On "Some Current Misinterpretations of Carnot's Memoir"

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(Received April 5, 1954)

Although Carnot's contributions to thermodynamics have been universally recognized, it is usually with the reservation that there were serious gaps in his proof. Careful study of his memoir shows that Carnot implicitly defined heat so as to make it equivalent to entropy. With this interpretation it may be shown that his logic was flawless, that he believed in the kinetic nature of heat, and that his theorems are based on the first and second laws of thermodynamics.

IN a recent article, Victor La Mer[1] presents an able and much needed defense of Sadi Carnot and his famous memoir.[2] I am in full agreement with the view that Carnot has been misinterpreted and consequently underrated. Still, I thought it might not be amiss to point out some of the confusions in the memoir and to show that they do not detract from its fundamental significance nor seriously affect its logical integrity. Otherwise, possible detractors might seize on these and deprecate the whole work.

That Carnot did make important contributions to physics has been universally recognized, but too often with the reservation that he believed in the substantive theory of heat and that, consequently, his proofs were invalid. As a matter of fact, Carnot's theorems follow rigorously from explicitly stated assumptions and his adherence to the kinetic theory of heat is clear and unmistakeable. His treatment of caloric makes it equivalent to entropy[3,4] and might well be used to modify and clarify the modern treatment. Carnot did state a conservation property for heat in circumstances that seemed to make it contradict the conservation of energy, but the contradiction is only apparent.

That Carnot was aware of the first two laws and that he used them implicitly is pointed out by La Mer, and yet in some respects he overstates the case. His statement that Carnot meant to distinguish between "chaleur" and "calorique" does not appear to be justified and the statement that he did not assert $\int dQ=0$ for the cycle needs clarification.

With regard to the first point, Carnot's footnote seems specific; it appears in the reprint of the original memoir, published in 1912. "Nous jugeons inutile d'expliquer ici ce que c'est que quantité de calorique ou quantité de chaleur (car nous employons indifféremment les deux expressions), ni de décrire comment on mesure ces quantités par le calorimètre" (p. 15). The reference to the calorimetric measurement is unmistakeable additional evidence that the two quantities were measured in the same way.

In addition, there are many cases where Carnot clearly uses the two words as synonyms in consecutive sentences; thus, when restating a proposition to clarify it, he frequently substitutes "chaleur" for "calorique" and *vice versa*. Two examples occur in his discussion of the dependence of efficiency of an ideal heat engine on temperature. Carnot says, "La quantité de *chaleur* due au changement de volume d'un gaz est d'autant plus considérable que la température est plus élevée. Ainsi, par exemple, il faut plus de *calorique* pour maintenir à 100° la température d'un certain quantité d'air dont on double le volume, que pour maintenir à 1° la température de ce même air pendant une dilatation absolument pareille" (p. 72). A little further on he states, "La chute de *calorique* produit plus de puissance motrice dans les degrés inférieurs que dans les degrés supérieurs. Ainsi, un quantité donnée de *chaleur* developerra plus de puissance motrice en passant d'un corps maintenu à 1°, à un autre maintenu à 0°, que si ces deux corps eussent possédé les degrés 101° et 100°" (p. 72).

As to the second point, La Mer's statement is correct if Q is taken to mean heat as defined today. However, Carnot did state as a fundamental assumption that the amount of heat

[1] V. K. La Mer, Am. J. Phys. 22, 20 (1954).
[2] Sadi Carnot, *Reflexions sur la Puissance Motrice du Feu* (Libraire Scientifique, A. Hermann & Fils, Paris, 1912). (Reimpression fac-simile conforme à l'edition originale de 1824.) All French quotations are from this source.
[3] H. C. Callendar, Proc. Phys. Soc. (London) 23, 153–189 (1911).
[4] A. C. Lunn, Phys. Rev. 14, 1–19 (1919).

contained in the body is not changed after a complete cycle; this is equivalent to the statement that $\int dQ = 0$, where Q is taken as "chaleur" in the sense that Carnot used it. The footnote reads: "Nous supposons implicitement dans notre démonstration que, lorsqu'un corps a éprouvé des changemens quelconques et qu'aprés un certain nombre de transformations il est ramené indentiquement à son état primitif, c'est-à-dire à cet état considéré relativement à la densité, à la température, au mode d'aggrégation, nous supposerons, dis-je, que ce corps se trouve contenir la même quantité de chaleur qu'il contenait d'abord, ou autrement, que les quantités de chaleur absorbées ou degagées dans ces diverses transformations sont exactement compensées" (p. 37). This statement is true if "chaleur" is interpreted as entropy and seems to imply that Carnot believed in the conservation of entropy in all cycles. However he uses the conservation property only for reversible cycles and this leads to important results.

The proof of his basic theorem illustrates this. It states, "La puissance motrice de la chaleur est indépendante des agens mis en oeuvre pour la réaliser; sa quantité est fixée uniquement par la température des corps entre lesquels se fait en dernier résultat le transport du calorique" (p. 38). ("The motive power of heat is independent of the agents employed to develop it; its quantity is determined solely by the temperatures of the bodies between which, in the final result, the transfer of the caloric occurs."[5]) The proof, which is scattered in several sections, is paraphrased here.

Given, a reversible engine which transfers an amount of caloric from a source at high temperature to a cold reservoir and supplies a certain amount of work. Suppose there were another such engine which utilized the same amount of caloric but produced more work. Then part of this work could be diverted to reverse the first engine, and "pour faire remonter, par la méthode qui vient d'être indiquée, le calorique du corps B au corps A, du réfrigérant au foyer, pour rétablir les choses dans leur état primitif···" (p. 20); that is, to return the caloric from the refrigerator to the hot reservoir and restore things to their original state. The net result would be the creation of work with no consumption of caloric or any other agent. This Carnot regarded as inadmissible and contrary to all the laws of physics. Essential to the proof is that the refrigerator as well as the hot reservoir were restored to their original state. And this followed only if we take Carnot's reference to the transfer of caloric as implying that the amount of caloric taken from the hot reservoir was also the amount of caloric received by the cold reservoir *in both cases*. Without this interpretation the proof is incomplete; with it, the proof is seen to be based on the two axioms, the conservation of energy and the conservation of caloric for reversible processes. In his comment that the motive power of the theorem refers to the maximum developable in each case, Carnot makes it clear that both engines are reversible.

As a matter of fact, the assertion that Carnot believed in the conservation of caloric for reversible processes is the only one consistent with La Mer's central theme, that caloric is really entropy. His statement[6] that "Carnot at least had in mind something like entropy when he spoke of 'chute de calorique'···" is a somewhat overcautious way of formulating the fact that Carnot's usage is actually based on a valid alternative definition of the concept of heat. This was set forth by H. C. Callendar[3] in 1911, and by A. C. Lunn in 1919.[4]

The orthodox view, that heat is (and always was) equivalent to work and that this fact was discovered by Black, Mayer, Joule *et al.*, is a misinterpretation of the logical sequence. Before the 19th century, there was only the intuitive view that heat was something that caused a temperature increase; the job of the scientist was to find out the cause of the temperature rise and this would be identified as heat. Unfortunately, there is no unique physical property or substance that satisfies this requirement; there are, in fact, three which are closely associated with a rise in temperature—what we *now* call heat, internal energy, and entropy—but for none of these is the relationship invariant.

In a situation like this, the physicist has two choices: he may abandon the original term, as was done in replacing quantity of motion with both momentum and kinetic energy; or he may arbitrarily identify the name with one of the

[5] Magie, *The Second Law of Thermodynamics* (Harper & Brothers, New York and London, 1899), p. 20.

[6] See reference 1, p. 26.

closely related concepts. Thus, Black tacitly identified heat with energy when he assumed it was conserved in mixture calorimetry; Joule established the identification and *defined* heat as the equivalent of mechanical work. Carnot, on the other hand, tacitly defined heat as a function of the state of the body which is conserved in reversible processes, thus identifying it with the modern concept of entropy. This procedure is unobjectionable; it is historically and logically fully as justified as Black's. The pertinent questions that may be asked are: (1) was Carnot consistent? and (2) is the definition fruitful?

Carnot was sufficiently consistent to provide an affirmative answer to the second question. After establishing several important properties of gases, he attempted to find the amount of work that can be obtained from a given amount of heat as a function of the temperature difference. In the two statements quoted previously he says that the amount of heat necessary to produce an isothermal change in volume increases with the temperature and deduces that the motive power of heat for a given temperature drop must be lower at higher temperatures. Both of these statements are, as Magie points out,[7] formally true of heat in the modern sense and not of entropy. Magie adds that the deduction is erroneous because of Carnot's use of the substantive theory of heat; however, a careful study of the proof shows that the theory is not involved and the result is a correct deduction from the data available; the conclusion, nevertheless, is incorrect (with caloric meaning entropy) because the experimental data were wrong. The data in question were the measurements of Delaroche and Bérard on the variation of the specific heat of air with density at constant temperature; these data show a small variation of the specific heat due to inadequate methods. Carnot clearly showed that he was suspicious of both the data and the conclusion and goes on to prove that if the specific heat of air is independent of its volume, then the motive power is the same at all temperatures. The proof and the conclusion are correct if the specific heat and motive power are both computed on the basis of entropy rather than heat (in the modern sense). Carnot's final result is equivalent to the statement that if we use the ideal gas temperature scale, then the efficiency of an ideal heat engine (reckoned on the basis of entropy) is strictly proportional to the temperature drop. This is a correct and important conclusion from the second law.

Nevertheless, it is true that Carnot did not carefully distinguish between heat or energy and entropy or, rather, between irreversible and reversible conservation. Thus, the statement in his footnote that it is unnecessary to explain the concepts of heat or caloric and the reference to the method of measurement shows his acceptance of Black's calorimetric definition. Furthermore, in his numerical computation of the work that can be obtained from an air or steam engine, he used the calorie (determined in the calorimeter) as a measure of entropy; he then correctly computes the maximum amount of work that can be obtained per calorie at various temperatures. This involves an implicit knowledge of Joule's constant; the value deduced from Carnot's computation is in error by only 10 percent; this was about 20 years before the principle of equivalence was supposed to have been discovered! That most of Carnot's results were not affected by the confusion was due to the fact that he was concerned exclusively with reversible processes.

That history decided against Carnot's definition can scarcely be considered a condemnation of his viewpoint, since it was made in partial ignorance of his views. The conservation of entropy for reversible processes was finally recognized and given its proper place with no thanks to Carnot. Callendar points out that the development of thermodynamics might well have benefited by the adoption of Carnot's definition. Entropy, as usually introduced, is a highly abstract concept, whereas, according to Carnot's method, it appears naturally as the work available per degree temperature drop.

Despite the subsequent misinterpretations of his conservation axiom, Carnot's immediate successors recognized their debt to him. In their hands his method proved a powerful tool in the development of thermodynamics and for discovering new results both experimental and theoretical. It was the latter-day emphasis on the mechanical definition of heat that put his memoir in the wrong light. Despite the minor errors that remain, the clarification of his views should restore Carnot to his proper position as the founder of modern thermodynamics.

[7] See reference 5, p. 38.