Comment on: "Sadi Carnot on Carnot's theorem".

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Abstract

Carnot established in 1824 that the efficiency η_C of reversible engines operating between a hot bath at absolute temperature T_{hot} and a cold bath at temperature T_{cold} is equal to $1-T_{cold}/T_{hot}$. Carnot particularly considered air as a working fluid and small bath-temperature differences. Plugging into Carnot's expression modern experimental values, exact agreement with modern Thermodynamics is found. However, in a recently published paper ["Sadi Carnot on Carnot's theorem", *Am. J. Phys.* **70**(1), 42–47, 2002], Güémez and others consider a "modified cycle" involving two isobars that they mistakenly attribute to Carnot. They calculate an efficiency considerably lower than η_C and suggest that Carnot made compensating errors. Our contention is that the Carnot theory is, to the contrary, perfectly accurate.

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1 Comment

Carnot established in 1824 [1] that the efficiency η_C of reversible engines operating between a hot bath at absolute temperature T_{hot} and a cold bath at temperature T_{cold} is equal to $1 - T_{cold}/T_{hot}$. He particularly considered air as a working fluid and small bath-temperature differences. If one plugs into Carnot's expression modern experimental values one finds exact agreement with the above formula. A recently published paper by Güémez and others [2] is useful in attracting attention to the early work on thermodynamics by Carnot. However, the "modified Carnot cycle" that they consider, involving two isobars, is not the one treated by Carnot. They calculate a considerably lower efficiency and suggest that Carnot made conceptual errors and employed incorrect data, the agreement being achieved by coincidence only. To the contrary, our contention is that the Carnot theory is perfectly accurate, and that his numerical estimates are fairly good. A related discussion was given in 1975 by Hoyer [3].

In his book "Réflexions sur la puissance motrice du feu", published in 1824, Carnot [1] presents calculations on the "motive power" of heat engines, defined as "the useful effect that an engine is capable of producing. The effect can always be expressed in terms of a weight being raised to a certain height. It is measured by the product of the weight and the height to which the weight is considered to have to be raised". Specifically, Carnot employed as the mechanical energy unit the energy required to lift a cubic meter of water by one meter in the earth gravitational field, that is, 9.81 kJ. As far as heat consumption is concerned, Carnot employed as a unit the heat required to raise one kilogram of water from 0 to 1°C (say, at constant pressure). Thus, the Carnot unit for heat is equal to 4.18 kJ.

Carnot [1, p. 80] considers an ideal heat engine whose working agent is a cylinder containing 1 kg of air initially at atmospheric pressure p=10.4 meters of water. The cold bath temperature is T_{cold}=0°C while the hot bath temperature T_{hot}=1°C [1]. Let us postpone physical explanations and consider the values of the work W performed per cycle and the hot-bath

[1] Initially, Carnot considered a hot-bath temperature of 0.001 °C, but later on switched to 1°C.

heat consumption Q as given in Carnot's book:

$$W = \Delta V \Delta p \qquad \Delta V = (\frac{1}{116} + \frac{1}{267})\, 0.77 \qquad \Delta p = \frac{10.4}{267}$$
$$Q = 0.267 \Longrightarrow \frac{W}{Q} = 0.00138 \text{ Carnot units.} \tag{1}$$

If we introduce into the above Carnot formula recent experimental values and convert heat into energy, we have instead

$$W = (\frac{1}{109.3} + \frac{1}{273.15})\, 0.773\, \frac{10.34}{273.15}$$
$$Q = 0.240 \Longrightarrow \eta = \frac{W}{Q}\frac{9.81}{4.18} = 0.00367. \tag{2}$$

in nearly exact agreement with the Carnot efficiency $\eta_C = 1 - T_{cold}/T_{hot} \approx 1/273.15 = 0.00366$.

The reasoning that led Carnot to the expression in (1) is sound. Figure 1 shows the reversible cycle 1-2-3-4-1 considered by Carnot in the pressure-volume diagram. The vertical axis corresponds to the change of pressure in the air-filled cylinder with respect to atmospheric pressure p_0, while the horizontal axis corresponds to the change in cylinder volume with respect to the volume at atmospheric pressure and $T = 0°$C, namely $V_0 = 0.773$ cubic meters. Because the relative changes of temperature and volume are small the cycle is a parallelogram. For obvious geometrical reasons the work performed per cycle, that is, the area enclosed in the parallelogram, is: $W = \Delta p\ \Delta V$, where Δp and ΔV are shown in the figure. This is also the area enclosed in the rectangular path shown in the figure. Let us emphasize, however, that this path is *not* the cycle considered by Carnot.

Δp is the change of pressure required to increase the temperature of 1 kg of air from 0 to 1°C, the volume being kept constant (path 4-4′). This quantity had been measured at Carnot's time by Gay-Lussac. The recent value is $\Delta p = p_0/273.15$, where $p_0 = 10.34$ meters of water. Carnot introduced the ratio γ of air specific heats at constant pressure and constant volume, which is also the ratio of the isothermal and isentropic compressibilities (see, for example, [4, p. 272]). According to the figure, the ratio of the slopes of the isotherms and adiabats is $\gamma = (1/109.3 + 1/273.15)/(1/109.3) = 1.400 = 7/5$. This is indeed the ratio of constant-pressure to constant-volume heat capacities of di-atomic molecules such as those comprising air (oxygen and nitrogen) in the temperature range considered. A slightly larger value of γ was used by Carnot on the basis of the sound-velocity measurements made at the time. Thus the volume change $\Delta V = (1/109.3 + 1/273.15)\ V_0$, where $V_0 = 0.773$ cubic meters.

To obtain the amount of heat Q supplied by the hot bath, Carnot noted that for small temperature differences the work performed is negligible compared to the heat consumption. It follows that one may assume, for that part of the calculation, that the heat received by the system almost vanishes in a closed cycle. Consider now the cycle 1-2-4-1 (triangular path). By definition, no heat is being transfered to the fluid along the adiabat 4-1. Therefore, the amount of heat Q received by the system along the path 1-2 is equal to the heat received along the path 4-2. The latter is the heat required to raise the temperature of 1 kg of air from 0 to 1°C at (constant) atmospheric pressure. Experimental values for this quantity were known at Carnot's time.

Carnot also correctly noted that, for small temperature differences, essentially the same values of W and Q are obtained if the cylinder volume is kept constant when being transfered from one bath to the other, that is, adiabats may be replaced by isochores, in that limit. However, when the cylinder is kept in contact with a bath and its volume changes as shown in the figure, the pressure necessarily varies. This is why the description of the Carnot cycle given in [1] "The cycle used by Carnot was composed of two isobarics and two isochorics" is erroneous. It is then not surprising that these authors calculate a much lower efficiency, namely, $\eta = 0.00089$, using modern data, and misinterpret the nature of Carnot's contribution, as far as air or other nearly ideal gases are concerned.

Carnot gave in a manuscript the mechanical equivalent of heat according to: 1 kilo-calorie of heat=370 kg.m (instead of the modern value of 426 kg.m corresponding to 1 calorie of heat=4.18 J). Because the energy of ideal gases depends on temperature only, Q is equal to the work $\Delta V\ p_0$ done along the isothermal path 1-2. If we replace Q in (1) by $\Delta V\ p_0$, ΔV drops out and we obtain, using the ideal gas law pV/T =constant, $\eta = \Delta p/p_0 = 1 - T_{cold}/T_{hot}$.

Readers interested in the history of Thermodynamics would do well in reading the La Mer papers (reference 6 of the commented paper) that appeared long ago in this journal.

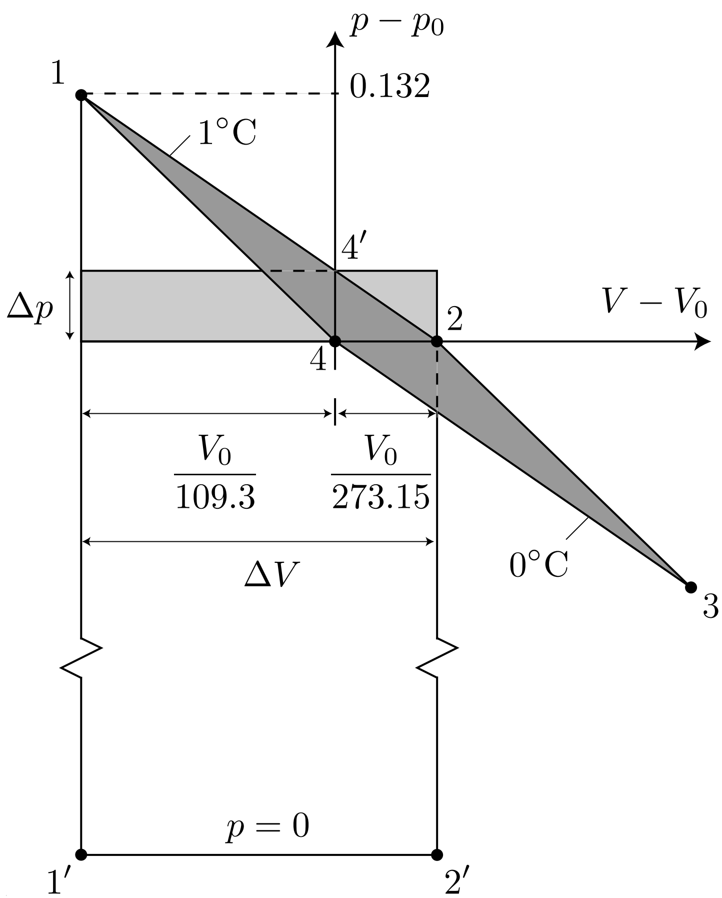

Figure 1: This figure represents at scale the reversible cycle (1-2-3-4-1) for air, considered by Carnot. Recent experimental values are shown. At the origin of the diagram ($T = 0$°C) the pressure is p_0=10.34 meters of water and the volume is $V_0 = 0.773$ cubic meters. The work performed is equal to the area enclosed in the paralelogram, also equal to the area enclosed in the rectangle, namely: $W = \Delta V\ \Delta p$. The heat consumption Q is approximately equal to the heat required to heat air from 0°C to 1°C at atmospheric pressure. The cycle efficiency $\eta \approx 1/273.15$.

References

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