

Sadi Carnot, ‘Founder of the Second Law of Thermodynamics’

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Abstract. Sadi Carnot was one of the giants of physics. Although he used the incorrect caloric theory of heat in his *Réflexions*, nevertheless he may rightfully be considered to be ‘the Founder of the Second Law of Thermodynamics’.

1. Introduction

Sadi Carnot (1796–1832) may rightfully be considered the ‘Founder of the Second Law of Thermodynamics’—despite having used the subsequently discredited caloric theory of heat in the only work he published during his lifetime, his *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* [1]. After the publication of his *Réflexions* he continued his research, and his *Notes* [2, 3] indicate that he abandoned the caloric theory for the mechanical theory of heat. These *Notes* were only published posthumously. In this paper we will try to show how Carnot’s theoretical ideas on heat engines in his slim (118 pages), partly incorrect, book secured for him a major position in the history of physics.

2. Historical background

Sadi Carnot had one of the shortest lifetimes, just 36 years, of any of the giants in the history of physics. Carnot’s period was that of the Industrial Revolution and the steam engine. Sadi was the son of Lazare Carnot, a prominent figure in the era of the French Revolution and Napoleon, and no mean scientist in his own right. Mendoza [4, p xii] attributed Sadi’s ability to generalize to his father and said of Carnot’s *Réflexions* that:

The Memoir transcended technical details because Sadi had inherited from his father the capacity to generalize, to see the fundamental processes animating a complicated mechanism. Thus he saw that in an engine—any engine—an amount of caloric fell from a high to a low temperature; he extended some of his father’s ideas on mechanics to apply to thermal processes—the impossibility of perpetual motion, the need to avoid irreversible changes.

Sadi was trained at the prestigious *École Polytechnique* from 1812 to 1814, following which he studied military engineering for two years at the *École du Génie* in Metz. In 1819 he was granted a permanent leave of absence from the army and embarked on a highly productive period of study and research in Paris. On 12 June 1824 his *Réflexions* book [1] was published

by Bachelier. After that, except for a short period when he returned to military service, Carnot continued his research in thermodynamics. He died at age 36 on 24 August 1832, a victim of a cholera epidemic.

Carnot's *Refléxions* was basically ignored by the community of his contemporaries in science at the time of its publication. We hazard the guess that this is because Carnot was outside of the scientific establishment. He had been trained as a military engineer and served in the army. How could a book written by such a person command the interest of the trained physicists of the period? J F Challey, in his article on Carnot for *The Dictionary of Scientific Biography* [5], writes that 'In 1828 a contemporary referred to Carnot as a "builder of steam engines", although there is no record of his formal connection with any firm'. We maintain that it was this association of the name of Sadi Carnot with engineering, as distinct from science, that delayed the recognition of Carnot's fertile ideas on thermodynamics.

Once the belated recognition of Carnot occurred, people had to deal with his use of the now obsolete caloric theory in the *Refléxions*, and more importantly, the absence in that work of the principle of conservation of energy. It was nevertheless recognized that after the publication of the *Refléxions* he had come to grips with both the mechanical theory of heat and with the First Law of Thermodynamics. The *Refléxions*, which had made so small a stir on its original publication in 1824, was republished in 1878 in a new edition [2], which also contained a letter from Sadi's brother, Hippolyte Carnot, to the French Academy of Sciences, and some of the unpublished *Notes* written by Sadi after the publication of his *Refléxions*. Hippolyte saw his brother as the founder of the science of thermodynamics. He wrote (English translation by H Erlichson):

We are therefore justified in saying that if, in his first work, published in 1824, he formulated the principle to which his name is preserved, by his later work he also discovered the principle of equivalence, which makes up, with the first, the fundamental basis of thermodynamics.

We will also have occasion to refer to a 1953 photographic reprint [3] of the original 1824 *Réflexions* including some of the material in [2], and to the most recent English translation of Carnot's *Refléxions* made by Robert Fox [6] in 1986.

3. Carnot's intention to study heat engines from a general viewpoint

Carnot opens his *Refléxions* by stressing the practical importance of heat engines [4, p 3]:

The study of these engines is of the greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world.

This kind of opening is what one would expect from a practical engineer enthusiastic about practical progress. But, shortly thereafter, we find [4, p 6]:

The phenomenon of the production of motion by heat has not been considered from a sufficiently general point of view. . . . In order to consider in the most general way the principle of the production of motion by heat, it must be considered independently of any mechanism or any particular agent. It is necessary to establish principles applicable not only to steam-engines, but to all imaginable heat-engines, whatever the working substance and whatever the method by which it is operated.

Here we have the voice of the scientist, not that of the engineer. And, in the very next paragraph, Carnot calls for a physical theory which can be used to achieve for heat engines what has been achieved for mechanical devices such as waterfalls or windmills [4, p 6]:

We shall have it only when the laws of physics shall be extended enough, to make known beforehand all the effects of heat acting in a determined manner on any body.

Here Sadi Carnot is calling for the establishment of the science of thermodynamics. The remainder of his book is his contribution to that new science. He is rightly called the 'founder of the Second Law of Thermodynamics'. It little matters that he erred in using the caloric theory in the *Réflexions* and only later in the *Notes* moved correctly to the mechanical theory of heat.

4. The search for a general thermodynamic principle in the difference of temperatures

Carnot fixed his attention on the 're-establishment of equilibrium in the caloric'. By this he meant that what was characteristic of a heat engine was the passage of the caloric (we remember that in the *Réflexions* Carnot thought of the caloric as a material fluid) from a higher temperature to a lower temperature. This passage of the caloric from a warm body to a cold body, what he referred to as the 're-establishment of the equilibrium of the caloric', was what he saw as a general guiding principle which was independent of the particular heat engine employed and independent of the working substance used in the heat engine cycle. It will be useful at this point to review the general principles of heat engines from a modern viewpoint in order to have a frame of reference for Carnot's ideas.

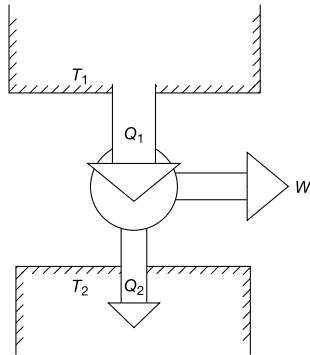


Figure 1. Schematic diagram of a heat engine.

Figure 1 is a schematic diagram of a heat engine. The engine operates between a high-temperature reservoir at the Kelvin temperature T_1 and a low-temperature reservoir at the Kelvin temperature T_2 . The engine operates in a cycle during which Q_1 units of heat are extracted from the high-temperature reservoir, Q_2 units of heat are delivered to the low-temperature reservoir, and the energy difference of $Q_1 - Q_2$ units appears as the work done per cycle by the engine. The conservation of energy (First Law of Thermodynamics) is expressed by the relationship

$$W = Q_1 - Q_2. \quad (1)$$

The efficiency of the engine is expressed as

$$e = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}. \quad (2)$$

For a reversible cycle (Carnot cycle) the ratio of the heats is the same as the ratio of the absolute temperatures:

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \quad (3)$$

Hence, the efficiency of a Carnot engine is

$$e = \frac{T_1 - T_2}{T_1}. \quad (4)$$

From a retrospective point of view, impossible of course for Carnot to see, equation (4) clearly indicates how he was on the right track in assigning difference of temperature between the high- and low-temperature reservoirs as the determining factor in heat engine efficiency. He clearly understood that one had to have a low-temperature reservoir in order to have a heat engine, stating [4, pp 7–8]:

According to this principle [of re-establishment of caloric] the production of heat alone is not sufficient to give birth to the impelling power [the work done by the engine]: it is necessary that there should also be cold; without it, the heat would be useless ... Wherever there exists a difference of temperature, wherever it has been possible for the equilibrium of the caloric to be re-established it is possible to have also the production of impelling power.

By 're-establishing the equilibrium of the caloric', Carnot clearly means the re-establishment of thermal equilibrium between the caloric and the surroundings.

Carnot saw the motive power of heat in its ability to produce volume changes in substances. These volume changes produced the motive power; they 'drove' the piston of the heat engine. Carnot wrote [4, p 9]:

To heat any substance whatever requires a body warmer than the one to be heated; to cool it requires a cooler body. We supply caloric to the first of these bodies that we may transmit it to the second by means of the intermediary substance. This is to re-establish, or at least to endeavour to re-establish, the equilibrium of the caloric.

5. Carnot's first proof that no engine can be more efficient than the most efficient steam engine

The first important theoretical development in the *Réflexions* is Carnot's proof that there is a limit to the efficiency of a heat engine which is independent of the working substance, and which depends only on the temperatures of the reservoirs between which the engine operates. In the *Réflexions* Carnot gives two proofs that it is impossible to have a heat engine more efficient than the most efficient steam engine. The first proof was 'an approximation', and the second proof was a 'more vigorous'† demonstration".

In the first proof Carnot does a 'thought experiment' in which he has a cycle using water as the material of the cycle. A and B are two heat reservoirs, with A being at a higher temperature than B. He obtains motive power (work) by the following steps:

- (1) Use reservoir A to boil the water; the steam being formed is at the same temperature as A.
- (2) Use a cylinder fitted with a piston to permit the steam to expand (producing motive power) until its temperature drops to that of reservoir B.
- (3) Condense the steam isothermally at the temperature of reservoir B by exerting a constant pressure on it.

At the end of the three steps Carnot has water at the temperature of reservoir B. To complete the cycle he would have to heat the water to the temperature of reservoir A. We can assume that he does this to complete the cycle, and we will shortly see that he was well aware of the incompleteness of his cycle 1–3‡. Carnot's main purpose is to show that he can obtain motive power by having caloric pass from body A to body B.

† It should be noted that the word 'vigorous' in the Thurston translation was probably a typographical error for the word 'rigorous', corresponding to 'rigoureux' in Carnot's original French [3, p 22]. We also note that the Fox translation of Carnot's book has the correct translation of 'rigoureux' [6, p 70].

‡ In a footnote added to the Thurston translation, Mendoza wrote 'This is only a sketch and Carnot accidentally leaves the cycle incomplete' [4, p 10]. Fox commented that 'The cycle of operations, as conducted here, is of necessity incomplete. For, once the steam has been wholly condensed to water at the end of the third stage, it cannot be restored to its initial state simply by adiabatic compression' [6, p 122, note 19]. What Fox means is that adiabatic compression of the water will barely change its temperature. So closing Carnot's cycle cannot be done with an adiabatic; that is, the closed cycle will not consist of two adiabatics and two isotherms (see our discussion of closing the cycle with an isovolumic, reversible heating process).

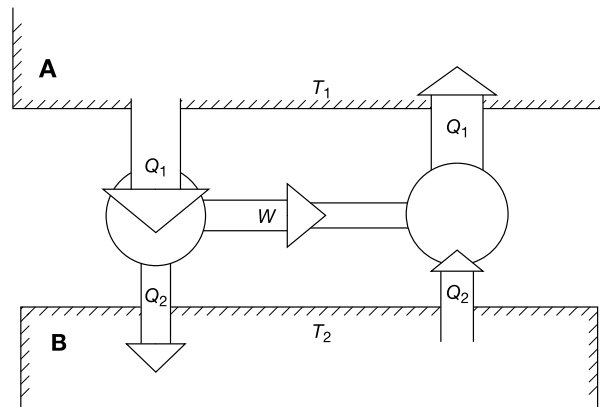


Figure 2. A reversible engine and reversible refrigerator coupled together and operating between reservoir A (top) and reservoir B (bottom).

Then Carnot imagines running the described operations in reverse order and having caloric move from B to A. This requires doing work equal to that obtained in the first series of operations, assuming no losses due to such things as friction. The first set of operations plus the second set would result in no net production of motive power and no net transfer of caloric between reservoirs. It should be noted that even though Carnot had at that point the incorrect view that the forward series of operations (the heat engine operations) resulted in a complete transfer of caloric, the combined set of operations on the modern, correct view would still result in no net transfer of heat and no net production of work. The combined operations on the modern view are shown in figure 2. It should also be noted here that in Carnot's description of the operations 1–3 he did not specifically mention anything about reversibility but it is clearly implied by his text. Indeed, the very words 'reverse operations' imply reversibility.

Now Carnot considers the hypothetical possibility that one can devise an engine which would produce more work than the engine using the operations 1–3. Such an engine could be coupled to a refrigerator as before and now a net amount of work would be produced by having the more efficient engine and the refrigerator operating sequentially. That is to say, if the more efficient engine produces work W' and the engine using operations 1–3 produces work W , a net amount of work $W' - W$ would be produced for each complete sequential operation. This conclusion would follow on either the caloric view or the modern view of heat. Since there would be no net heat transfer per complete cycle, and only the production of work $W' - W$, we would have a perpetual motion machine. Carnot rejected this as an impossibility, stating [4, p 12]:

Such a creation is entirely contrary to ideas now accepted, to the laws of mechanics and of sound physics. It is inadmissible. We should then conclude that *the maximum of motive power resulting from the employment of steam is also the maximum of motive power realizable from any means whatever.*

We have seen that Carnot's proof is independent of his assumption that all the caloric is transferred from the hot to the cold reservoir in a heat engine. Also, as mentioned previously, in creating his refrigerator Carnot has implicitly assumed reversibility of his cycle. Carnot makes reversibility even more important by asserting that it is the criterion for knowing that a heat engine is giving the maximum motive power obtainable from the given hot and cold reservoirs. In his own words he states that the condition for a maximum is [4, p 13]:

that in the bodies employed to realize the motive power of heat there should not occur any change in temperature which may not be due to a change of volume.

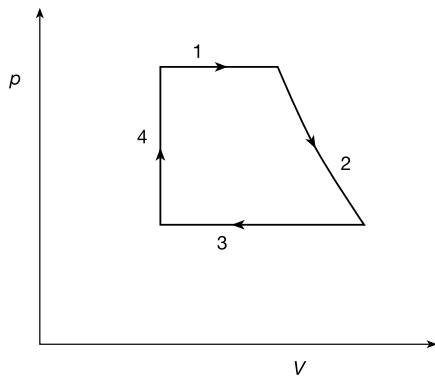


Figure 3. Carnot's operations 1-3 on water and steam.

This requirement by Carnot is equivalent to requiring reversible processes only. Carnot declares [4, p 13]:

Every change of temperature which is not due to a change of volume or to chemical action (an action that we provisionally suppose not to occur here) is necessarily due to the direct passage of caloric from a more or less heated body to a colder body.

That is, due to an irreversible flow of heat.

Carnot now turns to the incompleteness of his cycle of operations 1-3 (which shows that he was well aware of the incompleteness) by adding a final operation to complete the cycle, the operation of heating the water to the temperature of reservoir A by putting it into contact with that reservoir. Figure 3 shows Carnot's operations 1-3 on a p - V diagram. Now the operation Carnot proposed to complete the cycle 1-3 involves an irreversible heat flow, and therefore cannot be used to complete the cycle. Carnot proposes to remove this difficulty by assuming a temperature difference between A and B which is differentially small. From the standpoint of modern thermodynamics, this proposal has a problem. It can be readily seen that the efficiency of such a differential cycle, now treated as a Carnot cycle, would be zero. This follows from equation (4) when the difference $T_1 - T_2$ is differentially small. So this proposal would yield no motive work per cycle. Carnot did not deal with this problem. Instead, he assumed his theorem true for an infinitesimal cycle; that is, he ignored that for a differential cycle the work is zero, and proceeded to use an infinity of differential cycles between the two finite temperatures A and B in order to argue that he had proven his theorem for a finite temperature difference between the reservoirs[†].

Carnot brilliantly evaded the criticism of having using an irreversible heat transfer by using an infinite series of reservoirs. *This is standard modern practice in discussing a reversible process in which the temperature of the working substance changes by a finite amount—a 'tour de force' indicating how very modern Carnot was in his approach.* He said [4, pp 14-15]:

In fact, if it operated to produce motive power by the passage of caloric from the body A to the body Z, the temperature of this latter body being very different from that of the former, we should imagine a series of bodies B, C, D, . . . of temperatures intermediate between those of the bodies A, Z, and selected so that the differences from A to B, from B to C, etc, may all be indefinitely small. The caloric coming from A would not arrive at Z till after it had passed through the bodies B, C, D, etc, and

[†] The word 'd'ailleurs' in the French original was improperly translated as 'elsewhere' by Thurston in his statement that 'The proposition found elsewhere demonstrated for the case in which the difference between the temperatures of the two bodies is indefinitely small, may be easily extended to the general case' [4, p 14], and was never corrected in subsequent reprints of Thurston's translation. It should be translated as 'thus' or an equivalent word. Thurston's error was, however, corrected in Fox's translation, which reads 'The proof we have just developed on the assumption that the difference between the temperatures of the bodies A and B is infinitesimally small can easily be extended to the general case' [6, p 72].

after having developed in each of these stages maximum motive power. The inverse operations would here be entirely possible, and the reasoning of page 11 would be strictly applicable.

Now, it is true that adding up an infinity of differential cycles, each of which does zero work, would yield a finite cycle which does work. For example, we have closed Carnot's open cycle in figure 3 by an isovolumic heating of the water from the temperature of reservoir B to that of reservoir A. This proposed closing operation is shown as process 4 on the diagram. Although process 4 is a reversible process, so that Carnot's steam cycle now consists of all reversible processes, this cycle is not a cycle between only two reservoirs. We now have reservoirs A and B, and an infinite series of reservoirs between A and B for the isovolumic heating of process 4. Carnot's conclusion that his theorem is proven does not therefore follow and one has to await his more rigorous proof using air for a correct proof of his theorem.

6. Comparison of the motive power of heat with the motive power of a waterfall

Carnot draws an interesting analogy between the motive power of water and the motive power of heat [4, p 15]:

The motive power of a waterfall depends on its height and on the quantity of the liquid; the motive power 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.

It is of great interest to look at this statement retrospectively. We *now* know that the work of a heat engine is the difference between the heat extracted from the hot-temperature reservoir and that rejected to the cold; that is,

$$W = Q_1 - Q_2 = Q_1 \left(1 - \frac{Q_2}{Q_1}\right). \quad (5)$$

We also now know that

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}. \quad (3)$$

Substitution of (3) into (5) yields

$$W = Q_1 \left(1 - \frac{T_2}{T_1}\right) = Q_1 \left(\frac{T_1 - T_2}{T_1}\right). \quad (6)$$

Equation (5) depends on conservation of energy and equation (3) depends on the definition of the absolute thermometric scale. Both of these developments occurred after the publication of Carnot's *Réflexions*; indeed both occurred after Carnot's death. Carnot believed at the time of the writing of the *Réflexions* that $Q_1 = Q_2$ (caloric theory of heat). In spite of this Carnot asserted in the *Réflexions*, as we have just seen [4, p 15], that 'the motive power of heat depends also on the quantity of caloric used, and on ... the difference of temperature of the bodies between which the exchange of caloric is made'. In other words, Carnot stated that

$$W \propto Q_1(T_1 - T_2). \quad (7)$$

Is this not amazing when compared to equation (6) which depends on developments after Carnot's death?

More amazing still is the question which Carnot proposes at this point for later resolution [4, p 15]:

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 cold bodies; but we do not know whether it is proportional to this difference ... It is a question which we propose to examine hereafter.

The later resolution of this question, as we shall see, is that ‘the fall of caloric produces more motive power at inferior than at superior temperatures’ [4, p 36]. One way to introduce this resolution of Carnot’s question into proportionality (7) is to write the proportionality as

$$W \propto Q_1 \left(\frac{T_1 - T_2}{T_1} \right). \quad (8)$$

It can be argued that proportionality (8) was prophetically foreseen by Carnot at the time he wrote the *Réflexions*.

7. Second demonstration of Carnot’s theorem that the maximum work is independent of the working substance

Carnot now gives a second demonstration of his fundamental theorem. This demonstration is rigorous and the problems previously discussed about closing the cycle for Carnot’s first demonstration do not flaw his second demonstration. For the second demonstration Carnot takes a gas, such as air, through a cycle. The high-temperature reservoir is A and the low-temperature reservoir is B. Transfers of caloric† take place between the gas confined by the piston and cylinder and the reservoirs by using a diathermic wall. Carnot’s cycle consists of two isotherms at the temperatures of A and B, and two connecting processes. The cycle is shown on a p - V diagram in figure 4. These diagrams were introduced by Émile Clapeyron in 1834 (see his paper reprinted in [4, pp 71–105]).

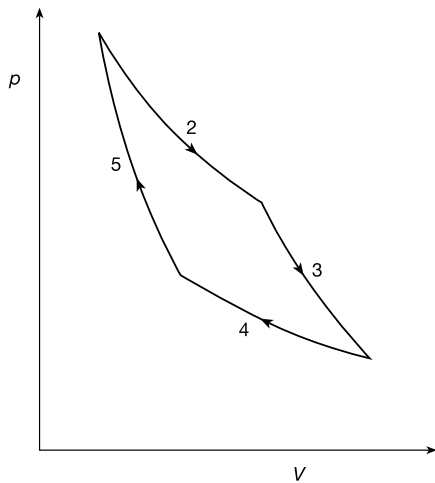


Figure 4. Carnot’s cycle shown on a p - V diagram.

We call special attention to processes 3 and 5. According to Carnot’s description, the air in the cylinder during these processes is thermally isolated and hence the processes are ‘adiabatic’ in modern terminology. It is of great interest that Carnot only used isotherms and adiabatics in his cycle. These are the limiting processes of thermodynamics, the one involving maximal heat transfer and the other involving zero heat transfer. Since the cycle is reversible, any reversible process other than isotherms and adiabatics would involve the description of the process by means of an infinite number of reservoirs between the starting temperature of the process and the final temperature of the process. This is a much more complex idea and Carnot sought simplicity rather than complexity.

† It is of interest to note that Mendoza here introduces a footnote, not present in Carnot’s original text, which says that ‘caloric’ may be taken to mean ‘entropy’ [4, p 17]. This is Mendoza’s interpretation (the same as La Mer’s in [7]), which we think is incorrect.

Carnot then tells us that his cycle has produced work; that is, it is a heat-engine cycle. Carnot further says of his cycle that the air has been [4, p 18]

employed in the most advantageous manner possible, for no useless re-establishment of equilibrium has been effected in the caloric.

Thus, he is telling us that all the processes in his cycle are reversible processes. In fact, his very next sentence is:

All of the above-described operations may be executed in an inverse sense and order.

After this Carnot establishes his theorem by the same method as he used in his first (non-rigorous) demonstration using the steam cycle. He imagines a more efficient engine, and combines it with a Carnot refrigerator. This combination would produce work with no other changes, which is impossible. Therefore the assumption of a more efficient cycle is impossible and Carnot once again asserts his theorem [4, p 20]:

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.

8. Carnot as the founder of thermodynamics

In this paper we have avoided any discussion of Carnot's work on the mechanical equivalent of heat. There can be no doubt that Carnot, after the writing of the *Réflexions*, abandoned the caloric theory of heat in favour of the mechanical theory of heat, and even made a correct approximate calculation of the heat equivalent of mechanical work. His brother Hippolyte, in the letter to the French Academy of Sciences, argued that Carnot should be considered the founder of thermodynamics because his *Réflexions* contained the essential theoretical basis for the Second Law of Thermodynamics, and the posthumous *Notes* transmitted by Hippolyte to the Academy in 1878 showed that he had come upon a correct appreciation of the First Law of Thermodynamics before there was a general agreement on this law by the scientific community.

We agree with Hippolyte on his first point about the Second Law but we must disagree with him on his second point about the First Law. Priority in time is not decisive unless there is public notice of that time priority, usually by means of publication. Carnot's *Notes* [2, 3] showing his rejection of the caloric theory and the statement of the mechanical equivalent of heat as 1 *dynamie* = 2.70 units of heat (i.e. 1 cal = 3.63 J, compared with the modern value of 1 cal = 4.187 J)† were first deposited in 1878 as noted above, and therefore had no influence on the development of thermodynamics, since the caloric theory had been decisively rejected and an accurate determination of the mechanical equivalent made before that date.

The historical significance of Carnot's work lies in his pathbreaking work on the concepts of the Second Law of Thermodynamics in the *Réflexions*. He saw the heat engine as a device operating in a cycle between two heat reservoirs. He correctly proved that it was impossible for any engine operating in a cycle between two given reservoirs to be more efficient than his theoretical Carnot engine operating in a cycle between those same reservoirs. He understood the importance of reversible heat transfers. He correctly told us that the efficiency of a Carnot engine with a fixed temperature difference between reservoirs would increase as the

† We remark that the value given by Mendoza for Carnot's determination of the mechanical equivalent of heat is not exactly correct. Mendoza gave this in a footnote as 3.7 J cal⁻¹ [4, p 68]. His translation of Carnot on this point is exact, the slight glitch undoubtedly occurred in his conversion of Carnot's number into modern terms. Carnot had said in his posthumously published *Notes* that a unit of motive power equalled 2.70 units of heat. The unit of motive power in Carnot's time was the 'dynamie', as mentioned by his brother Hippolyte in the 1878 letter to the Academy. The *dynamie* was the work to raise a 1 m³ of water to a height of 1 m. Since a 1 m³ of water has a mass of 1000 kg, and a weight of 9800 N, the dynamie is equal to 9800 J. The heat unit mentioned by Carnot was the kilocalorie. Thus, Carnot's mechanical equivalent as given in his *Notes* was that 2.7 kcal equalled 9800 J, or that the mechanical equivalent of heat was 3.63 J cal⁻¹, not the 3.7 J cal⁻¹ given by Mendoza.

temperature of the reservoirs was lowered. For all this pathbreaking work on the Second Law, Sadi Carnot does indeed deserve the title of ‘Founder of the Second Law of Thermodynamics’. We also note the evaluation of Robert Fox, who wrote rather recently that ‘the publication of the *Reflexions* marked the beginning of classical thermodynamics’ [6, p 1, note 2].

References

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