Sadi Carnot on Carnot’s theorem

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We reproduce the original calculations of Sadi Carnot that led him to formulate the so-called Carnot’s theorem. We rephrase Carnot’s calculations in SI units and compare his results with those obtained using modern data. © 2002 American Association of Physics Teachers. [DOI: 10.1119/1.1412642]

I. INTRODUCTION

In his book Reflections on the Motive Power of Fire (1824), Sadi Carnot presented calculations on the “motive power” defined as

\[ \text{motive power} = \frac{\text{work}}{\text{fuel consumed}} \]

He considered thermal cycles operating with different substances and, based on particular cases, formulated the following general propositions:

Wherever there is a difference in temperature, motive power can be produced.  

[…] the maximum amount of motive power gained by the use of steam [in a Carnot cycle] is also the maximum that can be obtained by any means whatsoever.

The motive power of heat is independent of the working substances that are used to develop it. The quantity is determined exclusively by the temperature of the bodies between which, at the end of the process, the passage of caloric has taken place.

According to this first statement, both a cold and a hot body are required to produce work. The second statement, equivalent to the second law of thermodynamics, says that a heat engine more efficient than the Carnot machine cannot exist. The third statement evolved to what is now called Carnot’s theorem.  

In spite of the recognition of Carnot’s contribution to thermodynamics, pedagogical presentations of his original work are scarce. Several authors discuss this work, but very few consider its quantitative aspects. Truesdell should be cited for his effort to put Carnot’s results in a modern perspective. On the other hand, Carnot’s booklet is difficult to read because of its terminology and units. This difficulty motivated us to present some of his original calculations, using modern concepts and SI units.

Carnot based his calculations on a cycle that differs from what became known as the Carnot cycle (two adiabatic and two isothermic processes, all reversible). The cycle used by Carnot was composed of two isobarics and two isochorics: we call it the “modified Carnot cycle.” We present his reasons and calculations and discuss their validity. We also show how the results change if we use current data.

In Sec. II we describe the processes that Carnot conceived to obtain “motive power.” In Sec. III we reproduce his calculations for five cycles, using air, water, and alcohol. In Sec. IV we discuss the results, comparing them with modern ones, and summarize the pedagogical relevance of Carnot’s work. In the Appendix we give some technical details.

II. MODIFIED CARNOT CYCLE

In his memoir, Carnot described the reversible cycle undergone by a fluid, with seven states, but equivalent to what is known today as the Carnot cycle. Two bodies were needed: body A (the hot source) at temperature \( T_A \), and body B (the cold source) at temperature \( T_B \). The original description of the cycle is intricate, but Carnot noted that such a cycle could be simplified if \( T_A \approx T_B \). In all his calculations, he considered a cycle with the following stages (Fig. 1):

Contact between the gas abcd and the body A; movement of the piston from cd to ef.

Removal of the body A; contact between the gas in abef with the body B; return of the piston from ef to cd.

Removal of the body B; contact between the gas and the body A; movement of the piston from cd to ef.  

In other words, the first stage is repeated, and so on.

Figure 1 shows the modified Carnot cycle in a \( (P,V) \) diagram. The process 1→2 is a quasi-static isobaric expansion at pressure \( P_f \) in contact with the hot reservoir; in 2→3, the temperature decreases at constant volume \( V_f \) (irreversible isochoric); the process 3→4 is a quasi-static isobaric compression at a lower pressure \( P_f \) in contact with the cold reservoir until the initial volume \( V_i \) is recovered; finally, in 4→1, the temperature increases at constant volume (irreversible isochoric) until the initial temperature is reached.

Carnot considered cycles for air, water, and alcohol with \( T_A - T_B = 1 \) °C, which is rather small in comparison with \( T_A \) and \( T_B \). As we shall see, replacing the Carnot cycle by the modified Carnot cycle is quite reasonable for water and alcohol, where liquid–vapor equilibrium phase transitions are present. On the other hand, the modified cycle is impossible for air if it is in contact with bodies A and B only.

Carnot implicitly defined the efficiency of the cycle as the ratio of the net (or useful) work delivered by the cycle to the heat taken from the hot reservoir:
In many cases, Carnot assumed that the area 1234 in Fig. 1 could be neglected in comparison with $Q_A$. For $W_N$ he took the difference between the work in processes 1→2 and 3→4. He knew that the work could be calculated from $W = P_{ext}\Delta V$, where $P_{ext}$ is the external pressure and $\Delta V$ the volume variation. Hence,

$$W_N = \Delta P \Delta V,$$  

where $\Delta P = P_f - P_i$, and $V_f = V_f - V_1$. This work is given by the area 1234 in Fig. 1(c).

### III. CARNOT’S CALCULATIONS

Carnot studied cycles with air between 0 and 1 °C, with water (liquid-steam) in three cycles between 99 and 100 °C, between 0 and 1 °C, and between 77 and 78 °C, and with alcohol (liquid–vapor) between 77.7 and 78.7 °C.

#### A. Cycle with air between 0 and 1 °C

Carnot considered 1 kg of air at 0 °C and volume $V_1(0{ }^\circ\text{C}) = 0.267$ m$^3$ (see Eq. 7). He fitted the temperature dependence of the steam volume, $v$, by the function [see Eq. (A7)]

$$v = 10^a(t) = 2268 - 19.64t \div 1000 + 3.30t,$$  

where $v$ is in liters per gram and $t$ in degrees Celsius. To calculate the steam pressure at 99 °C, Carnot first inserted this temperature in Eq. (8) and then introduced the resulting specific volume, $v_f(99{ }^\circ\text{C}) = 1.754$ m$^3$ kg$^{-1}$, together with the temperature, in the equation of state [see Eq. (A6)]

$$P_f(t) = \frac{3.52}{v_f(267 + t)},$$  

obtaining $P_f(99{ }^\circ\text{C}) = 734$ mm Hg. Because, on the other hand, $P_f(100{ }^\circ\text{C}) = 760$ mm Hg, he got the pressure increment:

$$\Delta P = 26 \text{ mm Hg} = 3.465 \times 10^3 \text{ Pa}.$$

In Table II (Appendix A 2) we summarize, in SI units, the data used by Carnot, not only for the present cycle but also for other ones.

The net work produced in the cycle by 1 kg of liquid water at 99 °C, which transforms into steam at 100 °C, was $W_N^{(2)} = 1.70 \times 0.36 = 5.890 \times 10^3$ J.
Moreover, Carnot knew that the heat required to transform into steam 1 g of liquid water at 100 °C was 550 kcal kg\(^{-1}\) (specific enthalpy of vaporization in Table II). Thus, \(Q_A^{(2)} = 299.0 \times 10^3\) J. The cycle efficiency was

\[
\eta^{(2)} = \frac{W_N^{(2)}}{Q_A^{(2)}} = 2.57 \times 10^{-3}.
\]

\section{C. Cycle with water between 0 and 1 °C}

Carnot next considered a cycle with liquid water in equilibrium with its steam, between 0 and 1 °C. He compared this efficiency with that of the first cycle with air between the same temperatures.

Taking \(t=1^\circ\) C in Eq. (8), one obtains the steam specific volume \(v_V(1^\circ\) C)\(=174.16\) l g\(^{-1}\)=174.16 m\(^3\) kg\(^{-1}\). Inserting this value and \(t=1^\circ\) C in Eq. (9), one has \(P_V(1^\circ\) C)=5.418 mm Hg. On the other hand, because from Biot’s data \(P_V(0^\circ\) C)=5.06 mm Hg, one finds \(\Delta P=0.358\) mm Hg=47.71 Pa.

Given \(v_L(0^\circ\) C)\(=1 \times 10^{-3}\) m\(^3\) kg\(^{-1}\), one has \(\Delta V = V_V(1^\circ\) C\)=174.16 m\(^3\). Introducing these pressure and volume increments in Eq. (2), the net work is \(W_N^{(3)}=8.310 \times 10^3\) J. Carnot did not explicitly present these calculations but obtained a value that is similar after convenient translation.

He assumed that the heat absorbed in the cycle was the sum of two contributions: One part would increase the water temperature from 0 to 100 °C at normal pressure, that is, 100 kcal kg\(^{-1}\); and the other would evaporate water at 100 °C, that is, 550 kcal kg\(^{-1}\). At his time, it was believed that the heat required to vaporize water was independent of the pressure: to vaporize water at 1 °C, one would need the same heat that would be required first to raise the water temperature, up to the normal boiling point, and then to vaporize it completely, always at normal pressure. The total heat absorbed in the cycle should be 650 kcal kg\(^{-1}\)=2717 kJ kg\(^{-1}\)

Finally, for this water cycle, the efficiency [Eq. (1)] was (Carnot arrived at a slightly different value)

\[
\eta^{(3)} = \frac{W_N^{(3)}}{Q_A^{(3)}} = 3.06 \times 10^{-3}.
\]

\section{D. Cycle with alcohol between 77.7 and 78.7 °C}

The next system studied by Carnot was 1 kg of ethylic alcohol. For alcohol, whose normal boiling point is 78.7 °C, he assumed that the vapor pressure at 77.7 °C was reduced by 760/25 mm Hg (see Appendix A 3): \(\Delta P=30.4\) mm Hg =4.05 \times 10^3\) Pa.

To obtain the volume variation when alcohol goes from liquid to vapor, one may use Eq. (9) adapted for alcohol. The overall numerical factor of that equation should be multiplied by the ratio of water and alcohol molecular weights:

\[
v(P,t) = 1.338 \frac{267+t}{P}.
\]

Actually, this equation was not used by Carnot. According to Eq. (12), the volume occupied by alcohol vapor near its boiling point, \(t=78.7°\) C, is \(v_V(78.7°\) C)\(=0.626\) m\(^3\) kg\(^{-1}\). Thus, \(\Delta V\sim V_V(78.7°\) C)\(=0.626\) m\(^3\), because \(v_L(77.7°\) C)\(=0.74\) \times 10\(^{-3}\) m\(^3\) kg\(^{-1}\). The net work in this cycle was \(W_N^{(4)}=2.54 \times 10^3\) J. Again, this work was not explicitly given by Carnot.

On the other hand, Carnot knew that the heat required to evaporate 1 kg of alcohol at its boiling point was \(Q_A^{(4)}=207\) kcal=865.3 \times 10^3\) J. The efficiency of the cycle was then

\[
\eta^{(4)} = \frac{W_N^{(4)}}{Q_A^{(4)}} = 2.94 \times 10^{-3}.
\]

Carnot again presented a slightly different value.

\section{E. Cycle with water between 77 and 78 °C}

To compare his results for alcohol and water, Carnot studied a fifth cycle with liquid water at 77 °C, which evaporates at 78 °C. First, he sought the specific volumes occupied by steam at those temperatures. Using Eq. (8), he found the specific volumes \(v_V(77°\) C)\(=4.005\) l g\(^{-1}\) and \(v_V(78°\) C)\(=3.849\) l g\(^{-1}\), respectively. Using Eq. (9) he could obtain the corresponding vapor pressures for water steam at those temperatures: \(P_V(77°\) C)=302.3 mm Hg and \(P_V(78°\) C)=315.5 mm Hg, respectively. Thus \(\Delta P=13.2\) mm Hg = 1.76 \times 10^3\) Pa. So the useful work performed in this cycle was \(W_N^{(5)}=6.77 \times 10^3\) J.

Following the method described in Sec. III C to calculate the heat absorbed by water at 77 °C that evaporates at 78 °C, Carnot obtained \(Q_A^{(5)}=572\) kcal=2390 \times 10^3\) J. Thus, the efficiency of this cycle was

\[
\eta^{(5)} = \frac{W_N^{(5)}}{Q_A^{(5)}} = 2.83 \times 10^{-3}.
\]

These calculations were not presented by Carnot. He just gave the cycle efficiency.

\section{IV. DISCUSSION AND CONCLUSIONS}

In Table I we list the efficiencies \(\eta\) obtained by Carnot for his modified cycles (Sec. III C), the efficiencies \(\eta’\) obtained using Carnot’s reasoning but contemporary data, and the efficiencies \(\eta_{CT}\) of the Carnot cycles calculated from Carnot’s theorem: \(\eta_{CT}=1-T_A/T_B\). (The data for water and alcohol are also summarized in Table II.) For air, \(\eta’\) is obtained in Appendix B.

For cycles with liquid–vapor phase transitions, Carnot obtained reasonable or even accurate values of the work, heat, and efficiencies. For the cycle with air, Carnot’s result deviates from the modern one (in this case, the Carnot cycle cannot be simply replaced by the modified cycle). In Appen-
Table II. Data in SI units used by Carnot for water and alcohol. Listed are vaporization pressures, vapor specific volumes, and specific enthalpies of vaporization at various temperatures. Modern thermodynamical data are given in parentheses. Water pressures were obtained from Eq. (A8). The steam specific volume and specific enthalpy variations of water were obtained from Ref. 21. Alcohol data are from Ref. 20.

<table>
<thead>
<tr>
<th>t (°C)</th>
<th>P_v (kPa)</th>
<th>v_v (m^3 kg^{-1})</th>
<th>∆h_v (kJ kg^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.6744 (0.6085)</td>
<td>174 (193.83)</td>
<td>2717 (2498.2)</td>
</tr>
<tr>
<td>77</td>
<td>40.29 (41.843)</td>
<td>3.85 (3.696)</td>
<td>2390 (2313.2)</td>
</tr>
<tr>
<td>88</td>
<td>97.83 (98.805)</td>
<td>1.70 (1.6736)</td>
<td>2299 (2256.6)</td>
</tr>
<tr>
<td>Alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>77.7</td>
<td>97.25 (97.645)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>78.7</td>
<td>101.3 (101.38)</td>
<td>0.626 (0.627)</td>
<td>865 (841.55)</td>
</tr>
</tbody>
</table>

In regard to the adiabatic compression of air, Carnot used the pressure data for equilibrium liquid—vapor water at various temperatures given in the *Traité de Physique* by Biot (1816). He assumed that steam obeys the ideal gas equation

\[ P = \frac{\epsilon}{v} \left( \frac{267 + t}{v} \right) \]

with \( \epsilon = 3.52 \). This value of \( \epsilon \) follows from the observation that vapor at atmospheric pressure occupies a volume 1700 times bigger than the volume of the corresponding liquid. The data for the steam specific volume and temperature were then fitted by Carnot using

\[ t = \frac{2268 - 1000 \log_{10} v_v}{19.64 + 3.30 \log_{10} v_v}, \]

which is Eq. (8). From here, Carnot was able to obtain steam volumes and pressures at different temperatures. In Table II we list Carnot’s data for water and also for alcohol.

APPENDIX A: DATA USED BY CARNOT

1. Air

For temperature increases of 1 °C, we quote Carnot:23

*By M. Gay-Lussac’s rule, direct heating at constant pressure must increase the volume of the air by 1/267 of its value at 0° centigrade.*

This increment of volume at constant pressure is given by

\[ \Delta V = \frac{\partial V}{\partial T} P \Delta T \]

For an ideal gas, \( \Delta V = (v/T) \Delta T \). Thus, for \( \Delta T = 1 \) K and \( T = 273.15 \) K,

\[ \frac{\Delta v}{v} = \frac{1}{273.15}, \]

close to the experimental value used by Carnot.

In regard to the adiabatic compression of air, Carnot wrote:25

The temperature of air will always rise by 1° centigrade when its volume is suddenly reduced by 1/116 of its original value.

In modern language, assuming that the process is isentropic,

\[ \Delta T = \left( \frac{\partial T}{\partial v} \right)_s \Delta v \]  

\((\Delta v < 0)\). If we use the reciprocity theorem and assume air to be an ideal gas, we have

\[ \left( \frac{\partial T}{\partial v} \right)_s = \frac{-P}{c_v} = -\frac{R}{v} \frac{T}{c_v}. \]

And supported by a result by Gay-Lussac, Carnot wrote about the isochoric heating of a gas:24

*By M. Gay-Lussac’s rule, this difference [between the air pressure at 1 °C and 0 °C] is one-thousandth of 1/267 of the elastic force of the gas...*

For an isochoric transformation of an ideal gas with \( \Delta T = 1 \) K and \( T = 273.15 \) K, we have

\[ \frac{\Delta P}{P} = \frac{\Delta T}{T} = \frac{1}{273.15}, \]

very close to the experimental value used by Carnot.

2. Water

Carnot used the pressure data for equilibrium liquid—vapor water at various temperatures given in the *Traité de Physique* by Biot (1816). He assumed that steam obeys the ideal gas equation

\[ P = \frac{\epsilon}{v} \left( \frac{267 + t}{v} \right) \]

with \( \epsilon = 3.52 \). This value of \( \epsilon \) follows from the observation that vapor at atmospheric pressure occupies a volume 1700 times bigger than the volume of the corresponding liquid. The data for the steam specific volume and temperature were then fitted by Carnot using

\[ t = \frac{3988.842}{(T - 39.47)}, \]

with \( P_v \) in kPa and \( T \) in K, fits modern data. In Fig. 2 we compare vapor pressures fitted by Carnot and vapor pressures obtained from Eq. (A8). Modern data used to compute the efficiencies \( \eta' \) in Table I are displayed in parentheses in Table II.
3. Alcohol

In Carnot’s words:26

At normal pressure pure alcohol boils at 78.7 centigrade. At this temperature, according to MM. Delaroche and Brard, 207 units of heat [1 unit of heat=1 cal] are required in order to vaporize one kilogram of alcohol. The vapor pressure of alcohol at a temperature 1°C below the boiling point is reduced by 1/25; it is 1/25 less than atmospheric pressure.

For alcohol, Carnot assumed that the vapor pressure increment between 77.7 and 78.7°C was ΔP = 760/25 = 30.4 mm Hg.

The boiling point of ethylic alcohol is 78.3 °C

The specific enthalpy variation in vaporization 20 is

For alcohol, Carnot assumed that the vapor pressure increment between 77.7 and 78.7°C was 30.4 mm Hg. Thus

We note, on the one hand, that the first heat cannot be neglected in comparison with the second, and on the other hand, that the second heat was not correctly estimated by Carnot (in process 1–2 the temperature increase is ΔT ~ 3.5 K and not ΔT=1 K as assumed by him). The efficiency of this cycle is

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The specific enthalpy variation in vaporization 20 is Δh_v = 841.55 kJ kg⁻¹. Because the alcohol molecular weight is 46.07 g mol⁻¹ and it is assumed to obey the Clausius–Clapeyron’s equation near the boiling point, one has

where P(77.7°C) = 760 mm Hg, so that P(77.7°C) ≈ 732 mm Hg. Thus ΔP = P(77.7°C) − P(77.7°C) = 28 mm Hg, very close to Carnot’s value.

APPENDIX B: CYCLE WITH AIR

Taking 1 kg of air (molecular weight 29 g mol⁻¹), assumed to be an ideal gas, one has for states 1, 2, 3, 4 in Fig. 1(c) (volumes in m³, pressures in 10⁵ Pa, and temperatures in K):

and the net work

Assuming air to be a diatomic ideal gas, the absorbed heats in the process at constant volume and at constant pressure are (c_v and c_p are molar specific heats)

We note, on the one hand, that the first heat cannot be neglected in comparison with the second, and on the other hand, that the second heat was not correctly estimated by Carnot (in process 1–2 the temperature increase is ΔT ~ 3.5 K and not ΔT=1 K as assumed by him). The efficiency of this cycle is

Quite different from Carnot’s value [Eq. (7)].

The efficiency of the standard Carnot cycle with two isothermics at T_B = 0 °C and T_A = 1 °C can be obtained directly from Carnot’s theorem:

Curiously, this value is closer to that found by Carnot. Analyzing the modified cycle, he was fortunate enough to obtain an efficiency that deviates only ≈10% from η_CT.

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6Electronic mail: tmanuel@teor.fis.uc.pt
8 See Ref. 1, p. 63.
9 See Ref. 1, p. 67.
11 See Ref. 1, pp. 76–77.
12 Although Carnot refers to the caloric theory of heat, his conclusions on heat engines do not depend on any caloric or mechanical theory of heat. For this discussion, see, for example, Refs. 7 and 14, and V. K. La Mer, “Some current misinterpretations of N. L. Sadi Carnot’s memoir and cycle. II,” Am. J. Phys. 23, 95–102 (1955); M. A. Hirshfeld, “Some current misinterpretations of Carnot’s memoir,” 23, 103–105 (1955).
EINSTEIN’S DOUBTS

The finality of death took five years. Einstein’s aneurysm had been diagnosed as early as 1950, and when doctors informed him that an operation might save his life, he said, “Let it burst.” Like Newton before his own death, Einstein was less worried about his physical demise than the constant nagging doubts about his theories. “There is not a single concept of which I am convinced that it will stand firm,” he wrote to an old friend, Maurice Solovine, in 1949, “and I feel uncertain whether I am in general on the right track.” And while his brain kept whirring with the problems of a unified theory, his body became frail and thin, wrinkles fell over him like elephant skin, and he began to slouch, as if with each new day he was carrying a slightly heavier pack on his back. “The strange thing about growing old is that the intimate identification with the here and now is slowly lost,” he wrote to the Queen Mother of Belgium in 1953, “one feels transposed into infinity, more or less alone, no longer in hope or fear, only observing.”