WHAT CARNOT'S FATHER TAUGHT HIS SON ABOUT THERMODYNAMICS

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Many traits and prejudices are brought down from generation to generation. The story of the development of the second law of Thermodynamics arguably started with a publication by a young man of a manuscript where the behavior of the recently appearing power-producing machines of his time was analyzed in a rational way. Thermodynamics, understood in its initial denotation as the study of the machines that produce mechanical power from heat, was spawning and was in dire need of a theoretical foundation to support it. This young man, Sadi Carnot, would eventually be considered one of the forefathers of modern thermodynamics, and its second law, one of the cornerstones of modern science. All of this, however, did not start from a clean slate....

At the start of the 18th century, waterwheels were well-established engines and a reliable source of mechanical energy; even today we have working examples of these machines, some modern versions powering the large hydroelectric plants in the world. Research[1] on waterwheels was mature in this age, the work of John Smeaton[2] stands out as an example of the comprehensive studies of the time, where detailed measurements of the different waterwheel configurations were compared among themselves, which led to conclusions with respect to the efficiencies[3] of water wheels. The concept behind a waterwheel is fairly simple and some of the empirical design features were described by Lazare Carnot, an illustrious and conflictive soldier, politician, and engineer, in his first work *Essai sur les machines en général*.[4] This book is based on the premise that all engines may be described by the same general equilibrium principles and that there are commonalities that may be englobed in some general rules. Lazare Carnot ignored "heat" engines in his essay, maybe not on purpose, but possibly out of the novelty and sheer rarity of such engines in 18th century France. Lazare Carnot's work is today largely forgotten. Speaking of waterwheels, and expressed in today's language, he was convinced that in the ideal waterwheel none of the energy would be lost (or dissipated), and the system could be made reversible if one were to actuate the waterwheel (inputting work) to raise water. His analysis is, by today's standards, accurate.

Further into the Napoleonic era, there was a generalized interest in understanding of the workings of the newer steam engines, which were beginning to appear in Europe promising an apparently inexhaustible source of mechanical power. In neighboring Britain, an effective alternative to natural (wind

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and hydraulic) and beast power was being explored. Steam engines were being built, although it is fair to say that there was little more than empiricism driving their development. Steam engines appeared to have an enormous potential in terms of the scalability along with the sheer availability and portability of their mechanical power output. The massive steam engines, now in display in museums,[5] were the size of small houses and of impressive outputs (for the time). In a now famous letter[6] from Matthew Boulton, (arguably the entrepreneur behind the rise of the steam era in Britain), to James Watt, (his partner in business and the engineer behind the successful steam engine-based machines), Boulton is quoted saying, *"The people in London, Manchester, and Birmingham ... are steam mill mad. I don't mean to hurry you...,"* in an effort to make Watt aware of the immense capabilities and opportunities that his inventions were opening. The world was about to change rapidly and that story is well known.

Like father-like son, Sadi Carnot—the son of Lazare Carnot—was trained as a military engineer and also as a scholar. Following his father's footsteps, it was now the son's turn to write, and he chose to take on where his father left off, attempting to understand and describe the workings of these new steam engines being brought from Britain to France. I am convinced that Sadi took on his father's ideas and independently extrapolated them to these new machines that made power from a different source of flow: heat flow. It is a remarkable stroke of luck that the simple concepts behind a water wheel could be applied to a heat engine almost directly. Few recognize that the second law, as derived from Sadi Carnot's comments, was actually stated with the assumption that heat could be treated as water flowing from a height. An excerpt from Sadi Carnot's only book[7] reads remarkably similar to what his father must have taught him:

> *"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.... 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 ... the difference of temperatures of the bodies between which the exchange of [caloric] is made."*

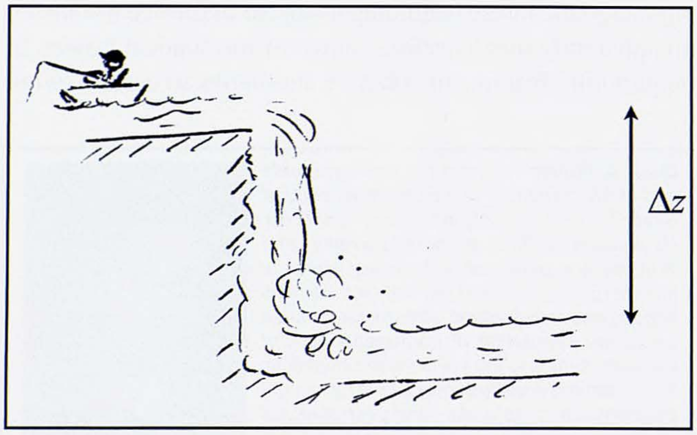

Figure 1. *A waterfall is described mainly by the height (Δz) of the fall.*

As usual with great discoveries, Sadi Carnot's ideas were not truly understood at his time and *Réflexions* was not immediately accepted by his peers.[8] The very unorthodox point of view and the implicit waterwheel analogy was most likely seen as implausible or irrelevant. The lack of enthusiasm of his peers was probably even a reflection of Carnot's own disbelief on his own ideas.[9, 10] Only posthumously (Carnot died of cholera when he was 36 years old) was the book noticed and brought to the attention of the scientists of the time. From a naïve point of view of an operator it would seem rather obvious that the performance of a steam engine would depend on the pressure of the steam rather than on its temperature. Although certainly pressure was the driving force of the pistons and moving parts, one needed to take a step back and look at the whole picture to understand that there were more overbearing principles to be sought. Sadi had made, by comparing his machines to the behavior of more classical mechanical engines, a link between the water height in a mechanical device to the temperature in a thermal device and the fact that power was done by the transfer of a "substance."

> *"The production of motive power is then due in steam engines not to an actual consumption of [caloric], but to its transportation from a warm body to a cold body...."*[7]

One must envisage the context in which the book was published: Thermodynamics[11] did not exist as a science, and the principle of conservation of energy (the first law of thermodynamics) was to be only formulated decades later. The prevailing theory of the time was centered around "caloric," a massless substance that could flow through physical boundaries and was presumably responsible for changes in temperature.[12] This, his main and key result, was also probably the principal reason for the initial demise of Sadi's theory. If the caloric theory was wrong, it would then follow that Sadi Carnot's theories would also have to be wrong. Only in hindsight can we see the clear correctness of some of the ideas in *Réflexions*. Sadi made no direct practical recommendations but expressed overall relationships that, placed in the proper context some 50 years later, would form the basis of today's thermodynamic theories. Excellent accounts of the historical developments with the link to modern nomenclature and concepts can be found in many places, notably the book by I. Müller[13] and the paper by M.J. Klein.[14]

The simplicity and clarity of some of Carnot's arguments can be used today to enlighten the study of classical Thermodynamics. Of course, now we benefit from the accumulated knowledge base and the fact that energy, as a concept, is understood colloquially and needs no further introduction. The first law and the interconversion of different forms of energy is a well-established principle, taught in most instances at high school level. This paper focuses on looking back and revisiting the hydraulic analogy with the aim of using it as an introduction to the description of a classical view of the second law of Thermodynamics.

THERMODYNAMIC ANALYSIS OF A WATERWHEEL

A modern pedagogical account of the efficiency of waterwheels has been presented by Denny.[15] Here, a simpler analysis will be drawn.[16] Consider the case of a waterfall as in Figure 1. Let us take as our control volume the waterfall plus the upstream and downstream sections of the river (leaving the fisherman out of the problem for the time being, although he is the only one with a problem). Since this is a steady state system, with no accumulation of either mass or energy, from the application of the first law one can write a rate-based version of the first law[17]

$$\dot{Q}+\dot{W}+\dot{m}\left(h+\frac{1}{2}vel^2+gz\right)_{upstream}-\dot{m}\left(h+\frac{1}{2}vel^2+gz\right)_{downstream}=0 \quad (1)$$

where $\dot{Q}$ and $\dot{W}$ refer to the rates of heat and work, $\dot{m}$ refers to the flow rate of water and the terms in parenthesis represent the intensive (enthalpy,[18] kinetic, and potential, respectively) contributions to the energy of the currents coming in and out of the control volume. If the river has a similar width and depth before and after the fall, the incompressible nature of the fluid will suggest that the average velocity, vel, of the water will be similar, thus the change in kinetic energy between the upstream and downstream of the river will be undetectable. One can further consider the fluid to be incompressible and isothermal, thus the enthalpy of the water will remain constant. Finally, since there is no work output, then the first law expression [Eq. (1)] simplifies to[19]

$$\dot{Q}=-\dot{m}g\left(z_{upstream}-z_{downstream}\right)=-\dot{m}g\Delta z \quad (2)$$

where g is the acceleration of gravity and z corresponds to a height. In other words, the change in potential energy [the right hand side

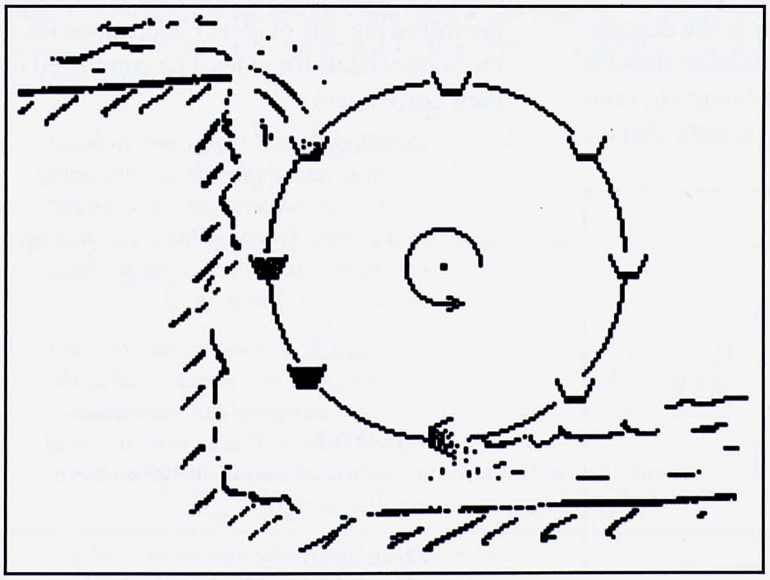

Figure 2. *A waterwheel may be placed at the mouth of the waterfall to extract mechanical work.[21]*

Like father-like son, Sadi Carnot—the son of Lazare Carnot—was trained as a military engineer and also as a scholar.

of Eq. (2)] is dissipated in the form of heat to the environment.[20] (Figure 2, Reference 21.)

It is interesting to note that nothing in these equations stops us from considering the inverse process, *i.e.*, a jump in water by extracting heat from the surroundings (and saving the fisherman). We see how it is our intuition[22] only that will suggest that water is displaced from top to bottom but it will not spontaneously travel upstream, surmounting the fall. The immediacy of the irreversible nature of the waterfall is apparent and with it the conclusion that there must be another physical law in action that has not been accounted for. The reason and need for a second law of thermodynamics is now very clear. When placing a waterwheel at the mouth of the waterfall (see Figure 2), we manage to extract work from the process. Making the same simplifications and assumptions as in the case of the free fall, but dismissing the heat losses to the ambient, application of the first law reveals that

$$\dot{W}=-\dot{m}g\left(z_{upstream}-z_{downstream}\right)=-\dot{m}g\Delta z\ . \quad (3)$$

Note that, of course, this is same amount of energy that the wheel-less fall dissipated in the form of a heat loss, which is now converted to work. This new process is intuitively reversible, suggesting that the energy is being converted efficiently.

It is the application of an entropy balance (*i.e.*, a second law analysis) that provides a further clue to interpreting the situation. An entropy balance on the river (with or without the waterwheel) provides the following information

$$\frac{\dot{Q}}{T}+\left(\dot{m}s\right)_{upstream}-\left(\dot{m}s\right)_{downstream}+\dot{\sigma}_{generated}=0 \quad (4)$$

where the right-hand side of the equation is zero since a steady state is considered. The term $\dot{\sigma}_{generated}$ is the rate of entropy generation in the system, which according to the second law must be either positive or, in the best case (of a reversible process), null. Using again an incompressible fluid model for water (*i.e.*, a constant heat capacity, C) the change in entropy between the upstream and downstream is a thermodynamic state quantity,[23] dependent only on temperature and seen to be null if the system remains isothermal,

$$\left(s_{upstream} - s_{downstream}\right) = \int \frac{\delta Q_{rev}}{T} = \int \frac{dh}{T} = \int \frac{CdT}{T} = C\ln\left(\frac{T_{upstream}}{T_{downstream}}\right) = 0 \ . \qquad (5)$$

Thus, substituting this result in Eq. (4), the entropy generated by the process for the system without a waterwheel is,

$$\dot{\sigma}_{generated} = -\frac{\dot{Q}}{T} \ . \qquad (6)$$

Including the first law expression, Eq. (2) for the system without a waterwheel, one obtains,

$$\dot{\sigma}_{generated} = \frac{\dot{m}g\left(z_{upstream} - z_{downstream}\right)}{T} = a\Delta z \qquad (7)$$

where a= $\dot{m}$g/T is a positive quantity. Note the natural behavior (water falling down) implies a positive generation of entropy. In the awkward case where we consider the water to flow in "countercurrent," or upstream, the entropy generated will be negative and the process impossible both from the second law expression and from common sense. If we place a waterwheel the heat dissipation term in Eq. (6) is zero, [since now the change in potential energy is converted into work and no heat is dissipated to the surroundings; c.f. Eq. (3)] and the corollary from Eq. (6) is that the generation of entropy is null. The result tells us that the use of a waterwheel makes the energy conversion process efficient (we obtain work!) and that the process is reversible (there is no entropy generation). In particular it is the best scenario, *i.e.*, the maximum work is attainable. We see how accounting for the entropy generation can provide a handle on the determination of the reversible, irreversible, or impossible nature of a process.[24] It is of course possible to recognize and thus include in the above analysis scenarios where the entropy generated is between 0 and that of Eq. (7), *e.g.*, a situation where there is both work produced and energy dissipation in the form of friction or heat losses. Alternatively, one can flip the problem around and specify the entropy generated and from it calculate the relative amount of work (in fact one could end up requiring to input work into the system).

The above exercise highlights the importance of including the second law in any engineering analysis and the need for considering entropy in the description of any physical process. The example is intuitive, as many science students will understand the basic idea behind a waterwheel, while being rigorous enough to be presented with no unwanted assumptions. It does assume that the students have been exposed, at least initially, to working versions of the second law (or entropy balances). This is sometimes done in textbooks by stating, as an imposition, the existence of a property called entropy and performing the appropriate balances, to later justify it and/or argue its correctness. The waterwheel analogy is a simple exercise that can give "peace of mind" to the inquisitive souls who do not wish scientific dogmas and expect only proofs.

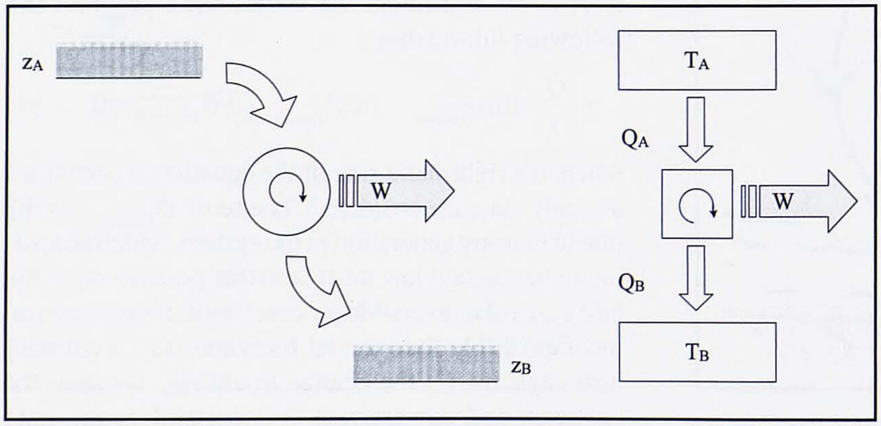

Figure 3. *Waterwheel (left) and heat engine (right) diagrams.*

THE HEAT ENGINE ANALOGY

Another avenue in the teaching of the second law is to attempt to "derive" from intuitive observations the relationship between entropy and the ratio of heat and temperature. To this end, most classical thermodynamics textbooks[25] will use, as their starting point, the description of a heat engine (see Figure 3, right) and discuss how certain types of these heat engines are commonplace and others are not. For example, according to these textbooks, it should be obvious to the readers that a heat engine that produces work continually from a unique source of heat is unbuildable (*i.e.*, consider Figure 3, right, with Q_B = zero). This is far from being intuitive and is a very poor starting point for any discussion, except maybe in the case of more experienced readers.

If instead we use the analogy between the hydraulic system and thermal system we may have a very useful starting point in the teaching of the second law. One can extract the following self-evident conclusions from the waterwheels (or at least be convinced of their correctness):[26]

> <u>Postulate 1:</u> *It is impossible to build a waterwheel that without consuming work raises water from a low height to a greater height. (This is a common experience, as we know water "falls" but does not "jump up.")*
>
> <u>Postulate 2:</u> *It is impossible to build a waterwheel that converts all of the potential energy of the river water to work. (There will always be water at a lower level that would have energy equal to mgz_B).*[27]
>
> <u>Postulate 3:</u> *The maximum work is obtained by an ideal waterwheel,* i.e., *one where no energy is lost by dissipation, friction, etc. This ideal*

machine has to be reversible. (This idea, although maybe not self-evident, is certainly unchallengeable.)

Postulate 4: *Regardless of the way we design the waterwheel, the maximum amount of work extractable depends exclusively on the difference in the height of the water streams. [c.f. Eq. (3), where no preconception is made on the nature of the mechanical device used to produce power.]*

An experienced lecturer will immediately recognize in these simple statements the analogue of the Clausius (postulate 1) and Kelvin-Planck (postulate 2), statements of the second law, and the two Carnot corollaries (postulates 3 and 4) as enunciated in most classical thermodynamics books[28] if only one exchanges "waterwheel" for "heat engine"; "raises water" to "transfers heat"; and so forth, as per the recipe in Table 1. Also, the translation from the waterwheel to the standard heat engine diagram (Figure 3) is seamless.

The analogy can be pushed further if one is to introduce the concept of efficiency, η. In engineering terms, efficiency is the ratio of the desired outcome divided by the cost of producing such effect (or the "costly" input).[29]

$$\eta = \frac{\text{desired outcome}}{\text{costly input}} \tag{8}$$

In the case of a waterwheel, the desired outcome is power at the expense of using water from a high altitude, so the efficiency could be expressed as

$$\eta = \frac{|\dot{W}|}{\dot{m}gz_{\text{upstream}}} = \frac{\dot{m}g\left(z_{\text{upstream}} - z_{\text{downstream}}\right)}{\dot{m}gz_{\text{upstream}}} = 1 - \frac{z_{\text{downstream}}}{z_{\text{upstream}}}, \tag{9}$$

where Eq. (3) is used to convert the power into the height difference. Using the analogy (Table 1), the efficiency of a heat engine should be, from Eq. (9)

$$\eta = 1 - \frac{T_B}{T_A}, \tag{10}$$

which is the expected result, rightfully known as the "Carnot efficiency." This can be compared to the original definition of the thermal efficiency;

$$\eta = \frac{|\dot{W}|}{|\dot{Q}_A|} = \frac{|\dot{Q}_A - \dot{Q}_B|}{|\dot{Q}_A|} = 1 - \frac{|\dot{Q}_B|}{|\dot{Q}_A|}. \tag{11}$$

Thus, by inspection of Eq. (10) and (11) one arrives trivially to the Kelvin relation,

$$\frac{|\dot{Q}_A|}{T_A} = \frac{|\dot{Q}_B|}{T_B}, \tag{12}$$

TABLE 1
Analogous Terms in Waterwheels and Heat Engines

Hydraulic system		Thermal system
waterwheel	~	heat engine
z	~	T
Source of water at z	~	Reservoir at T
Fall of water	~	Heat flux

which is the classical starting point for defining entropy as a state function.

As an ending note, it is fair to say that the above rendition of the Carnot description of waterwheels is by no means unique. In a recent paper,[30] Newburgh has developed a modern reinterpretation of Carnot's results and shown in a very detailed way how the "flow of caloric" can be reconciled and restated in terms of modern variables. Erlichson[31] presents the Carnot waterwheel results in terms of modern nomenclature. Thoma[32] has presented other analogies, including a circuit-based analogy.

COROLLARY

Nowadays no science student has any problem grasping the concept of energy. Curiously, it would be quite a difficult concept to explain, had it not been introduced by colloquial usage from an early stage. No student thinks of energy as something "with matter" and the risk of improperly employing the waterwheel analogy is minimal. In spite of this, it is important to make it clear that the analogy proposed is actually a "crutch" that allows the understanding of the concepts of efficiency and entropy generation, and it should not be taken at face value. All simplifications and generalizations inevitably can be abused. Even the commonplace rendition of entropy as the disorder of a system can be terribly misleading.[33]

It is important to note that the analysis of these concepts does not parallel the historical developments, but rather stems from the modern analysis of those ideas.[34] Carnot was not aware of the nature of energy nor the fact that heat and work are mere manifestations of energy transfer and its conversion. He did, however, recognize the waterwheel analogy and expressed it in the terms of the folklore of those days. Only after the acceptance of the concept of energy, mainly by the widespread disclosure of the works of Mayer and Joule, could the world start to relate the concepts of energy and temperature in a consistent way. The synthesis of modern classical thermodynamics, and the coinage of the word entropy, was later to be performed by Clausius, almost 40 years after Carnot's book.

ACKNOWLEDGMENT

I dedicate this paper to my father, who taught me all that is important to know.

REFERENCES

1. Note the context of the word "research." Waterwheels are as old as humanity, and actually boomed in Europe during the Middle Ages. They were empirically built, and even during the Carnot era, little was understood on how they could be improved.

2. Smeaton, J., "An experimental enquiry concerning the natural powers of water and wind to turn mills, and other machines, depending on circular motion," *Phil. Trans. Royal Soc.*, **51**, 100 (1759)
3. Efficiency, or first law efficiency as we understand it now in the thermodynamic sense, is the ratio of the desired energy outcome—work, divided by the energy disposed to produce it, c.f. Eq. (8). It is a concept that was only correctly coined a century later, and attributed to William Rankine. However, ad hoc definitions of efficiency were used at the time.
4. Carnot, L.N.M., *Essai sur les machines en général*, Paris (1783)
5. The Science Museum in London is a premier example; see <http://www.sciencemuseum.org.uk/ visitmuseum/galleries/energy_hall.aspx>
6. Smiles, S., *Lives of Boulton and Watt*, John Murray, London, p 293 (1865)
7. Carnot, S., *Réflexions sur la puissance motrice du feu et sur les machines propes a developer cette puissance*, Paris (1824). See the commented translation by E. Mendoza (ed.), *Reflections on the motive power of fire*; Dover, (1988)
8. The book was far from being a best-seller: it was to be sold at 3 Francs (roughly 45 US$ in today's money), but nobody was known to buy it at the time.
9. Cardwell, D.S.L., *From Watt to Clausius: The rise of thermodynamics in the early industrial age*, Cornell University Press, Ithaca, NY (1971)
10. Cardwell, D.S.L., "Science and the steam engine in the early nineteenth century reconsidered," *Tran. Newcomen Soc.*, **49**, 111 (1977)
11. Historically the word "thermodynamics" was coined from the Greek words τερμη (heat) and δυναμς (power) by Lord Kelvin in 1849 and was conceived as the science that would study the link between the production of mechanical power from heat. Today it is understood as the description of the physics of energy and entropy.
12. Fox, R., *The Caloric Theory of Gases*, Clarendon press, Oxford (1971)
13. Müller, I., *A History of Thermodynamics*, Springer, pp 59-71 (2007)
14. Klein, M.J., "Carnot's contribution to thermodnamics," *Phys. Today,* **27**, 23(1974)
15. Denny, M., "The efficiency of overshot and undershot waterwheels," *Eur. J. Phys.*, **25**, 193, (2004)
16. Müller, E.A., *Termodinámica Básica*, 2nd Ed., Kemiteknik (2002)
17. The energy and entropy equations are written here in terms of rate equations, as is preferred for open systems. The reader is referred to standard textbooks for a comprehensive treatment, *e.g.*, J.R. Elliott and C.T. Lira, *Introductory Chemical Engineering Thermodynamics*, Prentice Hall (1999) and/or S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th ed., Wiley (2006)
18. The enthalpy, h, is the sum of the internal energy, u, plus the flow term, pv.
19. The negative sign of Q is a consequence of an arbitrary sign convention that assigns the addition of energy to a system a positive value. Most engineering books will have an opposite convention. This, obviously, has no implication on the results.
20. It is reported that while on his honeymoon in the Alps, James Joule actually tried unsuccessfully to measure a temperature difference between the upper and lower parts of the Sallanches waterfall. Heat was to be found somewhere else.
21. This is a most absurd waterwheel, and just an artist's rendition.
22. Actually it is our experience that suggests the apparent impossibility of the event. The second law of Thermodynamics can be alternatively and equivalently formulated from the point of statistical mechanics, as worked out by Ludwig Boltzmann. From this point of view the inverse process is understood as a "highly improbable" event.
23. Entropy is a state function defined as the integral of the ratio of heat to temperature along a reversible path. The path does not have to be real; here we consider an isobaric path, where the heat is equal to the enthalpy change.
24. A negative, null, or positive generation implies an impossible, reversible, or irreversible process, respectively.
25. I will avoid being rude and pointing out particular authors, but I believe this to be a general statement.
26. As a class exercise, groups of students could be "coached" into developing these laws by themselves.
27. Here, as in the case of temperature, one must establish an absolute origin from where to measure heights. In the case of the gravitational potential energy, we could establish this (unattainable) limit $z = 0$ as being the center of the Earth.
28. See for example classical engineering textbooks as M.J. Moran and H.N. Shapiro, *Fundamentals of Engineering Thermodynamics*, 5th Ed., Wiley (2006) and/or C. Borgnakke and R.E. Sonntag, *Fundamentals of Thermodynamics*, 7th Ed., Wiley (2009)
29. For example, the efficiency of a student may be quantitatively measured as the ratio of the marks in their exam divided by the number of study hours.
30. Newburgh, R., "Carnot to Clausius: caloric to entropy," *Eur. J. Phys.*, **30**, 713 (2009)
31. Erlichson, H., "Sadi Carnot, Founder of the second law of thermodynamics," *Eur. J. Phys.*, **20**, 183 (1999)
32. Thoma, J., private communication, see <http://www.jthoma.ch/>
33. Lambert, F.L., "Disorder—a cracked crutch for supporting entropy discussions," *J. Chem. Ed.*, **79**, 187 (2002)
34. See the excellent paper by S.I. Sandler and L.V. Woodcock, "Historical observations on laws of thermodynamics," *J. Chem. Eng. Data*, **55**, 4485 (2010) ❒