work *with no other change* in the system or the surroundings.

Now, the hypothesis of Carnot, the second law of thermodynamics, is sometimes stated as follows: heat cannot, of itself, flow from a cold to a hot object. But, as we have just seen, these two statements are equivalent: first, that one cannot devise a process whose only result is to convert heat to work at a single temperature, and second, that one cannot make heat flow by itself from a cold to a hot place. We shall mostly use the first form.

So, if both engines are reversible they must both do the same amount of work, and we thus come to Carnot's brilliant conclusion: that if an engine is reversible, it makes no difference how it is designed, because the amount of work one will obtain if the engine absorbs a given amount of heat at temperature T_1 and delivers heat at some other temperature T_2 *does not depend on the design of the engine*. It is a property of the world, not a property of a particular engine.

This is the relation we were seeking. Although proved for a perfect gas engine, we know it must be true *for any reversible engine at all*.

Excerpt 2. Other Feynman statements

We will not consider the 1st Principle in this section, as Carnot did, although we use the term "Energy" in figure 2.

We will start our journey starting from Carnot ideas to let the reader appreciate his ingenuity.

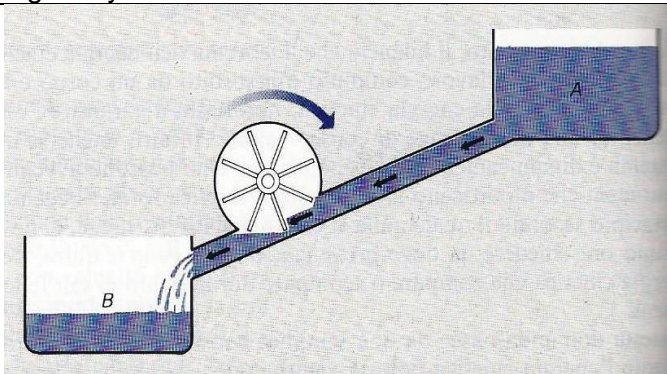


Figure 1. Transformation of the water Potential energy into Kinetic energy of the waterwheel, which can be used to do "work" by a mill, for example

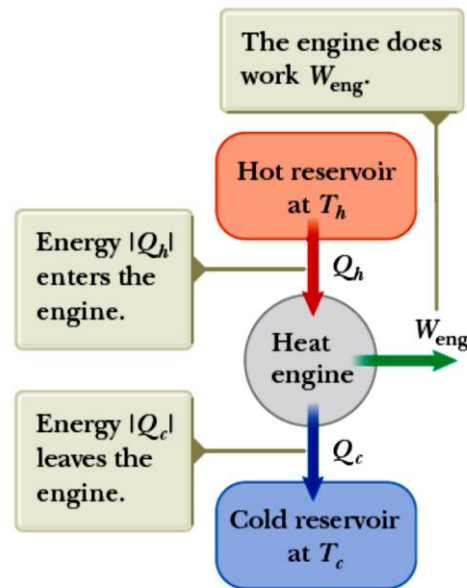


Figure 2. Schematic of a Heat Engine, operating from the temperature T_h to the temperature T_c . Transformation of "heat" into "work"

This is not the way most of the books present the Theory of Thermodynamics.

The two figures show the analogy between the waterwheel and the heat-engine.

We now (in these days) use the term Energy both for the Potential energy of water and Kinetic Energy for the wheel, providing the way to do “work”, as we use the term Energy both for the “heat” entering Q_h into the heat-engine and the “heat” leaving Q_c the heat-engine and the “work” done by the engine.

At the Carnot times the word Caloric was used for the word heat.

Note that Carnot erroneously assumed that the same caloric (heat) passes through the engine and extracts (produces) work by lowering its temperature, like how the same water flow passes through the waterwheel and produces work by lowering its elevation potential. This error, considering the knowledge at the time, in no way diminishes Carnot’s ingenious reasoning and conclusions about limiting, reversible processes and its accurate limitations of heat to work conversion. Notice, as well, that although, at that time, everybody thought that, according to the caloric theory, the quantities of “heat” Q_h and Q_c would have to be the same, **Carnot did not say that** the two “levels” (quantities) Q_h was equal to Q_c because he did not believe it; that, in spite of the analogy between the motive power 1) of a heat engine and 2) of a waterwheel; as in the waterwheel (see fig. 1 and 2) two levels of height of a waterfall are needed to get the wheel move, due to the water flow, the “caloric flow” causes the heat engine to generate work [the quantity of water discharged by the wheel at the bottom level is the same as originally entered at the top level; **Carnot did say** (See *the Carnot’s own wording, later*) that the “quantity of caloric (flow)” entering the engine was the same quantity as the “quantity of caloric (flow)” outgoing from the engine]. He invented an ideal reversible engine, named Carnot Engine, working according to the Carnot Cycle, made of two isotherm and two adiabatic lines.

Notice that Carnot assumed that it is impossible to “extract work” from heat at a single temperature. In other words, the process of making work go into heat can take place at a given temperature, one cannot reverse it to get the work back again.

Carnot did not consider the “mechanical” details of the engines and gave due attention to the “significant (“theoretical”) aspects” of heat engines; they were:

- A. Caloric (Heat?) is supplied in, at High temperature T_h [Q_h is the “level” of Caloric (Heat?) delivered to the engine]
- B. The engine transforms caloric into (mechanical) work
- C. Caloric (Heat?) is delivered out, at Low temperature T_c ($<T_h$) [Q_c is the “level” of Caloric (Heat?) delivered out of the engine]

The “levels” of Caloric (fig. 2), at the Carnot times, were the nowadays Potential Energy of the water (fig. 2): the temperature difference between the heat source and heat sink, like the waterwheel output dependence on the waterfall height difference.

Notice that the caloric “theory” was respectable at Carnot’s days, while it is obsolete nowadays.

Notice that Carnot could not say how much quantity of caloric (heat?) was Q_c , because he did not know the first Principle.

However, he did say:

“On peut donc poser an thèse générale que la puissance motrice est en quantité invariable dans la Nature; quelle n’est jamais, à proprement parler, ni produite, ni détruite. A la vérité, elle change de forme, c’est à dire quelle produit tantot un genre de mouvement, tantot un-autre; mais elle n’est jamais anéantie.”

Substitute the word “energy” to “puissance motrice (motive power)” and you see the Energy Conservation Principle. One can hardly believe it possible that it should have been written in the first quarter of the nineteenth century.

No heat engine, no matter how well constructed, can convert all the heat from the high-temperature reservoir T_h into work. Such an engine would be 100% efficient. Sadi Carnot was the first scientist to realise this and deduce an expression showing the limitations of heat engines.

We can say that this could be considered the Carnot statement of the 2nd Principle of Thermodynamics: **NO heat engine can be 100% efficient.**

2. Efficiency of Heat Engines

See the fig. 2 and its symbols; Carnot did say that “The ratio of the work obtained in a cyclic process (W_{eng}) to the caloric (heat?) taken from the high-temperature reservoir (Q_h , at T_h) is referred to as the efficiency of a heat engine”.

From the above cycle the efficiency of the Carnot cycle can be found out as:

Efficiency of the cycle=**Work output/Heat supplied**

Carnot, at its times, lacked the validity of the First Principle, the Energy Conservation.

Nevertheless, since he thought that the work depended on the “caloric flow” flowing in the engine and on the difference of the temperatures t_h (actually $t_h+273.15$) and t_c (actually $t_c+273.15$) [height of the caloric fall] the efficiency should be the following ratio

$$\eta = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} \quad (1)$$

where T_H and T_C are the absolute temperatures (in degrees Kelvin) of the high and low temperature reservoirs respectively.

The maximum engine efficiency dependence on the reservoirs' temperatures only, is functionally expressed by Equation (1).

A way to prove (1) is the following: **see the Carnot's own wording:**

When a gas passes without change of temperature from one definite volume and pressure to another volume and another pressure equally definite, the quantity of caloric absorbed or relinquished is always the same, whatever may be the nature of the gas chosen as the subject of the experiment.

This is a simple and logical, ingenious reasoning! The maximum, limiting efficiency of heat engine does not depend on the medium used in the engine or its design, but only depends on (and increases with) the temperature difference between the heat source and heat sink, like the water wheel output dependence on the waterfall height difference.

According to Fermi [2], the ratio of $Q_c/Q_h = f(t_h, t_c)$ is the same for all the reversible engines and that the function $f(t_h, t_c)$ is a universal function depending only on the two temperatures.

Consider two reversible engines A_1 and A_2 working between the temperatures $t_0 \rightarrow t_1$ and $t_0 \rightarrow t_2$ we have $Q_1/Q_0 = f(t_0, t_1)$ and $Q_2/Q_0 = f(t_0, t_2)$; dividing the two relations we have the consequence

$$\frac{Q_2}{Q_1} = \frac{f(t_0, t_2)}{f(t_0, t_1)} = f(t_1, t_2) \quad (2)$$

The functional relation [Markovian!]

$$f(t_0, t_2) = f(t_0, t_1)f(t_1, t_2) \quad (3)$$

whose solution is

$$\theta(t) = kf(t_0, t) \quad (4)$$

Considering a perfect gas working in a Carnot cycle it is proved that

$$\theta(t) = T \quad (5)$$

where T is the absolute temperature.

Hence, we retrieve

$$\eta = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} \quad (1)$$

where T_H and T_C are the absolute temperatures (in degrees Kelvin) of the high and low temperature reservoirs respectively.

Now we find the interesting probabilistic relation

$$\eta_{13} = \eta_{12} + \eta_{23} - \eta_{12}\eta_{23} \quad (6)$$

where η_{ij} is the efficiency of an engine working between the temperatures t_i and t_j .

Consider two reversible engines connected in series; engine A receives the heat Q_1 at temperature t_1 , delivers work W_A , and discharges heat Q'_2 . Engine B receives the heat Q'_2 ,

delivers work W_B , and discharges heat Q_3 to a reservoir at temperature $t_3 < t_2$. Their efficiencies are

$$\eta_{12} = W_A/Q_1 \quad \eta_{23} = W_B/Q'_2 \quad (7)$$

But by a simple mechanical linkage, A and B can be combined into a single reversible engine C, which receives heat Q_1 and delivers work $W_C=W_A+W_B$. So, we must have also

$$\eta_{13} = (W_A + W_B)/Q_1 \quad (8)$$

Now we elaborate the formula (8)

$$\begin{aligned} \eta_{13} &= \frac{(W_A + W_B)}{Q_1} = \frac{W_A}{Q_1} + \frac{W_B}{Q_1} = \frac{W_A}{Q_1} + \frac{W_B}{Q'_2} \frac{Q'_2}{Q_1} = \eta_{12} + \eta_{23} \frac{Q'_2}{Q_1} = \\ &= \eta_{12} + \eta_{23} \frac{Q_1 - W_A}{Q_1} = \eta_{12} + \eta_{23} \left[1 - \frac{W_A}{Q_1} \right] = \\ &= \eta_{12} + \eta_{23} (1 - \eta_{12}) = \eta_{12} + \eta_{23} - \eta_{12}\eta_{23} \end{aligned}$$

so, getting

$$\eta_{13} = \eta_{12} + \eta_{23} - \eta_{12}\eta_{23} \quad (6)$$

To see the probabilistic interpretation of the formula (6), let's consider two events A and B, whose probabilities are $p_A=P\{A\}$ and $p_B=P\{B\}$.

If the events are independent, we have that the probability of the "union" $A \cup B$ of the two events is

$$p_{A \cup B} = P\{A \cup B\} = P\{A\} + P\{B\} - P\{A\}P\{B\} = p_A + p_B - p_A p_B \quad (9)$$

If we identify the event $\{A\}$ as "the engine A has efficiency η_{12} " and the event $\{B\}$ as "the engine B has efficiency η_{23} " the series of engines A and B, given by "union" $C=A \cup B$ event provides that "the engine C has efficiency η_{13} " receiving heat Q_1 and delivering work $W_C=W_A+W_B$.

This is the **probabilistic interpretation of the Carnot Theorem (Principle!)**:

No heat engine operating between two heat reservoirs can be more efficient than a reversible heat engine operating between the same two reservoirs.

From (6) we derive

$$1 - \eta_{13} = (1 - \eta_{12})(1 - \eta_{23}) \quad (10)$$

Comparing (10) with (3) we see that it is the same functional relation formula.

So, we get again

$$\eta = \frac{T_H - T_C}{T_H} = 1 - \frac{T_C}{T_H} \quad (1)$$

where T_H and T_C are the absolute temperatures (in degrees Kelvin) of the high and low temperature reservoirs respectively.

References

- [1.] R. Feynman, 2006, *The Feynman lectures on physics*, New Millennium Edition, Published by Basic Books, A Member of the Perseus Books Group
- [2.] E. Fermi, 1936, *Thermodynamics*, book related to his lessons at Columbia University (N.Y.)
- [3.] Finzi B., 1959, Cosa è la temperatura (*what is the temperature*) *Periodico di Matematiche, serie IV, vol. XIV and Accademia.edu*

- [4.] G. A. Linhart, 1921, The Relation Between Entropy and Probability. The Integration of the Entropy Equation, Note at EUREKA CALIFORNIA, Received September 16, 1921
- [5.] G. A. Linhart, 1922, Correlation of Entropy and Probability, CONTRIBUTION FROM THE EUREKA JUNIOR COLLEGE, SCIENCE DEPARTMENT
- [6.] Galetto, F., 2019, The Mathematics of Thermodynamics. *Academia.edu & HAL*
- [7.] Galetto, F., 2019, Addendum to Mathematics of Thermodynamics. *Academia.edu & HAL*
- [8.] Galetto, F., 2019, Entropy of Linhart_a nonsense_PREAMBLE. *Academia.edu & HAL*
- [9.] Galetto, F., 2019, Linhart ideas on Entropy versus “classical Entropy”. Proof of Linhart nonsense. *Academia.edu & HAL*
- [10.] Galetto, F., 2019, Horstmann Thermodynamics versus Mathematics_FIRST part, Horstmann Errors on Thermodynamics. *Academia.edu & HAL*
- [11.] Galetto, F., 2022, Thermodynamics Maths with Fermi Feynman Finzi ideas, *Academia.edu*
- [12.] Galetto, F., 2022, Thermodynamics One Law from the four Principles, *Academia.edu*
- [13.] Galetto, F., 2012, QUALITY IN HIGHER EDUCATION COURSES, *International Journal of Advanced Quality, Vol. 40, No. 1.*
- [14.] Galetto, F., 2017, The SPQR («Semper Paratus ad Qualitatem et Rationem») Principle in Action. *Engineering and Applied Sciences.*
- [15.] Galetto, F., 2019, The Tetralogy of Thermodynamics, Thermodynamics made SIMPLE. 2019. *Academia.edu & HAL (02334857)*
- [16.] Galetto, F., 2016, *Reliability and Maintenance, Scientific Methods, Practical Approach, Vol-1, www.morebooks.de*
- [17.] Galetto, F., 2016, *Reliability and Maintenance, Scientific Methods, Practical Approach, Vol-2, www.morebooks.de*