
The Carnot Cycle and the Second Law

Paul J. Gans

*Department of Chemistry
New York University*

February 20, 2004

Credits

This material was created by Paul J. Gans for the course V25.0652, Physical Chemistry II given in the Chemistry Department at New York University in the Spring of 2004. Nevertheless this document stands on its own as a short explanation of the Carnot cycle and its importance.

Previous versions were set first using AT&T troff and later versions were set using GNU groff. The current version was typeset using the L^AT_EX typesetting system on a Linux-based computer using T_EX (Web2C 7.4.5) 3.14159 and L^ATeX2e Version 2001/06/01. Conversion to PostScript was done by dvips(k) 5.92b Copyright 2002 Radical Eye Software (www.radical-eye.com)

The HTML version of this document was produced using L^AT_EX2HTML, version 2002-2-1 (1.70) by Nikos Drakos; revised and extended by Marcus Hennecke, Ross Moore, Herb Swan and others producing markup for HTML version 3.2.

Graphs were prepared using, among other programs, grap-1.10, Ted Faber's implementation of the original *grap* package written by Brian Kernighan and Jon Bentley. Diagrams were created using GNU pic version 1.1.

Version History:

Version 1.0:	October, 1990
Version 1.1:	August, 1994
Version 1.2:	October 1995
Version 1.3:	October 1998
Version 2.0:	20 February 2004

Contents copyright © 2004 by Paul J. Gans. All rights reserved including but not limited to mechanical, electronic, and photographic reproduction and distribution. Reproduction for educational purposes is expressly allowed provided that this notice is maintained in the reproduced versions.

Contents

1	Sadi Carnot	4
2	The Steam Engine	5
3	A Thermodynamic Analysis of the Carnot Cycle	5
4	Kelvin and the Absolute Temperature Scale	8
5	The Second Law of Thermodynamics	10
6	How Good is an Ideal Carnot Engine?	11
7	There's More Than One Kind of Carnot Cycle!	13
8	Summary	14

1 Sadi Carnot

The view of the world in the early 1800's was very different from our view today. Dalton's atomic theory was brand new; Lavoisier's experiments had just put the phlogiston theory to rest;¹ and every educated person knew that heat was due to a mysterious fluid called *caloric*.²

Into this world was born a quiet man named Sadi Carnot. His life was short and undistinguished. His only mark was a small monograph entitled *Reflections on the Motive Power of Heat and on Machinery Appropriate for Developing this Power*. It was not at all a best seller, but the ideas it contained eventually changed the world.

Who was this peculiar fellow? He was born in 1796, the son of a very famous man, Lazare Carnot, a military engineer who had become a member of the ruling Directory during the first stages of the French Revolution and so one of the most powerful men in France. He was a strong anti-monarchist, a view he held all his life. His first child was born during this time. He was named Nicholas Leonhard Sadi Carnot, called Sadi for short.³ Lazare Carnot, already famous for a book he wrote on fortifications, was given the job of reorganizing the Revolutionary army and making it into a force that could repel the Allied invaders anxious to restore the monarchy. This army was the superb fighting tool later used by Napoleon.⁴ Sadi's younger brother Lazare Hippolyte was a writer and a radical politician. A nephew, Marie Francois Sadi Carnot, born to his brother after Sadi's death was named after him. This nephew later became the third President of the French Republic serving from 1887 to 1894, when he was assassinated by an Italian anarchist. Both Lazare Carnot (the father) and Marie Francois Sadi Carnot are today buried in the Pantheon in Paris.

But fame came to Sadi in more subtle ways. In 1812, at the age of 16, with Napoleon at the gates of Moscow, Sadi Carnot entered the *École Polytechnique* in Paris.⁵ Among its early faculty were such as Lagrange, Laplace, Fourier, Berthollet, Ampere, and Dulong,⁶ while its students at the time included Cauchy, Coriolis, Poisson, Gay-Lussac, Petit, Fresnel, Biot, Clapeyron, and Poiseuille, and of course, Carnot.⁷

In 1814 Carnot left the *École Polytechnique* to take a commission in the Corps of Engineers. But Waterloo intervened, Napoleon was defeated, the Empire collapsed, and the monarchy was restored. Lazare Carnot, who had been out of politics during the years when Napoleon ruled as Emperor, was

¹The phlogiston theory held that materials contained greater or lesser amounts of a substance called phlogiston. Phlogiston could be driven out of a material by heat. A typical example was the burning of wood. Anyone with half a mind (it was claimed in the late 18th century) could see that fire is nothing but light of escaping of phlogiston. What remains behind in dephlogistonated wood or ash. Curiously, when metals were dephlogistonated, what remained was *heavier* than the original metal. This didn't seem to bother anyone but Lavoisier.

²Caloric was believed to behave in a manner similar to water; it "fell" from materials at higher temperatures to materials at lower temperatures. People had all sorts of notions about caloric. Most said that it was conserved. Others thought that it could be created under proper conditions (such as explosions).

³Much of this material in this article is taken from John B. Fenn's *Engines, Energy, and Entropy*, W. H. Freeman and Company, 1982. This is a delightful book that I can recommend wholeheartedly to anyone who wants a different view of thermodynamics. Some of the historical material has been taken from a very interesting (and readable) article in the August, 1981 issue of the *Scientific American* while other historical material has been gathered from (mainly French) biographical encyclopedias.

⁴Lazare Carnot was totally out of sympathy with Napoleon's actions in becoming Emperor. Carnot saw little difference between an Emperor and a King.

⁵Founded in 1794 it is still one of the pre-eminent schools of the world.

⁶Lagrange, Laplace, and Fourier are well-known mathematicians (who can forget Fourier transforms), Berthollet (not to be confused with Berthelot) a famous chemist, Ampere remains well-enough respected to have become a unit of electrical current, and of course Dulong (and Petit) are fondly remembered by generations of chemistry students.

⁷Cauchy remains well-enough known to occur frequently in calculus books, Coriolis was a force to be reckoned with, Poisson a mathematician, Gay-Lussac discovered what is usually called Charles' Law, Petit worked with Dulong, Fresnel known for optics, Biot is known for several laws in physics, Clapeyron is quite notorious in physical chemistry, and Poiseuille famous in fluid dynamics. Few schools have had such distinguished members.

exiled by the newly revived monarchy and was never to return to France. Sadi found himself sent to do minor chores on garrison duty in the boondocks. Though he managed a transfer to the general staff school, he quickly realized that there was little future for him in the king's army and retired on half pay.

By 1823 the 29 year old Carnot, was living with his brother in Paris. In the next year he finished the manuscript of *Reflections on the Motive Power of Heat*, which was published in a small edition. He contracted scarlet fever in 1831, and, in 1832, at the age of 36, died of cholera. He never married and had no direct descendents.

2 The Steam Engine

Carnot spent much time thinking about steam engines. Steam engines are conceptually simple devices though complex in practice. Basically a steam engine is a cylinder fitted with a piston and several valves. One valve opens, letting hot steam into the cylinder. The piston is pushed outward. This step is essentially done at constant temperature, the temperature of the hot steam. The steam valve is then closed, but the piston allowed to continue moving outward. As it does, the steam cools. This step is basically adiabatic. The piston then starts to move back into the cylinder. As it does so a second valve opens and the now much cooler steam is pushed out of the cylinder. The temperature of the steam remains mainly unchanged in this step. The second valve then closes, but the piston continues to move inward until it returns to its original position. That step results in adiabatic heating of the residual steam, returning it to its original temperature.

The important thing to realize about this process is that it is *cyclical*. The piston returns to its original position and original conditions once each cycle. The net process is that hot steam is taken in, work is done, and cool steam is pushed out. Carnot realized that the process was cyclical. Further he understood that the steam was taken from a boiler and that the cool steam could be run through a condenser and the resulting liquid returned to the boiler. In principle no water would ever be lost.⁸ All that happened in a steam engine was that (a) heat from the boiler went into the engine, (b) work was done by the engine, and (c) heat was extracted from the spent steam and the water recycled. We can abstract this process as shown in Figure 1

The hot reservoir at a temperature T_2 represents the boiler. An amount of heat q_2 is taken from in by the hot steam and sent to the engine. In the course of one cycle the engine does an amount of work w . The spent steam is reconverted to water in a condenser at a temperature T_1 by the extraction of heat q_1 . The process then repeats.

This cyclic process is today known as a *Carnot cycle* in honor of Sadi Carnot.

3 A Thermodynamic Analysis of the Carnot Cycle

Let's make the Carnot cycle as simple as possible. Basically it is a four-part cycle: (1) steam at a temperature T_2 carries heat q_2 into the engine. As the steam enters the piston moves outward. We can assume that this process takes place at constant temperature, though this is an idealization. (2) The valve is closed and steam no longer enters. But the hot steam can still do work and the piston

⁸Most steam engines of the day did not condense the water as that added complications to an already complex system. So every so often more water had to be added to the boiler. Carnot realized that this was not a necessary part of the operation.

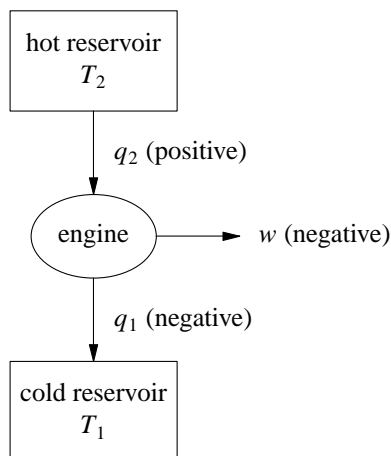


Figure 1: Heat and Work in a Steam Engine

still moves outward. This part of the cycle can be considered to be adiabatic, as no heat flows either into or out of the engine.

In order to have a cyclic process, the piston will have to be pushed back into the cylinder. Otherwise it will not be in position to be pushed out again. During step (2), which is adiabatic, the steam is cooled to a temperature T_1 . Of course, it still contains heat. In step (3) the cooler steam is pushed out of the engine into a condenser also at T_1 . This can be considered an isothermal process. Lastly, in step (4) the piston continues to move inward and, since it is no longer in contact with a heat source, adiabatically compresses the residual steam to T_2 . The piston is now back at its starting position and the process repeats.

Thus, in summary, the process is (1) an isothermal expansion at T_2 , (2) an adiabatic expansion to T_1 , (3) an isothermal compression at T_1 , followed by (4) an adiabatic compression to T_2 .

Lastly, we can make two further simplifications. One is to realize that we don't need the steam at all! We can fill the cylinder with any *working fluid* say an ideal gas.⁹ Then we put the cylinder in a constant temperature bath at T_2 let the piston move out. We remove it from all baths for the adiabatic steps, and use a constant temperature bath at T_1 for the compressions. This makes life simple.¹⁰ The other simplification is to assume that the entire process is reversible.¹¹

With an ideal gas as the working fluid, a $p - V$ diagram for the Carnot cycle would look like that in Figure 2. By the way, Figure 2 is a *real* Carnot cycle diagram.¹²

The cycle goes clockwise from the upper left through the points marked with diamonds. Call these points a , b , c , and d . We are looking for two things here. First, we would like to calculate the amount of heat used and the work done by the Carnot cycle. Second, we would like to compute the

⁹Available as always in your local Chemistry Department Stock Room.

¹⁰Life is never simple, no matter what it says here.

¹¹Of course, making the steps reversible means that each step takes an infinite amount of time. This is not too practical in a real engine!

¹²Not one of the made-up ones that occur in textbooks and on classroom blackboards. Note how narrow the center of the diagram is! The working fluid is one mole of an ideal gas. The upper left hand point is at a temperature of 400 K and a volume of 20 liters. The pressure is 1.641 atm. The next point (going clockwise) is at 400 K and 30 liters with a pressure of 1.094 atm. The next point is at 300 K, 61.58 liters, and 0.400 atm. And the last point is at 300 K, 41.06 liters, and 0.600 atm. The stretched-out appearance of the diagram is real, but makes the individual lines hard to see. That's why the texts and the blackboards lie and draw fake diagrams.

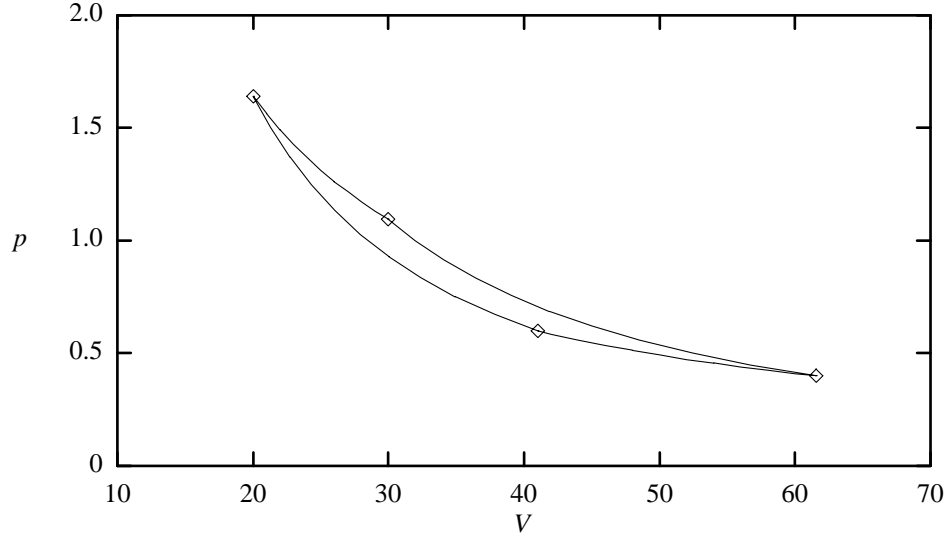


Figure 2: A Carnot Cycle: Volume V in liters, pressure p in atm.

efficiency of the cycle.

1. Starting at T_2, V_a, p_a , reversibly and isothermally expand to V_b . Since the process is isothermal and the gas ideal:

$$\Delta U = 0, \quad w_2 = -q_2 = -nRT \ln \frac{V_b}{V_a}. \quad (3.1)$$

2. We are now at T_2, V_b and p_b . The expansion is reversible adiabatic to a final temperature of T_1 . Hence:

$$q = 0, \quad w = \Delta U = n \int_{T_2}^{T_1} C_V dT. \quad (3.2)$$

3. The current state is T_1, V_c , and p_c . Isothermally and reversibly compress to V_d . Then:

$$\Delta U = 0, \quad w_1 = -q_1 = -nRT \ln \frac{V_d}{V_c}. \quad (3.3)$$

4. The state is now T_1, V_d , and p_d . Finally, a reversible adiabatic compression to T_2 .

$$q = 0, \quad w = \Delta U = n \int_{T_1}^{T_2} C_V dT. \quad (3.4)$$

Note that in the adiabatic steps $q = 0$ and w and ΔU cancel out. Thus only the isothermal steps contribute to the totals for the cycle. Of course, overall, ΔU is zero, as it must be for a cyclic process. The overall work w_{cycle} is:

$$w_{\text{cycle}} = w_1 + w_2 = -nRT_2 \ln \frac{V_b}{V_a} + nRT_1 \ln \frac{V_c}{V_d}. \quad (3.5)$$

There is a relationship between V_a, V_b, V_c , and V_d , but it is not obvious. It stems from a relationship for adiabatic processes. In such a process, acting from temperature T_α to T_β , we have:¹³

$$C_V \ln \frac{T_\beta}{T_\alpha} = -R \ln \frac{V_\beta}{V_\alpha} \quad (3.6)$$

¹³Assuming ideal gases, constant heat capacity, and a reversible process.

which comes from the fact that in an adiabatic process q is zero and hence $\Delta U = w$, or $nC_V dT = -pdV = -nRTdV/V$. This rearranges to $C_V dT/T = -RdV/V$, from which equation 3.6 follows.

If we use equation 3.6 to describe the adiabatic expansion, we get

$$C_V \ln \frac{T_1}{T_2} = -R \ln \frac{V_c}{V_b} \quad (3.7)$$

and if we also use it to describe the adiabatic compression we get:

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_a}{V_d} \quad (3.8)$$

If we invert the temperature ratio in equation 3.8 it becomes identical to the temperature ratio in equation 3.7. Thus

$$C_V \ln \frac{T_1}{T_2} = -R \ln \frac{V_c}{V_b} = -R \ln \frac{V_d}{V_a} \quad (3.9)$$

from which, cancelling the $-R$ terms and exponentiating, we have $V_c/V_b = V_d/V_a$. A slight rearrangement then gives

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \quad (3.10)$$

This allows equation 3.5 to be rewritten as:

$$w_{\text{cycle}} = -nR(T_2 - T_1) \ln \frac{V_b}{V_a}. \quad (3.11)$$

The efficiency of a steam engine is a very practical thing. It is a measure of the heat input to the engine relative to the work output. The heat input is a cost, the work output is a gain. The efficiency ϵ of a Carnot cycle is defined then to be:

$$\epsilon = -\frac{w_{\text{cycle}}}{q_2}. \quad (3.12)$$

The minus sign is present to make ϵ positive. We can use equation 3.11 for w_{cycle} and equation 3.1 for q_2 to get

$$\epsilon = -\frac{w_{\text{cycle}}}{q_2} = \frac{nR(T_2 - T_1) \ln V_b/V_a}{nRT_2 \ln V_b/V_a}, \quad (3.13)$$

which reduces to the very simple (and famous):

$$\epsilon = \frac{T_2 - T_1}{T_2} \quad (3.14)$$

It is interesting that the efficiency depends *only* on the temperature and not on the size of the engine (the number of moles of gas present) or the *stroke volume* (the distance the piston moves), or the *compression ratio* V_b/V_a . Only the temperatures matter.

4 Kelvin and the Absolute Temperature Scale

Much later Kelvin¹⁴ (in 1851) published a paper that put Carnot's work into context with that of Rumford and Joule. It was Kelvin who set forth the principle now called the First Law of

¹⁴Born William Thomson. Professor of Natural Philosophy at Glasgow, and a true genius, he made a fortune on his contributions to transatlantic telegraphy, for which he was knighted in 1866. He became Baron Kelvin of Largs in 1892. He retired in 1899 and died in 1907. He published more than 300 papers in mathematics and physics.

Thermodynamics. Kelvin is also responsible for the absolute temperature scale (which temperature unit now bears his name).

We can trace Kelvin's idea by looking at heat instead of work. If w_{cycle} in equation 3.13 is replaced by $-(q_2 + q_1)$ (to which it is equal, we get:

$$\epsilon = \left[1 + \frac{q_1}{q_2} \right]. \quad (4.1)$$

If we recognize that q_2 is a positive number while q_1 is negative, we can write equation 4.2 as:

$$\epsilon = 1 - \frac{|q_1|}{|q_2|} \quad (4.2)$$

where $|$ denotes absolute value. But the efficiency ϵ is a function only of the temperature, so

$$\frac{|q_1|}{|q_2|} = f(t_1, t_2), \quad (4.3)$$

where $f(t_1, t_2)$ is some function of temperature, where t is not necessarily the absolute temperature.

Let us put two Carnot cycles together so that the low temperature isothermal expansion of one is the high temperature isothermal compression of the other. Such a setup is illustrated¹⁵ in Figure 3. The high temperature cycle is $ABCF$ operating between T_3 and T_2 . The low temperature cycle is $FCDE$ operating between T_2 and T_1 . And, indeed, there is a third cycle present, $ABCE$, operating between T_3 and T_1 . Now if the heats q^{16} connected with the three isotherms are $|q_1|$, $|q_2|$, and $|q_3|$,

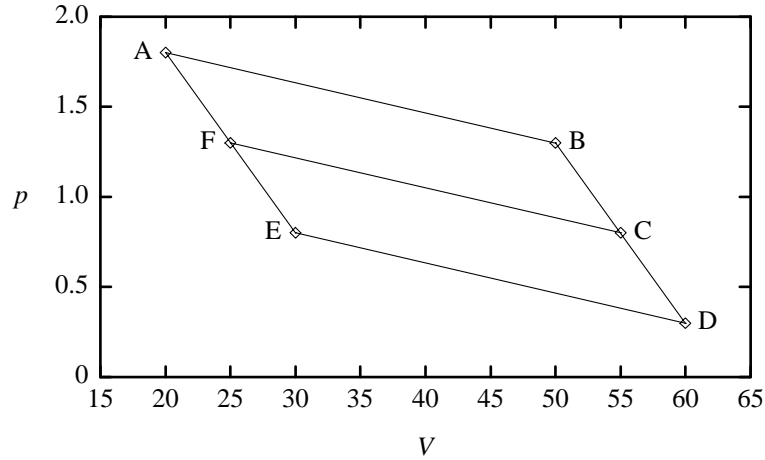


Figure 3: Three Carnot Cycles

then from equation 4.3 we have as a simple algebraic fact:

$$\frac{|q_1|}{|q_3|} = \frac{|q_1|}{|q_2|} \frac{|q_2|}{|q_3|}. \quad (4.4)$$

Since, from equation: 4.3

$$\frac{|q_1|}{|q_2|} = f(t_1, t_2) \quad \frac{|q_2|}{|q_3|} = f(t_2, t_3) \quad \frac{|q_1|}{|q_3|} = f(t_1, t_3), \quad (4.5)$$

¹⁵Note that these are very schematic. They are much more like the diagrams in texts and on blackboards.

¹⁶I use absolute value signs since we are only concerned with the *magnitudes* of the heat.

we must have

$$f(t_1, t_3) = f(t_1, t_2)f(t_2, t_3). \quad (4.6)$$

Now each f in equation 4.6 is the same function. Only the names of the variables have changed. It is easy to see that if

$$f(t_i, t_j) = \frac{T_i}{T_j}, \quad (4.7)$$

equation 4.6 will be satisfied.¹⁷ It can be shown¹⁸ that this is the *only* solution, except for a constant factor. That is, kT could be used in place of T where k is a constant.¹⁹

Kelvin proposed that the T 's defined here be used to set up an *absolute* temperature scale. He also showed that this T is the same as the T in the ideal gas law.²⁰ The constant k was set by fixing the triple point of water as being 273.16 K.

5 The Second Law of Thermodynamics

Nowhere in the discussion above has the Second Law of thermodynamics appeared. I hid it. It was really there all the time. In the second section, when I discussed the steam engine, I assumed that some heat will be lost to a cold reservoir. Why must this be true? Kelvin postulated the second law of thermodynamics in the following form:²¹

A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible.

This doesn't look at all obvious. The key is the word *only*. A steam engine can absorb heat and do work, but the process leaves the piston pushed out. This is a result in addition to the doing of work. Kelvin is saying that you cannot take heat from a hot object and convert it all to work without producing some other change in the universe. Because of this I included a low-temperature constant temperature bath in our Carnot cycle.

The statement of the Second Law that I prefer is one that agrees with everyone's experience:²²

*If heat flows by conduction from body **A** to another body **B**, then a transformation whose only final result is to transfer heat from **B** to **A** is impossible.*

Heat will, of course, only flow by conduction from A to B if A is at a higher temperature than B . Then, of course, you cannot get the heat to flow back from B to A spontaneously. You will have to produce some other change in the universe as well.

These two statements of the Second Law, the first due to Kelvin, the second to Clausius, are equivalent. Fermi gives a non-mathematical argument that is quite convincing:²³ He argues:

¹⁷Don't take my word for it. Do the substitution and prove it to yourself!

¹⁸These four words always introduce a cop-out. Of course it can be shown or I wouldn't be talking about it. But I'm not going to show it because it is (a) too long, and (b) too messy a proof. One proof is given in K. G. Denbigh, *The Principles of Chemical Equilibrium*, 3rd Edition, Cambridge University Press, 1971.

¹⁹Because the k 's would cancel out in equation 4.7!

²⁰A proof of this (which is long but not complicated) can be found in Joseph de Heer, *Phenomenological Thermodynamics*, Prentice-Hall, 1986, page 115.

²¹Quoted from Enrico Fermi, *Thermodynamics*, Dover Publications, 1956, page 30.

²²Also take from Fermi, *ibid*.

²³More Fermi. see the citation above.

“Let us first suppose that Kelvin’s postulate were not valid. Then we could perform a transformation whose only final result would be to transform completely into work a definite amount of heat taken from a single source at the temperature t_1 . By means of friction we could then transform this work into heat again and with this heat raise the temperature of a given body, regardless of what its initial temperature t_2 , might have been. In particular, we could take t_2 to be higher than t_1 . Thus the only final result of this process would be the transfer of heat from one body (the source at temperature t_1) to another body at a higher temperature, t_2 . This would be a violation of the Clausius postulate.”

That rather convincingly demonstrates that if Kelvin was wrong, Clausius must also be wrong. To fully establish that the two statements are the same, we must also show that if Clausius is wrong, Kelvin must be wrong.

Again, quoting Fermi:

“Let us assume, in contradiction to Clausius’ postulate, that it were possible to transfer a certain amount of heat Q_2 from a source at the temperature t_1 to a source at a higher temperature t_2 in such a way that no other change in the state of the system occurred. With the aid of a Carnot cycle, we could then absorb this amount of heat Q_2 and produce an amount of work L . Since the source at the temperature t_2 receives and gives up the same amount of heat, it suffers no final change. Thus the process just described would have as its only final result the transformation into work of heat extracted from a source which is at the same temperature t_1 throughout. This is contrary to the Kelvin postulate.”²⁴

Thus the two statements are equivalent. Either can be taken as a statement of the Second Law.

6 How Good is an Ideal Carnot Engine?

Why bother with Carnot engines at all? The answer is that an ideal reversible Carnot engine is the most efficient heat engine possible that operates between two temperatures T_2 and T_1 . This rather remarkable statement is not hard to prove.

Consider the setup in Figure 4. There are two constant temperature baths, the high temperature bath at T_2 and the low at T_1 . There are also two Carnot engines, the *regular* one and the *primed* one. We will take the primed engine to be an ideal reversible Carnot engine running with efficiency ϵ' . It will be run backward.²⁵ The other engine, the regular one, runs in the forward (regular) direction. It absorbs an amount of heat $|q_2|$ and discharges $|q_1|$ to the cold reservoir.²⁶ It produces an amount of work $|w|$.

Let us assume that the regular engine is *more* efficient than the primed engine. That is:

$$\epsilon > \epsilon'. \tag{6.1}$$

²⁴It is interesting to note that Fermi uses a capital Q for heat while I use a lower case q . He also uses a lower case t where I use a capital T . Does this explain why Fermi won a Nobel Prize and I haven’t?

²⁵Because it is reversible it can be run backward as easily as forward!

²⁶Absolute values are used since the signs of each of these quantities tends to confuse the issue. While q_2 is positive, q_1 is, in fact, negative. Watch the words in the explanation. They will tell which way the heat is flowing.

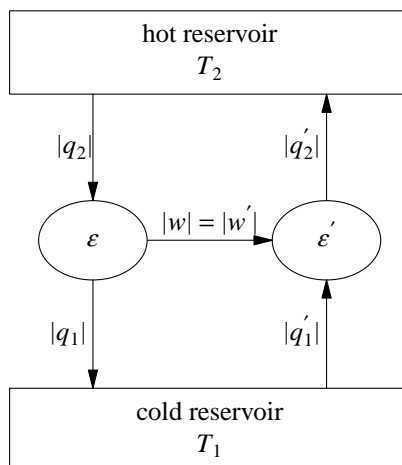


Figure 4: Two Coupled Cycles

This engine is run backwards: work w' is input, heat $|q'_1|$ is drawn into the engine from the cold reservoir, and heat $|q'_2|$ is discharged into the hot reservoir. It is important to realize that the amount of work absorbed by this engine can be *any amount whatever*. This is an ideal reversible Carnot engine, its work output is given by equation 3.11 and is directly proportional to n , the number of moles of ideal gas in the engine. By adjusting n we can make the work used by the ideal engine anything we wish.²⁷

The argument now follows de Heer in the book cited above. First we adjust the output of the regular Carnot engine so that the work input by it is just exactly what is produced by the primed engine. In other words:

$$|w| = |w'|. \quad (6.2)$$

The result is a cycle in which there is no net work output. An amount of heat $|q_1| - |q'_1|$ is *added to* the cold reservoir. Similarly, an amount of heat $|q_2| - |q'_2|$ is *removed from* the hot reservoir.²⁸ Now since ΔU *must* be zero for the cycle, these two amounts of heat must be equal, since there is no work. So

$$|q_1| - |q'_1| = |q_2| - |q'_2|. \quad (6.3)$$

Now rewriting equation 3.12 using absolute values, the efficiencies are defined as:

$$\epsilon = \frac{|w|}{|q_2|} \quad \epsilon' = \frac{|w'|}{|q'_2|}. \quad (6.4)$$

Since the regular engine is assumed to be *more* efficient:

$$\frac{|w'|}{|q'_2|} < \frac{|w|}{|q_2|}, \quad (6.5)$$

and, since the works are equal:

$$\frac{1}{|q_2|} < \frac{1}{|q'_2|}, \quad (6.6)$$

or

$$|q_2| < |q'_2|. \quad (6.7)$$

²⁷Of course $|q'_2|$ and $|q'_1|$ are *also* directly proportional to n and will change if n changes.

²⁸With this much of a clue, stop reading and see if you can figure out the rest of the argument.

Now using equation 6.7 in equation 6.3, it is clear that the right hand side of equation 6.3 must be negative!. Thus heat is not being removed from the hot reservoir, rather it is being pumped in from the cold reservoir with *no other change taking place in the universe*. Heat is flowing from cold to hot, which is impossible. Thus the assumption that the regular engine is more efficient than an ideal reversible Carnot engine is wrong. No engine can be more efficient than an ideal reversible Carnot engine.

7 There's More Than One Kind of Carnot Cycle!

We've looked at the Carnot cycle from the point of view of a steam engine. Steam engines take many forms including jet engines, gas turbines, and the working parts of a nuclear energy plant.

For a steam engine what is important is the heat taken from the hot reservoir, q_2 and the work w produced by that heat. So we define the efficiency in terms of those two quantities.

But consider: What if we call the cold reservoir a "refrigerator" and the hot reservoir the "kitchen" ? Then we are interested in pumping heat from the cold reservoir to the hot one. That will take work, but it can be done by running a Carnot cycle in reverse. While only the signs of the various quantities change,²⁹ the result is quite different. Here we care about the heat moved from the cold reservoir q_1 and the work w needed to move it. Now we have:

$$\eta_{\text{refrig}} = \frac{q_1}{w}, \quad (7.1)$$

where η is called the *coefficient of performance* and the larger it is, the better. The needed quantities are given by equations 3.3 and 3.11. Putting these into equation 7.1 and doing the same manipulations we did above, we get:

$$\eta_{\text{refrig}} = \frac{q_1}{w} = \frac{-nRT_1 \ln(V_d/V_c)}{-nRT(T_2 - T_1) \ln(V_b/V_a)} = \frac{T_1}{T_2 - T_1}. \quad (7.2)$$

A typical refrigerator at 277 K (40°F) with a room at 295 K (72°F) has a *maximum* coefficient of performance of 15.4. Of course a real refrigerator will have a lower performance. One way of improving the performance would be to lower the room temperature (since there will then be a smaller temperature difference to work against) or raise the temperature of the refrigerator (which risks spoiling what is inside of it) or both.

Another increasingly important use for a (reverse) Carnot cycle is to use it as a *heat pump*. A heat pump heats a house, taking in heat from the outside (cold reservoir) and pumping it into the house (hot reservoir). The coefficient of performance here is:

$$\eta_{\text{heatpump}} = \frac{q_2}{w} = \frac{T_2}{T_2 - T_1}, \quad (7.3)$$

where the manipulations are the same as in equation 7.2. Taking the same numbers as above, but with the house being at 295 K and the outside being at 277 K, we get $\eta = 16.4$. Now this is an amazing figure. If we heated our house by electricity, we'd get one joule into the house for every joule consumed. But if we used an ideal heat pump, we'd get 16.4 joules into the house for every joule spent!³⁰ What we are doing is using the energy to pump heat instead of simply converting it to heat. But of course the input electrical energy also turns up as heat in the process. Sadly, real heat pumps are not so efficient, but nevertheless all commercial ones offer an efficiency advantage over a simple electric heater.

²⁹For instance, the work w will now be *positive* since it must flow into the engine.

³⁰Take equation 7.3 and multiply through by w , which we can take as the electrical input to run our engine.

8 Summary

What's been done here?³¹ We've discussed steam engines and Sadi Carnot's life, both good things to know for your general education, but not too useful in real life. We've set up and analysed a special heat engine called a Carnot engine and shown, rather remarkably that (1) its efficiency depends *only* on the temperatures involved, (2) that *no* other heat engine operating between the same two temperatures can be more efficient, and (3) that while steam engines may no longer run on railroads, Carnot cycles still have their uses.

We've also seen where the absolute temperature scale comes from.

Perhaps most importantly, we've shown that the mysterious³² Second Law is actually more intuitively obvious than the First. Everyone has noticed that hot objects cool and never spontaneously heat. That's it: heat travels on its own from hot to cold, never the other way around. We've shown that this can be stated in several different ways; in particular that whenever one runs a heat engine, *heat must be wasted*.³³ People who run steam engines³⁴ are not "wasting" heat from these engines just to drive conservationists crazy,³⁵ it is the second law of thermodynamics that is driving them crazy.

Lastly, and most importantly, the Second Law gives a *direction* to energy flows. Using this, thermodynamics can predict the direction of chemical and physical reactions – a very powerful tool.

But that is beyond the scope of these notes.

³¹Besides putting a lot of people to sleep.

³²At least to people in the humanities and social sciences.

³³That is, discharged to a cold reservoir.

³⁴This includes the local electrical producers, atomic power plants, and a host of others.

³⁵Though these companies may have other wasteful habits.