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Historical Article

Sadi Carnot's *Réflexions* and the foundation of thermodynamics

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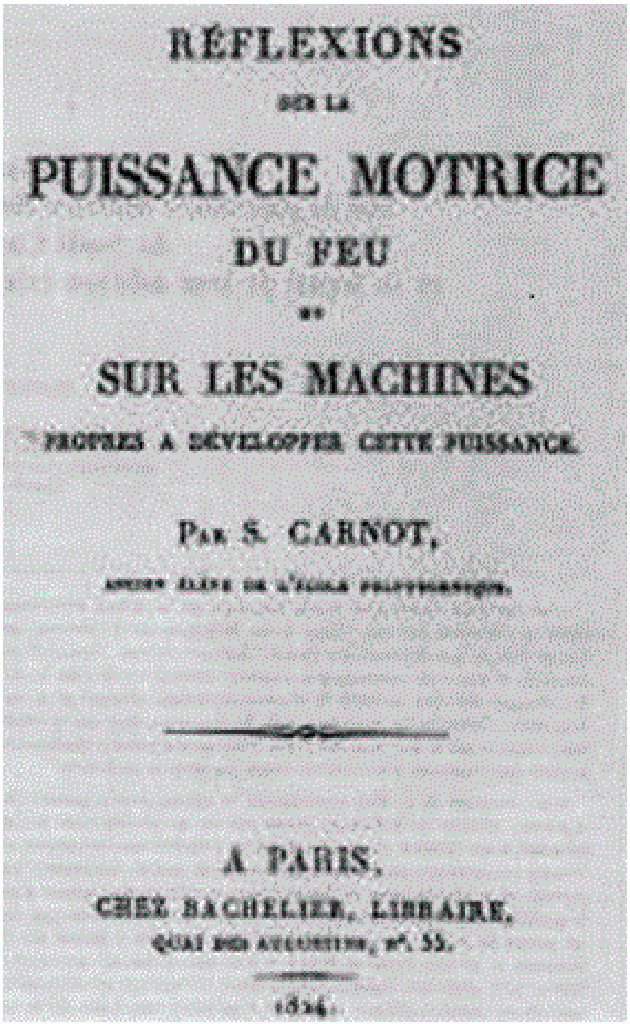
Abstract. The purpose of this article is to present a short review of Sadi Carnot work on heat engines and on the role his adherence to the caloric theory may have had. The essential points developed in the *Réflexions* are reviewed as forerunners of the science of thermodynamics. The antecedents that may have inspired the brilliant scientific insights of Carnot are reviewed together with the reception of the Carnot principles in the engineering and in the scientific community until the formulation of the two principles of modern thermodynamics.

1. INTRODUCTION

In several cases new important scientific theories have been outlined starting from models or interpretative schemes that later developments have shown groundless or partially incorrect. The limits of the starting bases were overcome by the intuition or the imagination of the scientists. An example of this twisted way in the advancement of science is the discovery of the periodic system of the elements by Dmitrij Ivanovich Mendeleev (1834-1907). In a meeting of the newly founded *Russian Chemical Society* (held on March 6, 1869) Mendeleev presented his periodic table of the elements, later published in the journal of the Society [1] and in a German edition [2] and included in Mendeleev's treatise *Principles of Chemistry* (1868-1870). Mendeleev arranged the 63 known elements in order of increasing atomic weight and the table showed the periodic recurrence of their physical and chemical properties, identifying group of elements with similar properties. The really innovative aspect of the table was in its heuristic power. In fact, in his ordering Mendeleev was forced to leave empty places corresponding to unknown chemical elements whose physical and chemical properties were predicted by Mendeleev. These unknown elements were actually discovered a few years later [3] and their properties were found to be in good agreement with Mendeleev predictions. Almost simultaneously a similar periodic table, including only 28 elements, was published by Lothar Meyer [4].

Today we know that the ordering of the elements in the periodic table is based on the atomic number and that the chemical and physical properties of the elements depend on the electronic structure of the atom. Nevertheless, the general idea of Mendeleev's periodic table has remained unchanged surpassing, almost unscathed, the revolution of quantum mechanics apart from the adaptations required to accommodate the numerous new elements discovered. Sadi Carnot's contribution to the foundation of thermodynamics can be analyzed along the same lines. In a historical period in which the first and second principle of thermodynamics and the equivalence between heat and work had not yet been established Nicolas Léonard Sadi Carnot (1796-1832), in his famous booklet *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* [5], published in 1824, (Fig. 1), was able to arrive at a substantial definition of the second principle, starting from the assumption of the caloric theory which attributed a character of materiality to heat. Even though, in addition to the erroneous nature of the current heat theory, various aspects of gas properties, such as the pressure-volume relationship along adiabatic transformations or the specific heats of gases, were not completely defined at the time on the basis of available experiments and theories, Carnot, starting from the study of the general characteristics of the thermal engines and the conditions for optimizing their performances, succeeded in defining general principles that would open the way to the establishment of thermodynamics as an autonomous science .


RÉFLEXIONS

SUR LA

PUISSANCE MOTRICE

DU FEU

ET

SUR LES MACHINES

PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,

ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,

CHEZ BACHELIER, LIBRAIRE,

QUAI DES AUGUSTINS, Nº. 55.

1824.

Figure 1. Front page of the original work of Carnot.

The work of Carnot and his *Réflexions* have been the subject of extensive and detailed studies (as it will be reported and discussed in the following) regarding, on the one hand, the original type of scientific reasoning underlying his conclusions and on the other the previous scientific knowledge and the later developments in thermodynamics. The aim of this work is to present a review of Carnot's contribution to thermodynamics and the various possible interpretations of his work. After a brief biographical profile of Sadi Carnot and an overview of the theories of heat, the essential points of the *Réflexions* will be revisited and subsequently examined with reference to possible scientific backgrounds and to the subsequent reception of the *Réflexions* in the scientific and engineering community.

2. BRIEF BIOGRAPHY OF SADI CARNOT

To better frame the work of Carnot in its historical context a brief biographical profile may be appropriate. The first information we have on Sadi Carnot can be found in the note of one of his fellow students of the École Polytechnique, and probably his friend, Michel Chasles [6] and in the obituaries of Claude-Pierre Robelin [7] and of Adolphe Gondinet [8], this latter reported by Pietro Redondi [9]. More substantial biographical information has been reported later by Paolo Ballada count of Saint-Robert, a Piedmontese engineer interested in thermal machines and industrialization processes [10], based on a letter from the grandson Adolphe of Sadi Carnot [11]. A similar but more informative letter dated 1878 from the brother Hippolyte Carnot has been reported by R.H. Thurston [12]. On the biography of Carnot, Birembaut has returned with new documentation [13] noticing various inaccuracies in his brother's story.

Sadi Carnot (Fig. 2) was born in Paris, June 1st, 1796. His father, Lazare Carnot (1753-1823), was a leading political figure during and after the French Revolution, deserving the name of Organizer of Victory due to the military successes during the revolutionary period. He was also a great mathematician and physicist and a cultivated poet and in honor of the persian poet Sadi of

Shiraz he gave the name to his first son. The mother was a gifted pianist. Carnot had a very reserved character but, whenever necessary, he was able to show great energy and decision. This results already from an anecdote of his childhood as reported by the brother Hippolyte [12]. His father often brought Sadi with him. On one occasion, when Napoleon Bonaparte enjoyed throwing rocks in the water to splash a group of ladies, including Madame Bonaparte, who were on a boat, the little Sadi did not hesitate to turn to the First Consul decisively: *Beast of a First Consul, will you stop tormenting those ladies?* The great tension of the moment vanished when Napoleon, followed by everyone present, burst into laughter. Sadi Carnot, after being initially instructed directly by his father Lazare [14], at age 16 was enrolled at the Polytechnic School having as professors, among others, Poisson, Thenard, Arago, Petit and Dulong [15]. After graduation he was admitted in 1814 in the Artillery and Engineering Application School of Metz as a cadet sub-lieutenant. He entered the military career in April 1817 with typical duties like inspecting fortifications, proposing and reporting on engineering plans. In 1818 he applied successfully for a position in a newly formed engineering corps at the Army Headquarters in Paris. This allowed him to attend courses of mathematical sciences, natural history, industrial art and political economy held in the College of France and Sorbonne. He had also the opportunity, as it will be discussed in the following, to make acquaintance with Clément at the Conservatory of Arts and Crafts. In 1821 he visited his father in exile at Magdebourg. Back in Paris and after completing various tasks as a military engineer he resigned as captain of the Military Engineering and developed a more direct interest in heat engines which led, in the following years, to publication of the *Réflexions*. In 1831 he resumed the study on the properties of gaseous substances encouraged by the appearance of two memoirs on the subject by Dulong. Unfortunately, in the same year he took scarlet-fever and fell seriously ill. Sadi Carnot died at age 36 in Paris by a violent attack of cholera on August 24, 1832.

Figure 2. Sadi Carnot at the age of 17.

3. CALORIC VERSUS MECHANISTIC THEORY OF HEAT

The type of reasoning used by Carnot in the *Réflexions* was based on the acceptance, albeit with significant distinctions, of the caloric theory. The theory of heat, with its evolution and oscillation between a materialistic and mechanistic view, has been discussed in great detail in many texts [16-19] and in many articles in scientific journals [20-23]. In this section only some points of this long history will be recalled to highlight how, even if the caloric theory was dominant in France at the time of Carnot, the two aspects of the heat theory tended to overlap in general and sometimes even in the same author, as it was indeed the case for Carnot.

Intuitively, the concept of heat is linked to that of fire. Fire was assumed as the prime element in the philosophy of Heraclitus, to explain the continuous becoming of natural phenomena, and had then become one of the four constitutive elements of Empedocles' philosophy. The fire instinctively arouses the idea of the motion of elementary particles emitted by the bodies and capable of producing the physical sensation of heat. From this point of view, it is remarkable that in the title of his *Réflexions* Carnot refers to fire: *la puissance motrice du feu*, a diction that in English translations will become *the motive power of heat*. Redondi [10] attached a particular significance to the use by Carnot of the word *feu* instead of *chaleur* as an attempt to give to the term a wider generality.

The concept of heat has remained scientifically undefined for a very long time because of a lack of experimental tools to measure and quantitatively define heat and make a clear distinction between heat and temperature. These shortcomings were overcome by thermometry and calorimetry. Confining the attention to chemistry, Hermann Boerhaave (1668-1738), a physician and chemist, introduced in the chemical laboratory a thermometer, built by Daniel Gabriel Fahrenheit (1686-1736), allowing to go beyond the sensory abilities in the control and understanding of heat [24]. For Boerhaave heat, or fire as he called it, was a subtle and imponderable fluid that interacted with matter to give rise to all that concerned heat [25]. However, the materialistic vision of Boerhaave had a dynamic character: the particles of heat were constantly moving and the increase in heat produced an increase in the movement of the particles.

Further progress in the study of heat was made with Joseph Black (1728-1799) who highlighted the conceptual difference between temperature and heat and invented the calorimeter to measure the amount of heat that develops in a chemical reaction [26]. An important discovery of Black was the observation that in the process of melting or boiling a substance absorbed heat without changing temperature arriving at the distinction between *latent heat* and *free* (or *sensible) heat*. Black also established that the specific heat differs for various substances. It is remarkable to note that James Watt (1736-1819), the instrument maker who perfected Newcomen's steam engine, was a student of Black.

Black was a follower of the *phlogiston* theory that had been developed by Johann Joachim Becher (1635-1682) and his pupil Georg Ernst Stahl (1660-1734). According to Becher [27] there were three elements, the *terra fluida* (or mercurial), the *terra pinguis* (or fat or combustible) and the *terra lapidea* (or vitrifiable). The combustible earth produced oils and fuels. Stahl [28] developed the master's ideas and called the combustible earth *phlogiston*. The *phlogiston* was volatile and tended to rise upwards. According to the theory, the metals were rich in *phlogiston* which was liberated during the calcination and their transformation into calxes (oxides). The process was reversible and by burning the oxides with coal the metal was regenerated with the reabsorption of the *phlogiston*. The *phlogiston* theory spread among chemists because of its ability to explain the phenomena of combustion, despite considerable inconsistencies. For example, since metals during calcination increase in weight, it was necessary to hypothesize that the *phlogiston* had a negative weight. Despite this, the *phlogiston* theory held up until Antoine Laurent Lavoisier (1743-1794) correctly interpreted the phenomena of combustion as reactions of substances with oxygen, the *dephlogisticated air* discovered by Joseph Priestley (1733-1804) and Carl Wilhelm Scheele (1742-1786) [29]. In discussing his new theory of chemistry and the critique of the *phlogiston* theory [30] Lavoisier was unable to abandon the theory of caloric although he still considered the caloric as one of the chemical elements. The caloric theory still survived for its extraordinary ability to explain many physical or chemical phenomena in a simple way. For example, Pierre Simon Laplace (1749-1817), a staunch supporter of this theory [31], on the basis on the theory of caloric was able to calculate the velocity of sound in gases. It is, however, remarkable that Lavoisier and Laplace in a joint article [32,33] adopt the caloric theory but, preliminarily, express severe doubts about the same theory with respect to a theory based on atomic movements.

In the Renaissance, with resumption of atomism, a more convinced connection of heat with the movement of the microscopic particles constituting matter gradually makes its way. Francis Bacon (1561-1626) adopts the atomistic philosophy of Democritus and in the *Novum Organum* [34] explicitly expresses himself on the nature of heat:

> *from the instances taken collectively, as well as singly, the nature whose limit is heat appears to be motion. This is chiefly exhibited in flame, which is in constant motion, and in warm or boiling liquids, which are likewise in constant motion… the very essence of heat, or the substantial self of heat, is motion and nothing else.*[1]

Also Galileo Galilei (1564-1642) did not disdain the atomistic theory of the constitution of matter and in the *Saggiatore* [35] he writes about heat:

> *…I incline very much to believe that [...] those materials that produce and make us feel the heat, which we call with general name of fire, they are a multitude of little bodies, in such a way figured out, moved with so much speed, which, meeting our body, penetrate it with their subtlety, and that their touch, made in their passage through our substance and felt by us, generates the effect that we call hot.*[2]

These conceptions, and similar ones we can find, for example, in Robert Boyle and Isaac Newton, must be considered intuitions rather than scientific theories. A progress in this direction will take place with Dan-

[1] [30], book 2, aphorism XX.

[2] original sentence in [35], section 48, which in Italian reads: … *inclino assai a credere che [...] quelle materie che in noi producono e fanno sentire il caldo, le quali noi chiamiamo con nome generale fuoco, siano una moltitudine di corpicelli minimi, in tal modo figurati, mossi con tanta e tanta velocità; li quali, incontrando il nostro corpo, lo penetrino con la loro somma sottilità, e che il lor toccamento, fatto nel lor passaggio per la nostra sostanza e sentito da noi, sia l'affezzione che noi chiamiamo caldo.*

iel Bernoulli (1700-1782) and the publication in 1738 of *Hydrodynamica* [36] a treatise on the dynamics of fluids which, in chapter X, proposes a kinetic model of a gas, consisting of spherical particles in rectilinear motion. For the interest of the present paper, the model assumes that heat increases the velocity υ of the particles and that both the pressure of the gas and its temperature are proportional to υ^2, that is to the kinetic energy. Even if the work of Bernoulli did not immediately undergo the resonance that deserved, it constituted an anticipation of the kinetic theory of gases that would take place only a century after its publication.

From an experimental point of view, doubts about the theory of the caloric had been advanced in 1798 by Benjamin Thomson (1753-1814), Count of Rumford, who, witnessing the reaming of the cannon barrels in the Munich arsenal, observed that large (apparently inexhaustible) quantities of heat developed in the process both in the cannon and in the boring shavings [37] without changes in the properties (and in particular of the specific heat) of the cannon or shavings. Similarly, in 1799 Humphry Davy (1778-1829) reported that the fusion of ice occurred by simply making friction between two blocks of ice at a temperature lower than the melting point [38]. Later, in 1842, Julius Robert Mayer (1814-1878) showed that the water temperature could be increased by one degree by simple mechanical stirring [39]. Although these experiments were not able to undermine the caloric theory, a preliminary form of kinetic theory continued to affirm its uncertain presence thank to work by John Herapath (1790-1868) and John James Waterston (1811-1883), with considerable hostility in the scientific community.

The seminal work of Bernoulli saw a definitive flowering with the work of James Prescott Joule (1818-1889) [40] and Rudolf Clausius (1822-1888) [41] and with the complete elaboration in statistical terms by James Clerk Maxwell (1831-1879) [42,43] and Ludwig Boltzmann (1844-1906) [44,45].

4. THE THERMODYNAMICS OF CARNOT

The *Réflexions sur la puissance motrice du feu et sur le machines propres à développer cette puissance* were initially printed in 1824 by Bachelier in Paris [5]; this edition can be easily accessed online. A second French edition was published in 1872 [46] and can be accessed in the Annales Scientiques de l'École Normale Supérieure at the site www.numdam.org/item/ASENS_1872_Among the English versions we already mentioned the translation edited by R.H. Thurston in 1897 [12]. An English critical edition by R. Fox [47], containing also the surviving manuscripts including the *Recherche d'une formule propre à représenter la puissance motrice de la Vapeur d'Eau*, first published by Gabbey and Herivel [48], has been published in 1986. Other notable English translations have been edited by Mendoza [49] and Magie [50].

The *Réflexions* begin by extolling the contribution of steam engines to the progress and wealth of England and the further advantages that could be foreseen for the development of civilization if technical improvements were able to increase their efficiency. However, Carnot realizes that

> *their theory* [of steam engines] *is very little understood, and the attempts to improve them are still directed almost by chance.*[3]

and remarks that

> *the phenomenon of the production of motion by heat has not been considered from a sufficiently general point of view.*[4]

Hence, the declared purpose of the work is of a theoretical nature, i.e., the identification of the principles and laws that regulate the phenomenon. The extraordinary nature of the *Réflexions* lies in the critical discussion of general principles without being anchored to a corresponding mathematical formulation so that the conclusions lend themselves to be framed in the scheme of the subsequent theory of thermodynamics.

4.1 The steam engine

After establishing the issues to be analyzed, namely:

a) if the motive power of heat is limited;
b) if the improvement of the steam engine can go beyond a certain limit;
c) if there is an agent more efficient than water vapor,

Carnot initially focuses the attention on the steam engine, schematically represented in Fig. 3. The water vaporizes in the boiler and the steam is admitted in the cylinder, thus causing the piston to move, and then, by further expansion cools back to water at the condenser temperature.

The first general statement rules out the possibility of a thermal engine, like the one depicted in Fig. 4a, in which heat from a single source is transformed in motive power. For the production of motive power two heat reservoirs at different temperatures are necessary:

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[3] [12], p. 42.
[4] [12], p. 43.

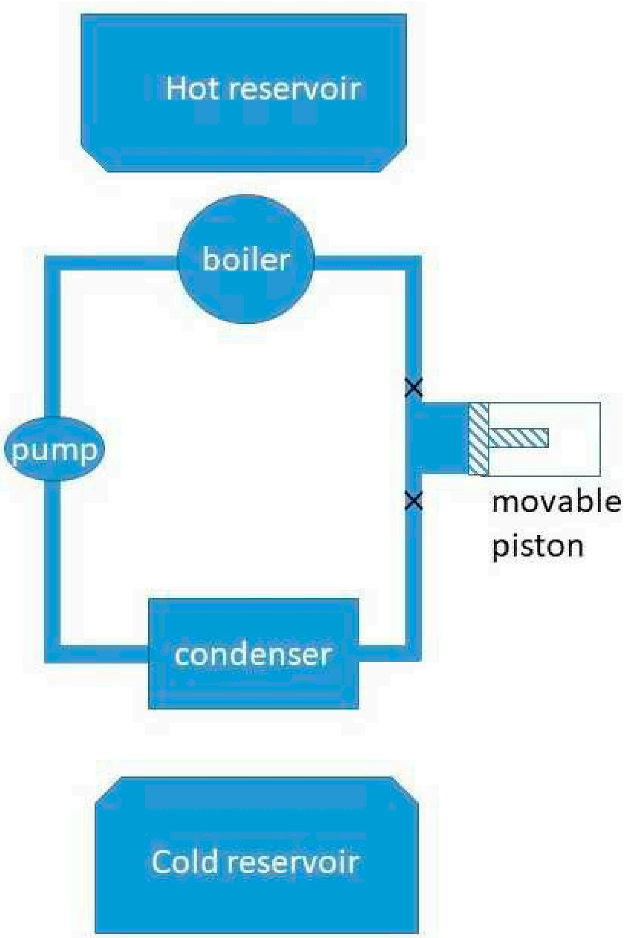

Figure 3. Schematic representation of the steam engine.

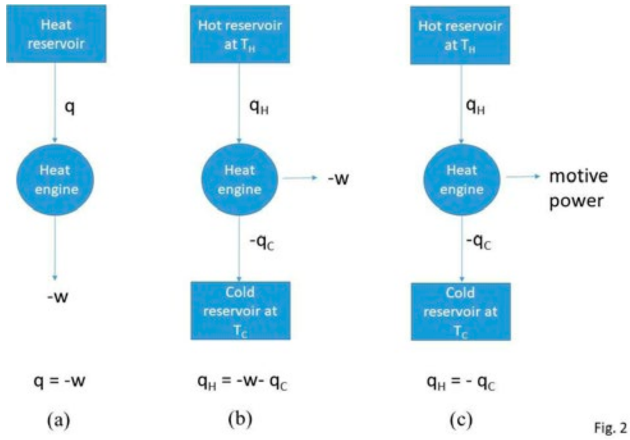

Figure 4. (a) a heat engine with a single heat source; (b) a heat engine operating between two reservoirs at T_H and T_C temperatures; (c) the steam engine according to the caloric theory of heat. In the three schemes q is the heat expended, -q the heat absorbed by the reservoir and -w the work done by the engine.

the production of heat alone is not sufficient to give birth to the impelling power: it is necessary that there should also be cold; without it, the heat would be useless. And in fact, if we should find about us only bodies as hot as our furnaces, how can we condense steam? What should we do with it if once produced? We should not presume that we might discharge it into the atmosphere, as is done in some engines; the atmosphere would not receive it. It does receive it under the actual condition of things, only because it fulfils the office of a vast condenser, because it is at a lower temperature; otherwise it would soon become fully charged, or rather would be already saturated.[5]

The heat flow from the furnace at high temperature T_H to the condenser at lower temperature T_C would not be by itself effective in producing motive power unless the heat transfer occurs through the mediation of an agent, the steam in the present case, able to expand under the action of heat. The temperature difference between the two reservoirs plays the role of a potential energy difference like the height in the waterfall:

*according to established principles at the present time, we can compare with sufficient accuracy the motive power of heat to that of a waterfall. Each has a maximum that we cannot exceed, whatever may be, on the one hand, the machine which is acted upon by the water, and whatever, on the other hand, the substance acted upon by the heat. The motive power of a waterfall depends on its height and on the quantity of the liquid; the motive power of heat of heat depends also on the quantity of caloric used, and on what may be termed, on what in fact we will call, the height of its fall, * that is to say, the difference of temperature of the bodies between which the exchange of caloric is made. In the waterfall the motive power is exactly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power undoubtedly increases with the difference of temperature between the warm and the cold bodies; but we do not know whether it is proportional to this difference.*[6]

In transmitting the caloric from the hot to the cold reservoir the volume of the steam changes and this generates the motion of the piston in the cylinder. Besides steam, any substance that expands due to heat could be employed as an agent in the cyclic operation. In the context of the caloric theory as an indestructible fluid, the heat engine would work according to the scheme of Fig. 4c [51], while the correct thermodynamic functioning is that of Fig.4b.

After establishing these general criteria, Carnot moves on to the examination of the steam engine, iden-

[5] [12], p. 46-47.

[6] [12], p. 60-61.

tifying three successive phases described in detail in the *Recherche* [48]:

a) steam generation in the boiler absorbing heat from the high temperature source at T_H and expansion into the cylinder equipped with a movable piston by the opening of the upper valve;
b) further steam expansion and piston motion with upper and lower valves closed;
c) steam condensation at the refrigerant temperature T_C after the opening of the lower valve and return of the piston to the initial position.

It can be seen that, from the beginning, Carnot includes the adiabatic expansion (process b) according to the expansive principle of Watt introduced explicitly by Clément [52,53]. Supposing that the steam engine works without dispersion of heat and the conditions for maximum power output are satisfied, the mode of operation of the steam engine can be reversed. Calling the hot and cold reservoirs A and B, respectively, the direct and inverse operation of the steam engine can be compared: in the first the caloric is transferred from A to B and motive power is produced, in the second the caloric flows from B to A and motive power is expended. It is evident that acting on the same quantity of vapor and with no loss of caloric or motive power, the A → B and B → A amounts of caloric are equal as well as the direct and inverse motive powers, apart from the sign, so that the overall balance is zero. Alternating the two processes in opposite directions in an indefinite number of operations neither motive power is produced nor caloric is transferred. If a different process were available producing more motive power than that produced by the steam engine, all other conditions being equal, it would be possible to couple this process with the steam engine, to return at the initial conditions and to divert a portion of the motive power at the end of the reversed process. The net result would be creation of motive power from nothing. This is perpetual motion, contrary to the laws of mechanics and as such inadmissible. The conclusion is:

> *the maximum of the motive power resulting from the employment of steam is also the maximum of motive power realizable by any means whatever.*[7]

Carnot realizes that *the proposition should be considered only as an approximation*[8] and that a more rigorous demonstration is necessary. An important point is that the described process of the steam engine is not reversible since the agent at the end of the process has not recovered the initial state, which is a basic requirement for the comparison of the performances of engines with different agents. The closure of the cycle cannot be simply obtained by the direct contact of the cold liquid with the high temperature reservoir since this direct contact between bodies at different temperatures will cause a loss of motive power and the reverse process would be impossible. This problem is circumvented when the temperature difference between A and B is indefinitely small since in such a case the heat necessary to raise the cold liquid to the initial temperature is also negligibly small compared to the caloric producing power. In the more general case of a finite temperature difference one may imagine that a series of other reservoirs, C, D, E, …… could be inserted between A and B with infinitely small spacing between two adjacent reservoirs such that the caloric transfer from A to B occurs through intermediate steps each developing maximum motive power.

4.2 The Carnot cycle

The analysis continues to arrive at a more exhaustive demonstration of the general principle derived from the study of the steam engine which Carnot himself defined as approximate. To this end Carnot proposes an ideal thermal engine, the famous *Carnot engine*, which works in a perfectly cyclical manner and which uses a permanent gas, air, as an agent. This choice corresponded to a need felt in the environment of thermal engines to use an agent other than water that could be used at higher pressures and, hopefully, with fuel savings [16].

The starting experimental observation is that expansion causes a temperature fall, and compression a temperature rise, which can be compensated by absorption and release of caloric, respectively. The series of operations can be described with reference to the reproduction of the original Carnot drawing shown in Fig. 5a:

I) The gas, initially enclosed in the *abcd* volume (with *cd* the actual position of the piston), is in contact with the wall of the cylinder which freely transmits the caloric from furnace A. The gas is thus taken at the temperature T_H of the furnace.
II) The piston gradually moves isothermally up to the position *ef*.
III) The furnace is removed and the gas is fully isolated from external bodies. The piston moves from position *ef* to *gh*. During this adiabatic expansion the gas temperature decreases until it reaches the temperature of the condenser B.
IV) The gas is now placed in contact with the condenser B and isothermally compressed until the piston moves back from the position *gh* to *cd* recovering the initial volume but at the condenser temperature.

[7] [12], p. 55.
[8] [12], p. 56.

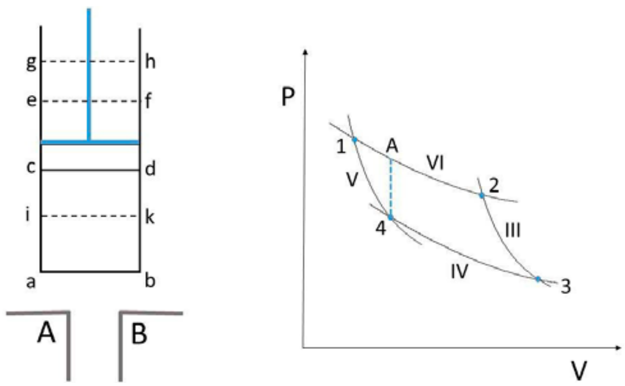

Figure 5. (a) the Carnot cycle as shown in the original drawing; (b) the usual representation of the Carnot cycle for a gas on the p-V diagram. Points A and 4 correspond to the initial volume and to completion of the isothermal compression.

V) The condenser B is removed. An adiabatic compression of the gas is carried out until the temperature rises to reach again the temperature of the furnace A. The piston moves from *cd* to *ik*.

VI) The gas is now placed in contact with the furnace A and the piston goes from *ik* to *ef*.

The cycle is successively repeated along the steps III, IV, V, VI. For the sake of clarity in Fig. 5b the usual representation of the Carnot cycle on a p-V diagram is shown. Problems connected with the correct closure of the cycle in the p-V diagram have been discussed by Klein [54], Kuhn [55], La Mer [56,57] and Tansjo [58]. Useful motive power is obtained since the elastic force (i.e., pressure) of the gas in the isothermal expansion is greater than in the isothermal compression so that the power produced in the first operation exceeds that consumed for compression:

> *the quantity of motive power produced by the movements of dilatation is more considerable than that consumed to produce the movements of compression.*[9]

By a line of similar reasoning as employed to show the impossibility to produce motive power greater than that by a reversible steam engine, the general conclusion, known as *Carnot's principle*, is reached

> *the motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperatures of the bodies between which is effected, finally, the transfer of the caloric.*[10]

The next basic question concerns the dependence of the motive power on the temperature of the two reservoirs and, in particular, whether a difference of motive power should be expected for a fall of caloric from 100°C to 50°C and from 50°C to 0°C. To this purpose, Carnot considers two air engines working between 100°C and (100 – h)°C and 1°C and (1 – h)°C, respectively, with h extremely small. The motive power results from that supplied by the air in the $V_1 \rightarrow V_2$ expansion minus that expended in the opposite compression and is the same for the two engines. Carnot easily comes to this conclusion, valid also within the later thermodynamic theory, in a long note ([12], p. 98). For the comparison between q_{100}, the heat necessary to keep air at 100°C during the expansion, and q_1, the equivalent quantity at 1°C, Carnot considers two different paths from the starting point, 1°C and V_1, to the final point, 100°C and V_2. One is performed by heating at V_1 up to 100°C and then expanding isothermally to V_2, the other by the reverse combination, i.e., expanding isothermally at 1°C to V_2 and then heating at V_2 up to 100°C. According to the caloric axiom the two amounts of heat are independent on the path and therefore

$$q_{V1} + q_{100} = q_1 + q_{V2}$$

where q_{V1} and q_{V2} are heats to increase the air temperature from 1°C to 100°C at the two different volumes V_1 and V_2, respectively. It was incorrectly established from measurements reported in previous years by Delaroche and Bérard on several gases that their specific heats depend on density, decreasing with increasing density [59]. Carnot acknowledges the result by saying that *"the capacity of gases for heat changes with their volume"* ([12], p. 78), increasing as the volume increases. Since $q_{V2} > q_{V1}$, it follows that

> *the quantity of heat due to a change of volume of a gas is greater as the temperature is higher*[11]

and as a consequence

> *the fall of caloric produces more motive power at inferior than at superior temperatures*[12]

because the amounts of heat are different ($q_{100} > q_1$), while the motive power is the same for the two engines. The conclusion happens to be correct, as everybody of us knows looking at the efficiency of thermal engines reported in all thermodynamic textbooks, but, as

[9] [12], p. 65.
[10] [12], p. 68.
[11] [12], p. 96.
[12] [12], p. 97.

already noted [16], the justification rests on the false assumption of the caloric conservation and on the misleading volume dependence of the specific heat of gases [59]. As to the latter point, it is correct to say that a word of caution about the experimental observations by Delaroche and Bérard in favor of this dependence was advanced also by Carnot and an invitation to further investigate about the law relating the motive power and temperature was clearly expressed in the *Réflexions*. In retrospect, the $q_{100} > q_1$inequality holds not because $q_{V2} > q_{V1}$ but because the heat absorbed in an isothermal expansion is equal to the work performed (for an elastic fluid behaving as an ideal gas) and the latter depends linearly on temperature.

The second problem analyzed is concerned with the evaluation of the motive power developed by the same amount of heat absorbed by agents such as air, steam or alcohol vapor at the same or at different temperatures. Here we mention only the case of steam. To this purpose the cycle of Fig. 5a is simplified to include only the two isothermal steps, expansion *abcd* → *abef* and compression *abef* → *abcd*, joined by two cooling/warming steps at constant volume. Starting with 1 kg of water, with specific volume ≈ $10^{-3}m^3Kg^{-1}$, and expanding, *abcd* → *abef*, under atmospheric pressure at 100°C, it was well known that the vaporization leads to a volume increase ≈ 1700 times the initial value, resulting in an increment $\Delta V \approx V_{steam}$= 1.7 m^3kg^{-1}. The reverse process, the compression *abef* → *abcd*, is assumed to occur in the cycle at 99°C at a slightly smaller pressure inducing steam condensation to water and volume decrement 1.7 m^3kg^{-1}. The motive power is ΔV times the difference Δp of the water vapor pressure at 100°C and 99°C, which according to data available to Carnot amounts to 26 mmHg or 0.36 m.w. (meter of water, 760 mmHg = 10.4 m.w.)[13]. The product ΔV·Δp is

1.7 m^3kg^{-1}· 0.36 m.w. = 0.611 units

The hot source delivers heat to the cycle since (a) at constant volume the temperature of the water must increase from 99°C to 100°C and (b) at 100°C the expansion step must absorb heat in order to be isothermal. The first contribution is much smaller than the second and is neglected by Carnot in the calculation of the total heat. Being experimentally known that 550 units of heat, i.e., 550 kcal, are necessary to vaporize 1 kg of water under atmospheric pressure, the conclusion is, through the simple proportion 550/0.611 =1000/x,

> *thus 1000 units of heat transported from one body kept at 100 degrees to another kept at 99 degrees will produce, acting upon vapor of water, 1.112 units of motive power*[14]

Next, the steam engine working between 1°C and 0°C is considered. Carnot was able to estimate[15] Δp = 0.358 mmHg and ΔV = 174 m^3kg^{-1} following the computational procedure described in footnote 13. The heat of vaporization of 1 kg water at 1°C is determined under the vapor tension at that temperature, p(1°C)=5.418 mmHg. According to Carnot, this is the same heat necessary to raise under atmospheric pressure the water temperature from 1°C to 100°C and then to vaporize completely water. The total heat delivered by the hot source to the engine at 1°C (and transmitted to the cold source at 0°C) is therefore (100 + 550) kcal·kg^{-1}= 650 kcal·kg^{-1}. It is easily found after convenient unit conversion of the ΔpΔV product from m^3kg^{-1}mmHg to m^3kg^{-1}m.w. that 1000 units of heat will produce 1.290 units of motive power. The soundness of this last number is obviously related to the estimate of the vaporization heat at 1°C but the strength of Carnot physical insight is shown by the comparison with the actual value: the enthalpies of vaporization at 100°C and 1°C are [61] 549.5 kcal·$kg^{-1}$and 597 kcal·kg^{-1}, respectively, so that the 650 kcal· kg^{-1} value differs from the last one only by ≈1/11.

4.3 Carnot and the caloric theory

In a note of the *Réflexions* Carnot explicitly states that a basic principle of his scientific reasoning is the assumption of the theory of caloric as an imponderable and indestructible fluid that, in a modern diction, is a function of state:

> *we tacitly assume in our demonstration that when a body has experienced any changes, and when after a certain number of transformations it returns to precisely its original state, that is, to that state considered in respect to density, to temperature, to mode of aggregation – let us suppose, I say, that this body is found to contain the same quantity of heat that it contained at first, or else that the quantities of heat absorbed or set free in these different*

[13] Data on vapor pressure of water at discrete values of temperature from 0°C to 100°C were already known [60]. Assuming that steam obeys the ideal gas law in the form p = c(267 + t)/v [p(mmHg), t(°C), v(liters) and c = 3.52 solving for c with v(steam) = 1700 liters at 100°C and 760 mmHg] Carnot found v(steam) at these temperatures and then fitted the calculated values to a known function of t(°C) in the range 0-100°C . The vapor pressure at the desired t(°C) was obtained applying the gas law equation and solving for p. For instance, p results 734 mmHg at 99°C [61].

[14] [12], p.104.

[15] Full details about the Carnot calculations on this as well as on all the others heat engines considered may be found in ref. 61.

transformations are exactly compensated. This fact has never been called into question.[16]

However, in the conclusion of the same note, Carnot explicitly expresses profound doubts about the same theory:

For the rest, we may say in passing, the main principles on which the theory of heat rests require the most careful examination. Many experimental facts appear almost inexplicable in the present state of the theory.[17]

In a subsequent step of the *Réflexions*, after calculating the motive power generated when 1000 units of caloric experience a thermal fall of 1°C in air, steam and alcohol engines, to demonstrate its independence from the agent, Carnot is again openly critical of the caloric theory:

The fundamental law that we propose to confirm seems to us to require, however, in order to be placed beyond doubt, new verifications. It is based upon the theory of heat as it is understood today, and it should be said that this foundation does not appear to be of unquestionable solidity.[18]

Therefore, while adopting the caloric theory, it is apparent that the theory does not appear to be well founded to Carnot [62]. For instance, with reference to the principles of the caloric theory he explicitly states that:

these theories furnish no means of comparing the quantities of heat liberated or absorbed by elastic fluids which change in volume at different temperatures.[19]

and in another passage he writes:

we do not know what laws it [the caloric] *follows relative to the variations of volume: it is possible that its quantity changes ….. with its temperature.*[20]

The extraordinary character of the *Réflexions* lies in the fact that, while officially adopting the caloric theory, Carnot is able to reach general conclusions that go beyond the starting hypothesis. This circumstance may well be highlighted by the closing mechanism of the thermodynamic cycle adopted by Carnot [54-58]. The set of six transformations that activate the ideal engine starts from point A in Figure 5b and the achievement of point 4, at the end of the isothermal compression and from which the adiabatic compression starts, is defined exclusively in terms of volume, without any reference to the heat exchanged. On the contrary, in the Clapeyron discussion [54,63] the cycle starts at point 1 of the p-V diagram and the end of the isothermal compression 3-4 is defined when the heat transferred to the condenser equals that absorbed during the expansion at high temperature, with explicit reference to the theory of caloric.

A certain ambiguity in the adhesion of Carnot to the caloric theory was already noted by Clausius [64]. In fact, after reporting the experimental tests showing that heat could not be considered as an indestructible fluid, he writes:

these circumstances, of which Carnot was also well aware, and the importance of which he expressly admitted, pressingly demand a comparison between heat and work, to be undertaken with reference to the divergent assumption that the production of work is not only due to an alteration in the distribution of heat, but to an actual consumption thereof; and inversely, by the consumption of work heat may be produced.[21]

After further discussing experiments in favor of the dynamic theory of heat, Clausius defines the Carnot's principle that "*no heat is lost*" only as an *additional* statement in his logical reasoning not affecting the conclusions drawn:

on a nearer view of the case, we find that the new theory is opposed, not to the real fundamental principle of Carnot, but to the addition "no heat is lost;" for it is quite possible that in the production of work both may take place at the same time; a certain portion of heat may be consumed, and a further portion transmitted from a warm body to a cold one; and both portions may stand in a certain definite relation to the quantity of work produced. This will be made plainer as we proceed; and it will be moreover shown, that the inferences to be drawn from both assumptions may not only exist together, but that they mutually support each other.[22]

However, Callendar [20] notes that Carnot's statement concerning a perfectly reversible cyclical process was actually misquoted by Clausius when he reports that Carnot

expressly states that no heat is lost in the process, that the quantity (transmitted from the fireplace to the condenser) remains unchanged[23]

[16] [12], p. 67.
[17] [12], p. 67.
[18] [12], p. 107.
[19] 12], p. 84
[20] [12], p. 62.
[21] [64], p. 2.
[22] [64], p. 4.
[23] The original Carnot statement: *Les quantités de chaleur absorbées ou degagées dans les diverses transformations sont exactement compensées*, is

According to Callendar [20] the bad interpretation of Clausius to identify "*compensated*" with "*equal*" may have been induced by the work of Clapeyron [63]. Callendar's conclusion is that the principles that Carnot reaches with regard to reversible processes are independent of the caloric theory. Considerations of this type can be applied to the description of Carnot's work by Maxwell [65]. Maxwell starts the cycle from the point 2 in the p-V diagram with an adiabatic compression up to the temperature of the cold source, again without reference to the heat exchanged.

Apart from the unpublished manuscript reported in ref. 48, Carnot did not publish anything else on the theory of heat and thermal engines after the *Réflexions* and some considerations or speculations have been advanced as an explanation [16,47]. It is possible that the increasing dissatisfaction with the caloric theory caused in Carnot some embarrassment when discussing with influential figures of the scientific milieu, which did not support the idea of destroying the fundamental axioms of the theory inherited from the founding fathers, Lavoisier and Laplace [30-33]. A second concern was perhaps bound to the assessment of the validity of the *Réflexions* and to some uncertainty about the parts of the work which could be saved after the collapse of the old theory. Although most of Carnot's ideas overcame untouched tens of years, it was necessary to wait the experimental results of Joule and the theoretical considerations of Kelvin and Clausius to reach the final objective, a giant effort for a single man. It has been observed [47] that in the remaining years of his life Carnot was probably disappointed and frustrated not being able to reconcile the published work with the ideas, freshly growing in his mind, tightly relating heat and work. A sad conclusion has been drawn that these years had elements of tragedy more than of triumph for Carnot, contrary to what we are inclined to think on the basis of his anticipation of the future laws of thermodynamics.

The doubts of Carnot on the theory of caloric are expressed more explicitly in his scientific notes which are more or less contemporary to the *Réflexions* [12,47,49]. With reference to the radiant heat, which is clearly associated to motion, Carnot poses the problem:

> *could a motion (that of radiant heat) produce matter (caloric)? Undoubtedly no; it can only produce motion. Heat is then the result of motion.*[24]

From a more general point of view Carnot position is as follows:

> *is heat the result of a vibratory motion? If this is so, quantity of heat is simply quantity of motive power. As long as motive power is used to produce vibratory movements, the quantity of heat must be unchangeable; which seems to follow from experiments in calorimeters; but when it passes in movements of sensible extent, the quantity of heat can no longer remain constant.*[25]

4.4 The physics of gases

The physics of gases presented in the *Réflexions* has been critically reviewed and discussed [47] (see notes 42, 46, 53, 61 and 63 of the Commentary). The sharp insight into the matter, despite the Carnot's adherence to the conservation of caloric as a fundamental axiom of the theory, is shown by the following examples. Considering a cycle where the two isothermal operations occur at temperatures differing only slightly, the adiabatic contributions to the total motive power may be legitimately ignored with respect to those from the isothermal operations. If different gases are used in the cycle, ensuring that they go exactly through the same states of pressure and volume, the same motive power will be obtained since the gases obey the same law. By the Carnot principle this means that the caloric absorbed at higher and released at the slightly lower temperature is the same whichever the gas used. The proposition follows:

> *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.*[26]

In modern terms, the same follows from the first principle, $\Delta U = q + w$, and the fact that the internal energy U of an ideal gas depends only on temperature. In an isothermal process $\Delta U = 0$ and $q = -w$. The statement follows since all ideal gases perform exactly the same amount of work in the same reversible isothermal process. Proceeding further, for one mole of an ideal gas expanding isothermally from V_A to V_B the heat absorbed from the surroundings is given by $RT \ln(V_B/V_A)$. Carnot expresses the same result with the proposition

> *when a gas varies in volume without change of temperature, the quantities of heat absorbed or liberated by the*

translated as: *the quantities of heat lost and gained in the various processes cancel one another out*, by Fox [47] and as: *the quantities of heat absorbed or set free in these different transformations are exactly compensated* , by Thurston [12].

[24] [49], p. 63, Selection from the posthumous manuscripts of Carnot.

[25] [49], p. 67, Selection from the posthumous manuscripts of Carnot.

[26] [12], p. 72.

gas are in arithmetical progression, if the increments or the decrements of volume are found to be in geometrical progression.[27]

and represents the volume dependence in analytical form by the equation

$s = A + B \log V$[28]

As a second result, it was known at his time that by adiabatic compression the temperature of the atmospheric air rises by 1°C when the volume V reduces to V – (1/116) V while, on the other hand, the isobaric heating of air by 1°C increases the volume to [V + (1/267) V]. The amount of heat absorbed in the last process is c_p, the specific heat of air at constant pressure, since Δt = 1°C. The final state of the isobaric process may be reached alternatively through a second trajectory which involves first the adiabatic compression by 1°C and then the isothermal expansion to the final volume. Due to the conservation axiom the amount of heat remains c_p but now is entirely expended in the isothermal process, being the compression adiabatic. A second point along the isotherm curve may be certainly reached at constant volume heating air by 1°C and increasing pressure from p to [p + (1/267) p] and in this case the heat absorption is equal to c_V, the specific heat of air at constant volume. Going again through the second trajectory but stopping now along the isotherm at a volume equal to the initial volume, the heat absorbed in this portion of isotherm expansion is c_V. As the variations are small with respect to the original volumes the amount of heat may be reasonably taken as proportional to these variations and therefore c_p/c_V= (1/116 + 1/267)/(1/116) = 1.43, not far from the value measured by Gay-Lussac and Welter, 1.3748, reported elsewhere [31]. It should be noted that the argument is valid also in later thermodynamics and made explicit by the expression $c_p/c_V = 1 - (\partial V/\partial T)_p/(\partial V/\partial T)_{ad}$ [47]. In addition, taken c_p as unity, $c_V \approx 0.7$. The difference, 0.3, represents the amount of heat due to the increase of volume when air is heated by 1°C at constant pressure. Since this increase of volume is the same for all gases, also the heat absorbed, $c_p - c_V$, is the same whichever the gas. Provided that the gases are at the same pressure and temperature it follows that

the difference between specific heat under constant pressure and specific heat under constant volume is the same for all gases.[29]

[27] [12], p. 81.
[28] [12], p. 90.
[29] [12], p. 76.

4.5 The mechanical equivalent of heat

As already noted, in the unpublished notes Carnot clearly refuses the caloric theory to such an extent to identify heat as a form of work (or energy):

heat is simply motive power, or rather motion which has changed its form. It is a movement among the particles of bodies. Wherever there is destruction of motive power there is at the same time production of heat in quantity exactly proportional to the quantity of motive power destroyed. Reciprocally, wherever there is destruction of heat, there is production of motive power.[30]

and goes as far as to propose a numerical estimate of the mechanical equivalent of heat:

according to some ideas which I have formed on the theory of heat, the production of a unit of motive power necessitates the destruction of 2.70 units of heat.[31]

The reported value (which rigorously is the thermal equivalent of work), once the appropriate conversion factor is inserted, is equivalent to a mechanical factor of 3.7 joule/cal, quite close to the actual value, 4.184 joule/cal. The theoretical justification of this number was however not advanced and successively various reconstructions have been attempted [47,49]. One possible procedure, suggested by Décombe [66] and cited in ref. [49], is particularly simple and makes use of the only data present in the *Réflexions*. It has been seen in the previous Section that ($c_p - c_V$) is the difference between the quantities of heat expended for 1°C increase under constant pressure and volume, respectively, and that this difference fully accounts for the increase of volume in the first case. This difference results to be 0.3 if c_p is taken as unit heat. Since c_p of air is 0.267 that of water ([12], p. 100), the heat ($c_p - c_V$) absorbed by the air for a 1°C increase under constant pressure is 0.267·0.3 = 0.081 cal. On the other hand, work is performed by the air due to heat absorption. Starting with 1 kg of air, the volume at 0°C and 1 Atm, 0.77 m^3([12], p. 99), increases by 1/267 for a temperature increase of 1°C at the constant pressure of 1 Atm. The work is $1 \cdot 0.77 \cdot 10^3/267$ ℓ Atm = 2.88 ℓ Atm. With the conversion factor from ℓ Atm to tonne-meter (the unit of work to which Carnot refers [66]) the result is 0.03 tonne-meter. Since the heat and work estimates are relative to 1 kg of air, it follows that a work of 1 tonne-meter is performed when air absorbs 0.081/0.03 = 2.7 kcal of heat.

[30] [49], p. 67, Selection from the posthumous manuscripts of Carnot.
[31] [49], p. 68, Selection from the posthumous manuscripts of Carnot.

5. SCIENTIFIC ANTECEDENTS OF SADI CARNOT

For a historical overview of the work of scientific innovators, it is important to identify the background that may have inspired or facilitated their discoveries. The problem, from a general point of view, can be framed by paraphrasing the famous line of John Donne that no man is an island, entire of itself. Indeed, Isaac Newton, the most famous of the innovators of science, said of himself that he had seen farther because he was travelling on the shoulders of giants.

In this perspective it seems unlikely that Sadi Carnot was a solitary innovator as claimed, for example, by Cimbleris [67]. Considering the topic of the work of Carnot, the thermal engines, any antecedent must be sought primarily in the world of technical and engineering literature [52,68-72]. Moreover, the formation of Carnot at the École Polytechnique and, above all, at the École de Metz was mainly of a technical nature, although, as described by Taton [15], considerable attention was also paid to a formation of a scientific character. The importance of the formation process of Sadi Carnot for his subsequent scientific work has been discussed by Payen [73] and by Taton [15]. It is easy to assume that Sadi had a more exquisitely scientific preparation also in the initial phase of his formation under the guidance of his father Lazare.

A possible scientific influence of his father on Sadi was already taken into consideration in the memory of Saint-Robert [11] in 1868 drawing attention to the analogy between the fall of water in hydraulic machines [74,75] and the transfer of heat between the heat source and a refrigerant. This connection has since been discussed in detail by various authors [14,23,76-79]. According to Gillispie [76] and Gillispie and Pisano [77] the *Réflexions* by Sadi would have been inspired or would even be a continuation of the work of the father Lazare on mechanics and on hydraulic engines [74,75]. The authors reach this conclusion through the discussion of available documents as well as with a complex treatment that involves an epistemological and semantic analysis of the writing of Sadi Carnot [78]. The elements deriving from the father Lazare [75] would be, in particular, the idea of a cyclic character in the functioning of ideal engines and of the reversibility of the involved processes, the need to avoid improper dispersion of the work by friction and, correspondingly, of heat by direct contact, the denial of the possibility of a perpetual motion, the extension of the physical principles of operation of particular engines to general cases and the discursive nature of the arguments. In fact, in the *Réflexions* an analysis or mathematical deduction of the principles enunciated by Carnot is found only in a long note [79]. It is now clear that, since mechanics was one of Sadi Carnot's scientific interests, he certainly had to know his father's work. In fact, the clearest correspondence between the *Réflexions* and the work of Lazare Carnot is found in the explicit analogy between the fall of water from a certain height in hydraulic engines and the transfer of heat between a high temperature source and a low temperature sink in thermal engines. The analogy has been discussed in some detail by Muller [14] as the real scientific inheritance of Sadi Carnot from the father. Apart from this, the conclusions of Gillispie and Pisano [77] appear absolutely plausible but in many cases they seem to be based mostly on circumstantial evidence. For example, when it is recalled that Sadi subjected some points of the *Réflexions* to his brother Hippolyte to check their readability for non-experts [12] the authors conclude in a dubitative or presumptive way: *The brothers could scarcely have failed to talk then of their father's science*[32]. In this regard, it should be noted that Lazare Carnot is never quoted or mentioned in the *Réflexions*, a strange circumstance in the normal scientific practice. Gillispie and Pisano [77] take this circumstance as a possible evidence that perhaps the *Réflexions* were actually the work of Lazare Carnot, which would then have been simply completed by the son who would have considered it useless to quote his father, the true author of the work.

The possible influence on the thought of Carnot by Nicolas Clément and Charles Bernard Desormes, but above all the first, is based on more certain documentary elements. In the first instance, we find three quotations of Clément and Desormes in the *Réflexions*. The first is related to an experiment, confirming previous Poisson data, on the gas temperature during compression[33]. The second concerns the experimentally established law (in English known as the Watt law) which states that the saturated water vapor, with the same weight, always contains the same amount of caloric whatever the temperature at which it is formed[34]. In modern terms this law is equivalent to say that the enthalpy of saturated steam is conserved at all temperatures [49] and implies that the vapor, adiabatically expanded or compressed, maintains the initial saturation state. The third quotation, the most important from our point of view, is in reference to adiabatic expansion and occurs when Carnot states that for better performance of a steam engine not only is an initial high pressure important but also, subse-

[32] [77], p. 78.
[33] [12], p. 73.
[34] [12], p. 92.

quently, progressively decreasing pressures[35]. In a note, Carnot acknowledges that the related Clément's law is indeed fundamental in the steam machine theory and he has come to the knowledge of the unpublished article of Clément by the author's kindness. With the help of this law, and of the one mentioned above, it is possible to calculate the work in an adiabatic expansion or compression of the saturated vapor. In absence of a caloric flow between vapor and surroundings the heat content is constant and the pressure and temperature of the vapor change in such a way to maintain the saturation conditions. The two parameters may thus be related following well known saturation tables such as those of Dalton. Then, the volume is found assuming the vapor obeys the Boyle and Gay- Lussac laws. Once the correspondence between pressure and volume is established at each temperature the strategy to calculate the adiabatic work is straightforward. The note in question clearly indicates a relationship of frequentation and, perhaps, of friendship between Carnot and Clément. In fact, even in the biographical note of the brother Hippolyte [12] we find that Carnot was familiar with Clément.

The possible debt of Carnot to Clément has been discussed in detail by Fox [52] and associated with the idea of the expansive principle, first conceived by Watt and then developed by Clément. The principle concerns the advantages that can be obtained in the efficiency of the steam engine allowing to continue the expansion after the initial supply of steam. While Watt considered this further expansive phase to be substantially isothermic, Clément, departing from the commonly accepted view, clearly defines it as adiabatic. It comes to this conclusion on the basis of a thought experiment in which a vapor bubble is introduced to the bottom of a cylinder, generating mechanical work measured by the water that flows from the top of the cylinder. The bubble continues to rise in the cylinder, expanding and letting other water to flow out of the cylinder corresponding to additional motive power.

A similar but more detailed analysis of the relationship between Carnot and Clément is reported by Lervig [53]. In particular, Lervig reports on the participation of Carnot to at least some lessons of the Clément's course on Industrial Chemistry at the *Conservatoire des Arts et Métiers*. This results from the set of notes to the course written in the years 1824-28 by a certain J.M. Baudot (partially reported by Lervig) which clearly show that Carnot was well acquainted with Clément and his scientific work (and in particular with the aforementioned Clément's law and with the phases of expansion [*détente*] and compression in the steam engine). In these notes the lecture of January 20, 1825 is reported where Clément says that Carnot, one in the audience of the course, has dealt with the principles of thermal engines [53]

> *… mais un des auditeurs de ce cours, M. Carnot, off.er du génie, ancien élève de l'École Polytechnique, a eu le courage et l'heureuse idée d'aborder cette intéressante question dans un ouvrage fort remarquable qu'il vient de publier sous le titre de Réflexions sur la puissance du feu.*[36]

In the note of March 8, 1827 Carnot is further mentioned by Clément as distinguished mathematician

> *la formule algébrique n'est ici que comme sujet d'exercice pour ceux qui voudront l'employer … Elle lui a été donnée, dit-il, par un mathématicien distingué.*[37]

Lervig, more explicitly than Fox, advances the hypothesis that in fact it was Carnot that influenced Clément at various points, as in the numerical examples contained in the notes taken by the mathematician L.B. Francoeur attending as a student the 1823-24 course (also these reported in part in ref. 53). The remarkable conclusion of the Lervig analysis is relative to the condensation phase of the steam engine and states that it was an idea entirely due to Carnot that in the evaluation of the total work the (negative) contribution of the isothermal work of compression must be taken into account. This conclusion is supported by an in-depth study of the Francoeur notes and by the accurate reconstruction of calculations present in the long abstract of the Clément and Desormes lost memoir describing the theory of the steam engines. Also, no hint about the condensation term is found in the notes taken by Baudot in the successive years [53].

In a simpler and more direct way the search for antecedents of Carnot can be conducted on the basis of the cites in the *Réflexions*. Gouzevitch [69] discussed the influence Prony and Betancourt (mentioned in *Réflexions*) may have had on Carnot for the emphasis these authors have put both on the need for a theoretical treatment of the thermal engines and on the necessary presence of a hot source and a low temperature sink [69].

6. THE RECEPTION OF CARNOT'S IDEAS

Carnot's *Réflexions* had a very limited initial fortune for various reasons. Carnot, like many at the time,

[35] [12], p. 115.

[36] [53], p. 185.

[37] [53], p. 188.

was an amateur scientist not introduced into the important circuits of scientific communication. Moreover, already in his presentation in the front page of the book he defined himself simply, with an understatement, an *ancien élève de l'École Polytechnique*. The book was presented by Pierre Simon Girard, a well-known engineer, at a meeting of the *Académie des Sciences* on 14 June 1824 to the presence of many important scientists but only in oral form and therefore the book was not published in the *Mémoires* of the Academy, which would have guaranteed the necessary publicity. This was not afforded either by a subsequent written presentation by Girard himself in the *Revue Enciclopédique* [80]. In an obituary of 1832 Robelin [7] attributed in part the scarce diffusion of the work to the difficult style of Carnot:

> *unfortunately, this writing ….. could be accessed by only few readers, and lacked the degree of utility it entailed.*[38]

Actually, the *Réflexions* were published at the expenses of Carnot in a very limited number of copies so that later, in 1845, William Thomson (Lord Kelvin) found it impossible to find a copy despite his research at all booksellers in Paris [81]

> *I went to every book-shop I could think of, asking for the Puissance Motrice du Feu, by Carnot. 'Caino? Je ne connais pas cet auteur' … 'Ah! Ca-rrr- not! Oui, voici son ouvrage', producing a volume on some social question by Hippolyte Carnot [Sadi's brother]; but the Puissance Motrice du Feu was quite unknown.*[39]

and he was initially acquainted with Carnot's work only through Emile Clapeyron [82]

> *Having never met with the original work, it is only through a paper by M. Clapeyron, on the same subject, published in the Journal de l'École Polytechnique, Vol. xiv. 1834, and translated in the first volume of Taylor's Scientific Memoirs, that the Author has become acquainted with Carnot's Theory.*[40]

In the next ten years after publication the book had a footnote citation in a treatise by Jean Victor Poncelet [83] where the analogy was made between the properties of gases and those of the caloric intended as a gas-like material.

Apart the biographical note prepared by his brother [12], Sadi was scarcely referenced also in books on the Carnot family and in other contexts. In a two-volume biography of the father [84], Hippolyte barely alluded to the Sadi's work. The family history by Maurice Dreyfous [85] reported primarily on Lazare, Hippolyte and Sadi, Hippolyte's son, which was the fourth President of the Third Republic, murdered in 1894 by the Italian anarchist Sante Ieronimo Caserio. François Arago, secretary for life of the Academy of Sciences, mathematician, physicist and politician wrote a historical note on steam engines [86] with the purpose of denying the thesis that the steam engine was entirely an English invention and emphasized the role of Denis Papin while completely ignoring Sadi's contribution.

As regards the success of the *Réflexions*, it is of course necessary to consider the dual nature of Carnot's work defined by Redondi [9] as "*un défi théorique à la pratique*" (a challenge of theory to practice) and to look at its reception both in the engineering environment and application and to its impact as a moment of foundation of the science of thermodynamics. The first aspect has been considered in detail by Redondi [9,87]. On the basis of a new documentation, reported as a group of annexes accompanying his work, Redondi brought to attention numerous explicit references to Carnot, also as explicit quotations of the *Réflexions*, in works by engineers and technicians, even though there is no evidence of practical applications of Carnot's principles. In particular, Redondi mentions an *Essai sur le machines à feu* (1835) by M. Boucherot, an *Emploi de l'air comme moteur* and a *Machine à air à effet alternative* (1838) both by F. Bresson. These are all projects submitted to the *Académie des Sciences*. These, and other technological projects mentioned by Redondi, have the common purpose of proposing the air at high pressures as an agent of thermal engines and therefore constitute a logical reference to the ideal air engine of the *Réflexions*. Of particular interest may be the air engine proposed by Boucherot, the *pyraéromoteur*, a new variant of the *pyreolophore* proposed by the Niepce brothers in 1800, an antecedent of the internal combustion engine, mentioned by Carnot in the *Refléxions*. Of course, Clapeyron, the first true communicator of Carnot's ideas, was also an engineer but his interest in the *Réflexions* was not really technical. But this is another story [88-93] that is discussed in the ref. [47], p. 110-111.

6.1 the Clapeyron contribution to the diffusion of the Carnot theory

It was in 1834 that a detailed exposition of the *Réflexions* appeared in the *Journal de l'École Polytechnique* by Clapeyron [63]. In the *Mémoire sur la Puissance Motrice du Feu* the verbal analysis of Carnot, sometimes

[38] [7], authors' translation of the French obituary.
[39] [81], p. 458.
[40] [82], p.100.

cumbersome, was substituted by the symbolism of the calculus and use was made of the indicator diagram of Watt, since then the familiar p-V diagram, to discuss the Carnot cycle. As the law relating pressure and volume in an adiabatic process was unknown to Clapeyron, the analysis was restricted to cycles with very small temperature difference between isotherms. Making reference to Fig. 5(b) Clapeyron assumes that the two isotherms, 1 → 2 and 3 → 4, are closely approaching each other at temperatures t + dt and t (degrees centigrade), respectively, and that the gas is allowed to expand, 1 → 2, and to compress, 3 → 4, by the volume increment/decrement dV. Due to the infinitesimal variations the two isotherms, 1 → 2 and 3 → 4, as well as the two adiabats joining them, 2 → 3 and 4 → 1, are essentially parallel segments and the area of the minute 1234 parallelogram is the *"quantity of action"* [63], i.e., the work performed due to the absorption of heat dQ during the 1 → 2 isotherm. As a fervent calorist Clapeyron points out that

> *successive states which the same weight of gas experiences are characterized by the volume, the pressure, the temperature, and the absolute quantity of caloric which it contains: two of these four quantities being known, the other two become known as a consequence of the former*[41]

Thus, the differential dQ may be defined as a function of p and V and the ratio between the *"quantity of action"* and dQ, which represents the maximum work for a unity of heat falling from t + dt to t, is determined by the expression

$$Rdt/[V(dQ/dV) - p(dQ/dp)]$$

where (dQ/dV) and (dQ/dp) are partial derivatives, the first at constant pressure and the second at constant volume. The constant R comes from the combination of the Boyle-Mariotte and Gay-Lussac laws for a given weight of an elastic fluid

$$pV/(267 + t) = p_0V_0/(267 + t_0) = R$$

where p, V, t and p_0, V_0 and t_0 are two different sets of values of pressure, volume and temperature and 1/267 is the (then) measured reduction/magnification factor of volume (1/273.15, actual value) for 1°C lowering/increasing at constant pressure. Through mathematical analysis the Q equation, Q = R(B – C ln p) with B and C unknown functions, is determined and, more important, the above defined ratio is found to be equal to dt/C. The Carnot principle says that C must depend only on temperature and not on the specific nature of the substance working in the cycle. The function B may in addition vary from gas to gas [63]. It follows that (1/C), called later the Carnot coefficient by Kelvin for its importance in the theory of heat and denoted by μ, is the maximum work due to a unit heat descending 1°C.

In another passage of the *Mémoire*, taking in consideration the saturated vapor as working substance, Clapeyron was able to derive the now famous "Clapeyron equation", a most remarkable fact in absence of the second law and the entropy concept. He observes that the maximum work performed with a unit input of heat when a liquid is vaporized in a cycle with infinitely close isotherms cannot be different from that obtained by any other substance between the same temperature limits, which was already shown to be dt/C. The following equation is obtained

$$k = (1 - \delta/\rho)\cdot(dp/dt)C$$

where k is the latent caloric contained in the unit volume of vapor and δ and ρ are the vapor and liquid densities. The comparison with the Clapeyron equation appearing in all textbooks of thermodynamics suggests that C coincides with the absolute temperature, a quantity not yet defined at that time.

Clapeyron not only recovered the Carnot *Réflexions* from obscurity but also introduced the point of true weakness of the theory, hinting at the possibility of *vis viva* (i.e., kinetic energy) destruction for the special case of direct contact of two bodies at different temperatures

> *caloric passing from one body to another maintained at a lower temperature may cause the production of a certain quantity of mechanical action; there is a loss of vis viva whenever bodies of different temperature come into contact*[42]

The *Mémoire* was translated into English in 1837 and into German in 1843, thus making the Carnot theory available for further analysis and development. As a mining engineer, Clapeyron was engaged in railroad engineering construction in France and abroad. Later Clapeyron was professor in the École des Ponts et Chaussées from 1844 to 1859 but alluded scarcely to the *Mémoire* in his courses and only briefly in 1847 in the scientific biography supporting his election to the Academy of Sciences [70].

[41] [63] middle sect. II.

[42] [63], end sect. II.

6.2 the Joule - Kelvin controversy and the approach to the second principle

A full recognition of the ideas contained in the Carnot *Réflexions* was granted only by the two founders of the second principle, Lord Kelvin and Rudolf Clausius. It it is worthwhile to first refer shortly to the point of view of Lord Kelvin's brother, James Thomson, about the Carnot's theory since it heavily influenced Kelvin's ideas in the following years. According to James [94], heat and work are proportional to one another in the sense that a given quantity of heat produces a given quantity of work and *vice versa* but the two entities cannot interconvert. It may help to go back to the waterfall analogy: as the fall from upper to lower height produces work with no loss of water, so the transfer of heat from high to low temperature produces work with heat conservation. This view was a source of strong debate, the two main actors being Joule, who in a series of experiments [95] in the years 1843-1844 had conclusively shown that work is converted into heat at a fixed ratio, and Lord Kelvin. Indeed, the defective point in the Clapeyron report on the Carnot theory was caught with penetrating criticism by Joule

> *I conceive that this theory, however ingenious, is opposed to the recognized principles of philosophy, because it leads to the conclusion that vis viva may be destroyed by an improper disposition of the apparatus. Thus Mr. Clapeyron draws the inference that "the temperature of the fire being from 1000ºC to 2000ºC higher than that of the boiler, there is an enormous loss of vis viva in the passage of the heat from the furnace into the boiler"* ([63], sect. VIII). *Believing that the power to destroy belongs to the Creator alone, I entirely coincide with Roget and Faraday in the opinion that any theory which, when carried out, demands the annihilation of force, is necessarily erroneous*[43]

The Joule's idea about the steam engine, substantially coincident with the modern interpretation, was clearly expressed

> *the steam expanding in the cylinder loses heat in quantity exactly proportional to the mechanical force which it communicates by means of the piston and on condensation of the steam the heat thus converted into power is not given back.*[44]

and led necessarily to the dramatic confutation of heat conservation, the basic principle of the caloric theory:

> *the theory here advanced demands that the heat given out in the condenser shall be less than that communicated to the boiler from the furnace, in exact proportion to the equivalent of mechanical power developed.*[45]

These considerations represent a turning point in the science of thermodynamics: the conversion of heat into work is apparently incompatible with the transmission of heat associated with the production of work. Kelvin knows Joule's results but the first reaction is of opposition [82]

> *In the present state of science no operation is known by which heat can be absorbed, without either elevating the temperature of matter, or becoming latent and producing some alteration in the physical condition of the body into which it is absorbed; and the conversion of heat (or caloric) into mechanical effect is probably impossible, certainly undiscovered.*[46]

adding in the footnote that Joule has reported

> *… some very remarkable discoveries which he has made with reference to the generation of heat by the friction of fluids in motion … seeming to indicate an actual conversion of mechanical effect into caloric. No experiment however is adduced in which the converse operation is exhibited; but it must be confessed that as yet much is involved in mistery with reference to these fundamental questions of natural philosophy.*[47]

Successively, Kelvin had a more cautious approach to Joule's conclusions trying, in a long note of [96], to answer the core question about thermal engines; what happens when heat flows by conduction from the hot to the cold body or in other words when the thermal engine has zero mechanical effect?

> *When thermal agency is thus spent in conducting heat through a solid what becomes of the mechanical effect which it might produce? Nothing can be lost in the operations of nature – no energy can be destroyed. What effect is then produced in place of the mechanical effect which is lost ? A perfect theory of heat imperatively demands an answer to this question; yet no answer can be given in the present state of science. It might appear that the difficulty would be entirely avoided by abandoning Carnot's fundamental axiom; a view which is strongly urged by Mr. Joule. If we do so, however, we meet with innumerable other difficulties, insuperable without further experimental investigation, and an entire reconstruction of the theory of heat from its foundation."*[48]

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[43] [95], p. 188.
[44] [95], p. 189.
[45] [95], p. 189.
[46] [82], p. 102.
[47] [82], p. 102.
[48] [96], note 7.

As it is evident from these considerations, Kelvin maintained an open mind on the issue. On one hand he did not venture in the complete rejection of the Carnot's theory for the above mentioned difficulties to adequately replace the caloric theory; on the other he brought to completion three major achievements, the calculation of the maximum work in the cycle as a function of the temperature [96], the successful proposal for the absolute scale of temperature [82] and the discovery of the pressure dependence of the water freezing point [97,98], all of them representing brilliant results coming from the application of Carnot's theory.

The key work [96]: *Account of Carnot Theory of the Motive Power of Heat: with Numerical Results derived from Regnault Experiments on Steam,* already in title indicates that the author not only reviews the original study but also provides a strong basis for the theory using the data on latent heat of vaporization and pressure of saturated vapors collected by the great experimentalist Victor Regnault. Two expressions are obtained for the mechanical effect due to *"the transference of heat from one body to another at a lower temperature"* ([96], paragraph 11) in an engine operating with steam or air. By the Carnot principle the maximum work M is the same in the two cases. If H units of heat are allowed to fall from the body A at temperature $t + \tau$ to B at t, the result is, in the Kelvin notation,

$$M = (1 - \sigma)\ (dp/dt)(1/k)H\tau = E[p_0V_0/(Vdq/dV)]H\tau$$

where the $H\tau$ coefficient is denoted by μ and has the usual meaning of maximum work for a unit heat transmitted from A to B with 1°C gap (measured by an air thermometer). Thus, μ is given by

$$\mu = (1 - \sigma)\ (dp/dt)(1/k) = E[p_0V_0/(Vdq/dV)]$$

where the left expression is appropriate for the saturated steam (with σ the ratio of steam and water densities, k the latent heat of water vaporization per unit volume) and the right expression for air. Using Regnault data for (a) the pressure p of saturated steam in the range 0°C - 230°C and (b) the latent heat of vaporization per unit weight in the same temperature range; and assuming that the density of the vapor follows the law of ordinary gases up to 100°C and beyond may be estimated from pressure data, μ was found from 0°C to 230°C. The coefficient steadily diminishes increasing the temperature, consistently with the few scattered points obtained by Clapeyron using boiling water, sulphuric ether, alcohol and turpentine [63]. Kelvin was fully aware of the great generalization embodied in this calculation but, at the same time, he worried about its physical basis, emphasizing the request of experimental confirmation

> *in paragraph 30 some conclusions drawn by Carnot from his general reasoning were noticed; according to which it appears, that if the value of μ for any temperature is known, certain information may be derived with reference to the saturated vapor of any liquid whatever, and, with reference to any gaseous mass, without the necessity of experimenting upon the specific medium considered. Nothing in the whole range of Natural Philosophy is more remarkable than the establishment of general laws by such a process of reasoning. We have seen, however, that doubt may exist with reference to the truth of the axiom on which the entire theory is founded, and it therefore becomes more than a matter of mere curiosity to put the inferences deduced from it to the test of experience.*[49]

The second important point is concerned with a fundamental quantity like temperature which is expected to be defined in a general way rather than looking at specific properties of a substance, so as to make its definition independent of any kind of material [82]. On the basis of the Carnot theory the mechanical effect due to the transmission of heat from a hot to a cold body does not depend on the nature of the working medium but only on the temperatures of the two bodies. Further, the maximum work done by a unit heat falling 1°C is given by μ. From μ data on steam and few others on different substances [96], μ is found to decrease as the temperature, measured by the air thermometer, increases. The Kelvin proposal was that μ, rather than other physical properties, must be used to fix the temperature scale. The central point of the proposal is that a degree is defined by the amount of maximum work done by a unit heat falling down this degree, irrespective of the temperature value. This is equivalent to say that μ becomes constant through the whole temperature range. In Kelvin's own words:

> *In M. Clapeyron paper various experimental data, confessedly very imperfect, are brought forward, and the amounts of mechanical effect due to a unit of heat descending a degree of the air-thermometer, in various parts of the scale, are calculated from them, according to Carnot's expressions. The results so obtained indicate very decidedly, that what we may with much propriety call the value of a degree (estimated by the mechanical effect to be obtained from the descent of a unit of heat through it) of the air-thermometer depends on the part of the scale in which it is taken, being less for high than for low temperatures. The characteristic property of the scale which I now propose is that all degrees have the same value; that is, that a unit of*

[49] [96], paragraph 41.

heat descending from a body A at temperature T° of this scale, to a body B at the temperature (T–1)°, would give out the same mechanical effect, whatever be the number T. This may justly be termed an absolute scale, since its characteristic is quite independent of the physical properties of any specific substance.[50]

Finally, a curious question was raised by Kelvin, possibly representing a fatal argument to endanger Carnot's theory. It is known that water ices at 0°C under atmospheric pressure with volume expansion. In this process the latent heat is released while in the opposite process, i.e., melting under the same conditions of temperature and pressure, an equal amount of heat is absorbed with volume contraction. Therefore, at least in principle, it may be thought of an ice engine in which heat does not flow from a hot to a cold body but between bodies at the same temperature, i.e. 0°C, with the result that *"mechanical work would be given out without any corresponding expenditure"* ([97] p.156). It was the brother James, who succeeded in showing that under pressure the melting point of water is lowered allowing Kelvin to escape from this impasse [97]. Thus, for an ice engine properly operated, it is necessary to run with the cold body at a temperature lower than 0°C otherwise the freezing process stops when freezing water starts to exert a pressure. The theoretical estimate of the temperature lowering with pressure was proposed considering a cyclic ice engine, analogous to the steam engine, which was working with the following steps:

1) isothermal (and isobaric) compression of ice at 0°C and 1 Atm until one cubic foot of water is obtained from ice, absorbing heat from a reservoir (*"an indefinite lake of water at 0°C"*) ([97], p. 160);
2) adiabatic compression of the water/ice mixture to pressure p_a(pounds/squarefoot) above that of the atmosphere. At the end of the process the temperature of the mixture is −t(°C);
3) isothermal (and isobaric) expansion causing the complete freezing of water and the heat release to a reservoir at − t(°C) (*"a second indefinitely large lake at −t(°C)"*) ([97], p.160). According to the caloric theory, of which James Thomson was a follower, *"continue the motion till all the heat has been given out to the second lake at −t(°C), which was taken in during Process 1 from the first lake at 0°C"* ([97], p. 160);
4) adiabatic expansion to the original values of temperature and pressure to close the cycle.

It should be noted that James Thomson predicted the temperature lowering with two independent strategies and not making recourse to the laws of thermodynamics. In the first the work is calculated considering the area enclosed by the cycle in the p-V diagram, i.e., $p_a \cdot (V_{ice} - V_{water})$; in the second, being known to James the thermal units Q to melt one cubic foot of ice and the value of μ at 0°C, the same work was calculated as the product Q·μ·t. The final expression is [97]

$$t = 0.0075n$$

where t (degrees centigrade) is the lowering of the water freezing point with respect to 0°C and n is the pressure (atmospheres) above one atmosphere. The theoretical estimate was confirmed by the experimental measurements performed by Kelvin [98]. It may be concluded that the validity of the Carnot theory was supported also by the discovery of an unsuspected new physical effect and the admiration of Kelvin for this result was expressed by words which go beyond the brotherhood relation

In this very remarkable speculation, an entirely novel physical phenomenon was predicted in anticipation of any direct experiments on the subject; and the actual observation of the phenomenon was pointed out as a highly interesting object for experimental research.[51]

6.3 the second principle of thermodynamics: the final statements

Given the circumstances, it may be conjectured that a critical revision of the Carnot theory was not a primary objective for Kelvin. It was Clausius in a historical paper [64] that conclusively solved the problem of the Joule – Carnot antinomy at the expenses of the principle of heat conservation. While Kelvin sees insurmountable difficulties if the caloric theory is abandoned, Clausius in a quite illuminating passage of the paper states:

I believe, nevertheless, that we ought not to suffer ourselves to be daunted by these difficulties; but that, on the contrary, we must look steadfastly into this theory which calls heat a motion, as in this way alone can we arrive at the means of establishing it or refuting it. Besides this, I do not imagine that the difficulties are so great as Thomson considers them to be; for although a certain alteration in our way of regarding the subject is necessary, still I find that this is in no case contradicted by proved facts. It is not even requisite to cast the theory of Carnot overboard; a thing difficult to be resolved upon, inasmuch as experience to a certain extent has shown a surprising coincidence therewith.[52]

[50] [82], p. 104.

[51] [98] p. 165.

[52] [64], p. 3.

The option by means of which Joule's conversion of heat to work and Carnot transmission of heat from a hot to a cold body are reconciled is rejection of heat conservation. However, a question remains: how can the Carnot principle still be valid if the caloric theory is *"cast overboard"*? According to Clausius, the production of work in a thermal engine is due to the transmission of heat from a warm body A to a cold body B with heat consumption. Following Carnot, the maximum work is obtained if the two bodies never come in contact each with the other (in our terms, if the cycle is reversible). Reversing the engine, i.e., by consumption of the maximum work, heat is transferred from B to A. Alternating the direct and reverse cycles the work production (direct) and consumption (reverse) are equal. The same may be repeated for the heat consumption and production. The two bodies go back to the initial conditions and no total work is done. Let us now consider two different working substances K and K' with the former producing a larger amount of maximum motive power. Equivalently, we may assume that if the two substances develop the same amount of work, K' transfers from A to B a larger amount of heat, Q_B', than K, Q_B. Operating the engine with K and K' in the direct and reverse cycle, respectively, works are cancelled but B will transfer in the reverse operation more heat to A than received in the direct operation. In conclusion, an amount of heat Q_B'-Q_B is passed from a body at low temperature to a body at high temperature without any other change

> *Hence by repeating both these alternating processes, without the expenditure of force or other alteration whatever, any quantity of heat might be transmitted from a cold body to a warm one; and this contradicts the general deportment of heat, which everywhere exhibits the tendency to annul differences of temperature, and therefore to pass from a warmer body to a colder one.*[53]

This constitutes the first historical statement of the second principle of thermodynamics. As a consequence, the Carnot principle is justified even if the principle of heat conservation does not hold anymore. With its elimination, other concepts such as "latent heat" and "total heat of a body" must be dismissed or critically revised. The "latent heat" of vaporization, for instance, had in the old theory the meaning of caloric fluid surrounding the particles of vapor as if a composite particle was formed. According to Clausius heat actually disappears and is converted into the expansion work from liquid to vapor

> *… we can form a notion as to the light in which latent heat must be regarded. Referring again to the last example* [the liquid – vapor transition] *we distinguish in the quantity of heat imparted to the water during the change the sensible and the latent heat. Only the former of these, however, must we regard as present in the produced steam; the second is, not only as it name imports, hidden from our perception, but has actually no existence; during the alteration it has been converted into work.*[54]

As to the "total heat of a body", i.e., the sum of the sensible and latent heat, this property is dependent, according to the caloric theory, on the parameters which characterize the state of the body. It follows that, going from one state to another and then back to the original, the total heat is zero. On the contrary, Clausius argues that during the cyclical transformation work may be done or absorbed by the body and the total work may not be necessarily equal to zero, as it is indicated by the occurrence of volume change in the body. This work must correspond to a well defined amount of heat, on the basis of the Joule principle of equivalence.

Clausius summarized the theory of heat by means of the two principles [64, 99]:

1) *in all cases where work is produced by heat, a quantity of heat proportional to the work done is consumed; and inversely, by the expenditure of a like quantity of work, the same amount of heat may be produced.*[55]
2) *heat cannot by itself pass from a colder to a warmer body.*[56]

Kelvin acknowledged the dynamical theory of heat one year later [100]. From his point of view the two basic propositions are

1) *When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.*[57]
2) *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*[58]

The first proposition is essentially the Joule principle of equivalence, as it is in the Clausius statement. As to the second, it is a fair acknowledgment to declare Clausius' priority:

[53] [64], p.103.

[54] [64], p. 5.
[55] [64], p. 4.
[56] [99], p. 45.
[57] [100], p. 178.
[58] [100], p. 181.

It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius.[59]

At the same time it is a point of honor to say

I may be allowed to add, that I have given the demonstration exactly as it occurred to me before I knew that Clausius has either enunciated or demonstrated the proposition.[60]

and to note that the two formulations of the second principle are different only in the form, either of them being a consequence of the other. The crucial argument of the Kelvin second proposition is that heat absorbed cannot be integrally converted to work performed in a cyclic process. Suppose that a thermal engine is operating between temperatures t_1 and t_2, being $t_1 > t_2$, and both higher than the temperature t_0 of the coldest of the surrounding bodies, for the sake of clarity the environment. The amount of heat delivered to the body at t_2 is wasted unless it acts as input heat in a second thermal engine operating between t_2 and t_3, being $t_2 > t_3$ and both still higher than t_0. It is a result of the Kelvin enunciation that this step-by-step conversion of heat to work may proceed until the temperature of the environment is reached and that the work produced is $Q_1 + Q_0$, where Q_0 is the (negative) amount of heat delivered to the environment. As the proposition may be of no immediate comprehension, it was exemplified by a note

"If this axiom be denied for all temperatures, it would have to be admitted that a self-acting machine might be set to work and produce mechanical effect by cooling the sea or earth, with no limit but the total loss of heat from the earth and sea or, in reality, from the whole material world".[61]

Probably, Kelvin was motivated to reformulate the principles of Clausius to express his own ideas in his own way on the issue. In the second place the enunciation contains the Kelvin answer to the difficult question concerning the sort of the mechanical effect which does not appear when the two bodies are put in direct thermal contact. The work is *"irrecoverably lost to man, and therefore wasted although not annihilated"*.[62]

7. CONCLUSIONS

A question that has frequently been debated in the history of science and technology is whether science has been the driving force behind technological development or whether, on the contrary, the development of technologies has been the stimulus for new scientific knowledge. Even if the question, posed in this way, appears too schematic, it has aroused the interest of many scientists and historians of science. A case in point is the statement by Lawrence Joseph Henderson (1878- 1942), reported by Charles Coulston Gillispie [101] that:

Science owes more to steam engine than steam engine owes to science.[63]

On the other side, Hermann von Helmholtz is more cautious on the immediate or direct transfer of scientific findings to technology [102]:

Whoever in the pursuit of science seeks after immediate practical utility may rest assured that he seeks in vain.[64]

but Ludwig Boltzmann [103], and others as well [104], seem more convinced of the primacy of science:

There is nothing more practical of a good theory.

In such a hypothetical dispute Carnot and his *Réflexions* place themselves in an intermediate and more balanced position. In fact, as we have already discussed, even if Carnot's initial inspiration is derived from the consideration of technology and the practice of steam engines, an object that is so eminently technological, its line of reasoning is anchored on a logical and principle level. So much so that, even with long induction times, the work of Carnot has influenced and oriented the definition of the principles of thermodynamics rather than an immediate improvement of the thermal machines.

The truly extraordinary aspect of the work of Carnot is that, although starting from a theory of heat that already known results and subsequent experiments would have proved wrong, has led to the identification of extremely fruitful principles for the elaboration of the theory of thermodynamics.

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[59] [100], p. 181.
[60] [100], p. 181.
[61] [100], p. 181.
[62] [100], p. 189.
[63] [101], p. 357.
[64] [102], p. 93.

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