LECTURE 10 (2004-02-06)

Light bulb filaments

Alan Chapman set up a demonstration about light bulb filaments. Under the microscope, you can see that it has coils within the coils. The wire itself looks about $50\,\mu$m in diameter, which is reasonably close to the value predicted in problem C1 of sheet 2.

Adiabatic changes

Last time we got to

$$\frac{\Delta p}{p} = -\gamma \frac{\Delta V}{V}.$$

If you integrate both sides, you get

$$\ln p = \text{const} - \gamma \ln V.$$

This form is just the logarithm of the more familiar form:

$$pV^\gamma = \text{const}.$$

I prefer the fractional-change form: It shows more clearly that pressure drops more in an adiabatic expansion than in an isothermal expansion. This fact has an important consequence for the temperature. The ideal gas law says that $pV \propto T$. The fractional change in pV is the sum of the fractional changes in p and V (an idea used in lecture 9):

$$\frac{d(pV)}{pV} = \frac{\Delta p}{p} + \frac{\Delta V}{V} = (1-\gamma)\frac{\Delta V}{V}.$$

In air ($\gamma = 1.4$), a 5% increase in volume produces a 7% decrease in pressure and a 2% decrease in temperature. The sign is correct: Adiabatic expansions reduce temperature as the gas does work on the surroundings, or equivalently, as the gas molecules collide with a receding wall.

Rain shadows

Now imagine a mountain range and winds bringing moist air towards it (the moist air come from the ocean). As the air parcel rises up the mountain, the surrounding air pressure falls. Why? Because of gravity. One picture of air pressure (there are a few gotchas in this picture, but it's mostly right) is as the weight per area of a column of air above you. At higher altitudes less air sits on top of your head. So the pressure drops and the parcel expands until its pressure matches the external pressure. The expansion is adiabatic, so the parcel cools as it rises. Cooler air holds less water vapour. We'll sort out why in a minute, but let's take it as a given for now. What happens to the excess water vapour? It condenses into water and turns into rain! So the windward side of the mountain gets lots of rain.

As the dry parcel descends the other side of the mountain, the surrounding pressure increases so the parcel contracts. In this adiabatic expansion the temperature rises, as does the capacity to hold water vapour. Oh, not so good for the plants: The water-hungry air sucks up water from the ground, so it dries out (it gets 'anti-rain'). The net effect of the parcel of air is to transfer rain from the far side of the mountain to the windward side.

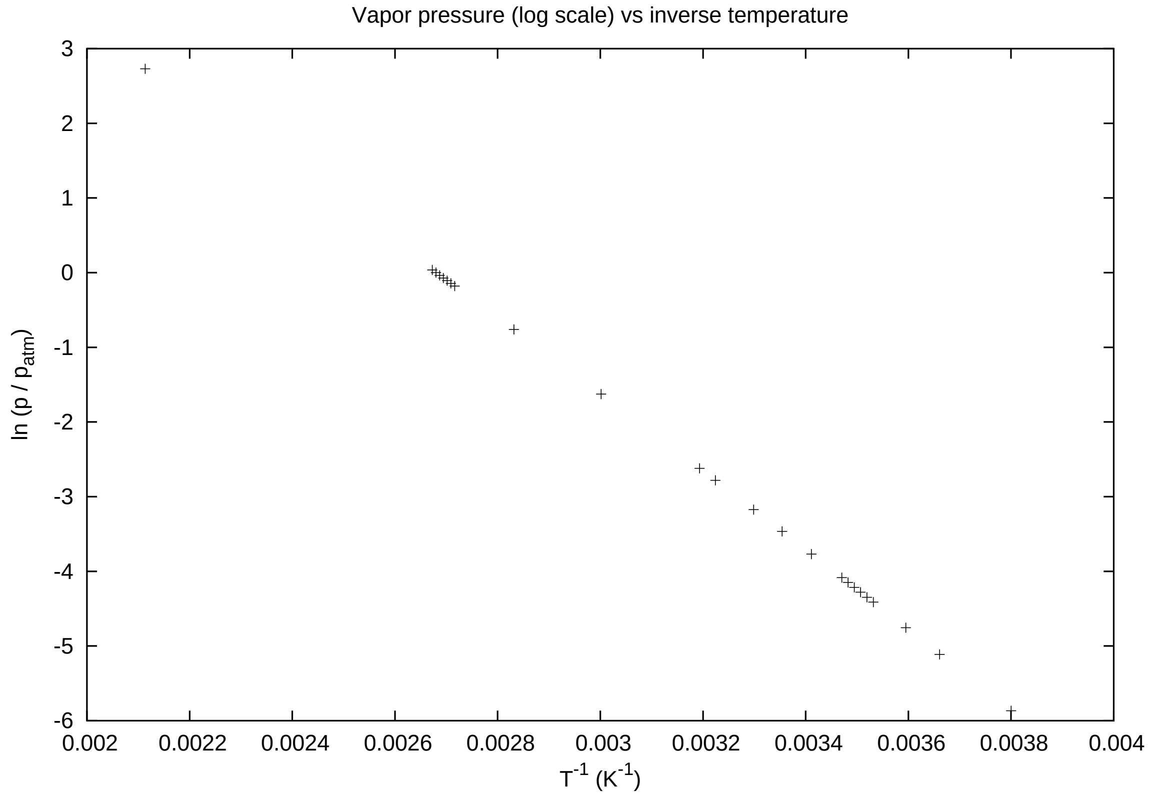
Adiabatic atmosphere

Knowing the pressure at the top of the mountain, we can calculate the temperature of the air parcel (using the adiabatic law). This temperature is also the temperature of the surrounding air in an adiabatic atmosphere (see problem B1 on sheet 3). How does an atmosphere become adiabatic?

Imagine an atmosphere where the temperature is constant with height. The pressure drops with height – because of gravity. You studied this *isothermal atmosphere* in IA physics as an example of the Boltzmann factor. It is stable as long as nothing disturbs it. Now add a tiny bit of convection: A bit of air near the ground heats up slightly (perhaps it's near a hot tarmac), so it becomes less dense than the surrounding air and therefore rises (buoyancy). As it rises, it follows the same life history as the air parcel going up the mountain: It expands (because of lower surrounding pressure) and therefore cools adiabatically. Heat flows in from the surrounding air, raising the temperature of the parcel and lowering the temperature of the surrounding air. This process of parcel circulation continues to reduce the temperature until the temperature at that height is what it would be in an adiabatic change. The isothermal atmosphere is *convectively unstable* and turns into an adiabatic atmosphere.

Vapour pressure

How does vapour pressure vary with temperature? Here is vapour pressure data for water:



Note the special axes. The pressure is on a log scale and the temperature is plotted as $1/T$. Those choices make the data fall on a straight line. So

$$\ln p = p_0 - \frac{T_0}{T},$$

where p_0 and T_0 are constants determined by fitting a straight line to the data. Thus

$$p \propto e^{-T_0/T}.$$

Why does the pressure have this form?

Boltzmann!

The answer is the Boltzmann factor: the same factor that you used last year to work out the pressure versus height in an isothermal atmosphere. It says that

$$\text{probability of being in a state} \propto e^{-E/RT},$$

where E is the energy of a state and R is the usual gas constant. Here the two states are gaseous water (steam) and liquid water. Imagine a box containing liquid water and vapour. The ratio of probabilities to be in vapour relative to liquid is

$$\frac{P(\text{steam})}{P(\text{liquid})} \propto e^{-\Delta E/RT},$$

where ΔE is the energy difference between vapour and liquid. It takes energy to remove a molecule from the liquid (you have to break hydrogen bonds) so the vapour has higher energy than the liquid ($\Delta E > 0$). As temperature changes, more liquid turns into vapour, but the amount of liquid hardly changes (gases are so much less dense than liquids). So $P(\text{liquid})$ is roughly constant, and then

$$P(\text{steam}) \propto e^{-\Delta E/RT}.$$

Furthermore, probability is proportional to density and pressure is proportional to density by the ideal gas law. So

$$p_{\text{vapour}} \propto e^{-\Delta E/RT}.$$

Looking at the graph, you can find that $T_0 \sim 5000\,\text{K}$ (see also problem B1 on sheet 4). In the exponential form above, $RT_0 = \Delta E$. So

$$\Delta E \sim 8\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1} \times 5000\,\text{K} = 4 \times 10^4\,\text{J}\,\text{mol}^{-1}.$$

One mole of water has a mass of 18 g, so

$$\Delta E \sim 4 \times 10^4\,\text{J}\,\text{mol}^{-1} \times \frac{1\,\text{mol}}{1.8 \times 10^{-2}\,\text{kg}} \sim 2\,\text{MJ}\,\text{kg}^{-1}.$$

Hmm, that looks familiar: It's the heat of vaporisation of water (lecture 3). This result makes sense, since it is the energy to remove a water molecule from the liquid to the vapour. Thus

$$p \propto e^{-L_{\text{vap}}/RT}.$$

The constant of proportionality is determined by setting $p = 1\,\text{atm}$ at $T = 100\,^\circ\text{C}$ (don't forget to convert to Kelvin!).

Results

Everywhere you find the results of Boltzmann and adiabatic expansions. In North America, winds bring moist air from the Pacific Ocean towards the east. They eventually hit the Rocky Mountains ($h \sim 3000\,\mathrm{m}$), dumping water on the western slopes and making them bountiful and green. From the solution to problem B1 on sheet 3, the temperature in an adiabatic atmosphere is

$$T = T_0\left(1 - \beta\frac{z}{H}\right),$$

where $\beta = 1 - 1/\gamma \approx 0.3$, $T_0 \sim 300\,\mathrm{K}$, and $H \sim 10\,\mathrm{km}$. So at the top of the Rocky Mountains, the temperature has dropped by

$$\Delta T \sim 300\,\mathrm{K} \times 0.3 \times \frac{3\,\mathrm{km}}{10\,\mathrm{km}} \sim 30\,\mathrm{K}.$$

Which seems reasonable. Even in summer, where perhaps $T = 30\,^{\circ}\mathrm{C}$ at the bottom of the mountains, the tops have a bit of snow (at least in the shady regions). What fraction of the water is dumped because of this temperature change? The fraction retained is given by

$$e^{-T_0/T_{\mathrm{final}}}\big/e^{-T_0/T_{\mathrm{initial}}}.$$

The initial temperature is say 300 K and the final temperature is 270 K. So the exponent in the Boltzmann factor goes from 5000/300 to 5000/270 (leaving out the minus sign). The first quotient is roughly 17, and the second is is roughly 10% higher (because 270 is 10% lower than 300). The exponent then changes by 1.7, and the fraction retained is roughly $e^{-1.7}$ or 0.2. So four-fifths of the water is dumped on the western slopes, and perhaps that much water is absorbed from the eastern slopes. No wonder it is so dry.

East of the Rocky Mountains is the Great Plains where farming is difficult because it is so dry. In the 1930s a further drop in rainfall turned parts of the Great Plains into a dust bowl: the dirt was so dry that winds could blow it around. Farmers went bankrupt and many families fled to California in mass migrations. Their sad tale is the subject of John Steinbeck's classic novel *The Grapes of Wrath.*

Here is a European example of rain shadows, from Mark Mazower, *The Balkans: A Short History* (Modern Library, 2000):

> Over millions of years, the play of the earth's tectonic plates pushed up a series of mountain ranges in the Mediterranean along the geological frontier between Europe and Africa. Stretching from the Iberian peninsula in the west to the ranges of southeastern Europe in the east, they eventually link up with the mountain chains of Asia Minor and central Asia. To their north, the great Eurasian lowlands extend with scarcely a break from Calais to the Urals. There rainfall is abundant, arable land is plentiful and numerous navigable rivers connect the interior with the sea. To the south, it is a different story: good farming land becomes scarcer, the ground is more broken and rainfall less frequent.
>
> The effect of mountains is felt everywhere from the skies to the sea. Rain shadows deprive much of the peninsula of the moisture found in Europe's continental climatic zone. Kolain in Montenegro has an average annual rainfall of 104 inches, while a little way east, Skopje in Macedonia has only 18 inches per year. A tiny

coastal strip running down the Dalmatian coast to western Greece enjoys sufficient rain to soften the impact of the harsh Mediterranean summers.

On Corfu the vegetation is luxuriant; the Cyclades, by contrast, are parched and dry. The former is able to support itself, the latter–as wartime starvation revealed–relies on food imports to keep going.

What is the Carnot cycle?

These so-often studied engines (ways of turning heat flow into mechanical work) are important not because a real engine looks that much like a Carnot cycle. Rather, they show the maximum efficiency an engine can have and then lead to the idea of entropy.

The ingredients are reservoirs at T_{hot} and at T_{cold} and an ideal gas whose volume can be varied with a piston. The piston is surrounding by vacuum, so if we don't want the piston to expand we have to lock it down. The gas has four states, and begins in state 1 with the piston locked:

State	*Temp*	*Volume*
1	T_{hot}	V_1
2	T_{hot}	V_2
3	T_{cold}	V_3
4	T_{cold}	V_4

It goes through four changes, steps A–D:

Step	*States*	*Type of change*	*Heat flow?*
A	$1 \to 2$	Isothermal at T_{hot}	Heat flows in (Q_{hot})
B	$2 \to 3$	Adiabatic	No heat flow
C	$3 \to 4$	Isothermal at T_{cold}	Heat flows out (Q_{cold})
D	$4 \to 1$	Adiabatic	No heat flow

Step A: Isothermal expansion at T_{hot}

Connect the gas to the hot reservoir (which could be for example a giant metal block at T_{hot}). Reservoir just means: 'huge object whose temperature does not change even as heat enters or leaves' (infinite heat capacity). Just as a voltage source means: 'ideal source that supplies the same voltage no matter how much current is needed.' Neither a true reservoir nor a true voltage exists, but they are useful approximations.

Nothing happens when you first connect the reservoir, since the gas was already at T_{hot}. The gas tries to shove the piston outward, but no luck because the piston is locked. Unlock the piston and let it *slowly* creep outward. To prevent it from accelerating, you must balance the pressure from the gas. As the piston moves outward, the gas does mechanical work against your force on the piston. Without the reservoir, the gas would cool as it expands (it would be an adiabatic expansion). The reservoir supplies the heat needed to keep the temperature constant. Call this heat Q_{hot}. We'll compute it later. In this step, the volume has grown and the pressure has fallen, but the temperature remained T_{hot}. The gas is now ready for the next step.

Step B: Adiabatic expansion from $T_{\text{hot}} \to T_{\text{cold}}$

Disconnect the reservoir and let the gas expand further. Without the reservoir to supply heat, the temperature drops in this adiabatic expansion. Keep expanding – and doing work on the environment – until the gas cools to T_{cold}. No heat flows in this step.

Step C: Isothermal compression at T_{cold}

Now attach the cold reservoir and squeeze the gas until it reaches a special volume (which we won't need to calculate). Without the reservoir the gas temperature would rise, but the reservoir maintains the temperature by sucking heat from the gas. Call this heat Q_{cold}. The compression requires mechanical work from the environment to do work against the gas pressure.

After this step, the gas has neither the starting temperature (T_{hot}) nor the starting volume (V_1). Alas! The fourth step fixes these problems and makes the four steps a cycle.

Step D: Adiabatic compression from $T_{\text{cold}} \to T_{\text{hot}}$

Now remove the reservoir and compress the gas until it reaches T_{hot}. If in step C you chose the right stopping volume (V_3), then when the gas reaches T_{hot} in this step it will also have the initial volume V_1. The cycle will then be complete and can start over. Never mind what the magic volume V_3 is. As you will see, adiabatic magic means that we don't need to compute it. All that matters is that such a volume exists.

Diagram of the Carnot cycle

Most texts plot the states of a Carnot cycle on a pV diagram. I prefer to use a log–log diagram. So I plot $\ln p$ versus $\ln V$. But I do not want to commit dimension crimes by taking the logarithm of a pressure. For an example of the trouble that would get me into:

$$\ln(10\,\text{Pa}) = \ln 10 + \ln\ \text{Pa}.$$

But what on earth is the logarithm of a Pascal? So I better make sure I use a dimensionless pressure. The most natural way is to plot $\ln(p/p_1)$, where p_1 is the pressure in state 1. Similarly, I plot $\ln(V/V_1)$ on the x axis. Thus for state 1, both logarithms are zero, so state 1 lies on the origin. I'll plot the other three states by going one step at a time. Figure 1 has the result.

Step A: Isothermal expansion at T_{hot}

In an isothermal expansion, $p \propto V^{-1}$, so

$$\ln p = \text{const} - \ln V,$$

where all the dimension crimes hide in the constant. So on the log–log diagram, an *isotherm* is a line of slope -1. Hence I plot state 2 some distance along such a line.

Step B: Adiabatic expansion from $T_{\text{hot}} \to T_{\text{cold}}$

In an adiabatic expansion, $p \propto V^{-\gamma}$, so on the diagram the system moves along a line of slope $-\gamma$. Because $\gamma > 1$ an *adiabt* is steeper than an isotherm. So I move along an adiabat and plot state 3.

Step C: Isothermal compression at T_{cold}

Now the system moves up an isotherm (slope -1) until it reaches state 4. As discussed above, we don't know where state 4 is, but we will choose it so that step D completes the cycle. How? By considering what happens in step D.

Step D: Adiabatic compression from $T_{\text{cold}} \to T_{\text{hot}}$

Now the system moves up an adiabat (they all have the same slope) to return to state 1. So state 4 is the intersection of the adiabat from state 1 and of the isotherm from state 3.

Plotting it all

Figure 1 puts together all the plotting.

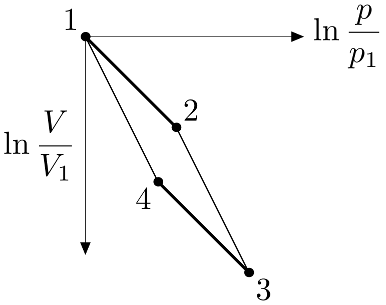


Figure 1. Carnot cycle on a log–log pV diagram. The two isothermal steps, with slope -1, are shown as thicker lines. The adiabatic steps have slope $-\gamma$.

Analysis of the Carnot cycle

There are many subtle points about the cycle, best brought out after analysing the heat flows and mechanical work. Only in steps A and C does heat flow: Q_{hot} is slurped from the hot reservoir, and Q_{cold} is dumped into the cold reservoir.

Computing Q_{hot} and Q_{cold}

These heat flows arose during the isothermal changes. The energy in an ideal gas depends only on temperature (and on the number of molecules, but the number never changes in any step). So the energy remains fixed during an isothermal change. But heat flowed, and heat is a form of energy. Where did that energy go? Oh, right, it all got turned into mechanical work. In step A, the incoming heat flow Q_{hot} is the mechanical work done by the gas in the expansion. In step B, the outgoing heat flow Q_{cold} is the mechanical work done on the gas during the isothermal contraction.

By computing the mechanical work, we can compute the heat flows. We know how to compute the mechanical work:

$$W = \int p\,dV,$$

which is a fancy way of saying work is force (from the pressure) times distance (from the volume change). For an ideal gas $pV = N_{\text{moles}}RT$ so

$$W = N_{\text{moles}}RT \int \frac{dV}{V} = N_{\text{moles}}RT \ln\left(\frac{V_f}{V_i}\right),$$

where V_f and V_i are the final and initial volumes, respectively. This value is easy to read on the log–log plot because it is just proportional to the x-axis distance between the final and initial volumes.

In step A, the initial and final volumes are V_1 and V_2, respectively, and the temperature is T_hot. The work done *by the gas*, and therefore the incoming heat flow (where the gas gets the energy to do the work), is:

$$Q_\mathrm{hot} = N_\mathrm{moles} R T_\mathrm{hot} \ln\left(\frac{V_2}{V_1}\right).$$

Careful about the sign! Q_hot should be positive. Luckily it is since $V_2 > V_1$. Similarly for Q_cold:

$$Q_\mathrm{cold} = N_\mathrm{moles} R T_\mathrm{cold} \ln\left(\frac{V_3}{V_4}\right).$$

Again a sign check. Q_cold should be positive since it represents the heat flowing out during the isothermal compression, and $V_3 > V_4$, so all is well.

Did you forgot the heat flows in steps B and D?

No, they are adiabatic and no heat flows.

Computing work done

After the four steps of the cycle, the gas is in its original state with its original (thermal) energy. The net heat flow, $Q_\mathrm{hot} - Q_\mathrm{cold}$, changed neither the state of the gas nor its energy. But heat flow is energy flow so the net heat flow must have turned into another kind of energy: mechanical work. This statement, which nobody today doubts, is another way of stating the *first law of thermodynamics* or conservation of energy. At the time of its discovery in the 19th century, debates raged on what heat was; was it a substance (the so-called caloric)? Nobody was sure. But especially now that we have microscopic models of matter, we can see that heat has a mechanical interpretation in the potential and kinetic energies of molecules.

Using the almost-obvious first law, the net work is

$$W_\mathrm{net} = Q_\mathrm{hot} - Q_\mathrm{cold} = N_\mathrm{moles} R \left(T_\mathrm{hot} \ln\left(\frac{V_2}{V_1}\right) - T_\mathrm{cold} \ln\left(\frac{V_3}{V_4}\right)\right).$$

Despair! We don't know either V_3 or V_4. But that's where the connecting adiabatic expansions save us.

Adiabatic magic

States 2 and 3, like states 4 and 1, are connected by an adiabatic change. Figure 1 shows the happy consequences. Because the figure is a parallelogram, the vector $\mathbf{r}_{12}$ is identical to $\mathbf{r}_{43}$. In particular, the x distance between states 1 and 2 is the same as the x distance between states 4 and 3. Since the x axis is logarithmic:

$$\ln\frac{V_4}{V_3} = \ln\frac{V_2}{V_1},$$

which is just what we needed to know. The simplicity of this method is why I like to plot pV on a log–log graph rather on the usual linear axes.

A more complicated way to get the same result is to wade through the algebra of the gas laws. Since $pV^\gamma = \text{const}$ for such changes and $pV \propto T$ always for an ideal gas, then by dividing these two relations you get

$$V^{\gamma-1} \propto T^{-1}$$

in an adiabatic change. So $V \propto T^{1/(1-\gamma)}$. The exponent itself will turn out not to matter, so for good hygiene I'll define

$$\alpha \equiv \frac{1}{\gamma - 1}$$

With that definition, the volume–temperature relation is

$$V \propto T^{-\alpha}.$$

For an expansion going from $T_\text{i} \to T_\text{f}$, the volume ratio is

$$\frac{V_f}{V_i} = \left(\frac{T_\text{f}}{T_\text{i}}\right)^{-\alpha},$$

where T_i and T_f are the starting and final temperatures, respectively. Let's check sanity. If the gas expands adiabatically, so $V_\text{f} > V_\text{i}$, then the final temperature is less than the initial temperature; this fact we know from the freezing of the bicycle U-lock. Since the exponent $-\alpha$ is negative, all is well.

Using this result for step B:

$$\frac{V_3}{V_2} = \left(\frac{T_\text{cold}}{T_\text{hot}}\right)^{-\alpha},$$

because the gas starts at T_hot and finishes at T_cold. And for step D:

$$\frac{V_1}{V_4} = \left(\frac{T_\text{hot}}{T_\text{cold}}\right)^{-\alpha},$$

since the gas starts at T_cold and finishes at T_hot. There's the magic we needed, because the two results combine to show $V_3/V_2 = V_4/V_1$ and therefore $V_3/V_4 = V_2/V_1$. This result is what we found so easily using the log–log diagram.

Using this result we can finally get the net work:

$$\begin{aligned}
W_\text{net} &= N_\text{moles}R\left(T_\text{hot}\ln\left(\frac{V_2}{V_1}\right) - T_\text{cold}\ln\left(\frac{V_3}{V_4}\right)\right)\\
&= N_\text{moles}R\left(T_\text{hot}\ln\left(\frac{V_2}{V_1}\right) - T_\text{cold}\ln\left(\frac{V_2}{V_1}\right)\right)\\
&= N_\text{moles}R(T_\text{hot} - T_\text{cold})\ln\left(\frac{V_2}{V_1}\right).
\end{aligned}$$

How simple! And it makes sense from what you know about real engines. Powerful car engines have a large *displacement* because it allows large volume changes. The T_hot in W_net means that engines run hot, and indeed much effort goes into making materials that withstand such heat for many, many cycles.

Efficiency

The efficiency of an engine is the ratio of work done to heat taken in (at the hot temperature):

$$\begin{aligned}\eta &\equiv \frac{\text{work done}}{\text{heat taken in}}\\ &= \frac{N_{\text{moles}} R (T_{\text{hot}} - T_{\text{cold}}) \ln\left(\frac{V_2}{V_1}\right)}{N_{\text{moles}} R T_{\text{hot}} \ln\left(\frac{V_2}{V_1}\right)}\\ &= 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}.\end{aligned}$$

More interesting than the efficiency

More interesting than the efficiency is a quantity suggested by this derivation. It's not the heat. Heat is not so interesting because, even though the system returns to the same state after one cycle, the incoming heat is not the same as the outgoing heat. It's therefore impossible to inspect a system and say: 'It has this much heat in it.' To see why, imagine that you could identify a property called 'heat'. After you one full Carnot cycle on your system, it will return to the original state, but the 'total heat' will be larger because more heat flowed in than flowed out! So 'total heat' cannot be a property of a system, and it is meaningless to ask what the total heat of a system is. (When you ask this question, you probably mean to ask for the energy of the system.)

But a close relative of heat can have a meaning. Here are the heats themselves:

$$Q_{\text{hot}} = N_{\text{moles}} R T_{\text{hot}} \ln\left(\frac{V_2}{V_1}\right),$$

and

$$Q_{\text{cold}} = N_{\text{moles}} R T_{\text{cold}} \ln\left(\frac{V_2}{V_1}\right).$$

Look at the close cousin Q/T for each heat flow:

$$\frac{Q_{\text{hot}}}{T_{\text{hot}}} = N_{\text{moles}} R \ln\left(\frac{V_2}{V_1}\right),$$

and

$$\frac{Q_{\text{cold}}}{T_{\text{cold}}} = N_{\text{moles}} R \ln\left(\frac{V_2}{V_1}\right).$$

These ratios are equal! In one cycle the system gains and loses equal amounts of this quantity. When Q is the heat flowing into a system, we call Q/T the *entropy change* of the system. So a cycle preserves the entropy of the gas: The incoming entropy all departs. Thus entropy can be a property of a system.

The second law of thermodynamics

You already know that heat flows from hot to cold. This empirical statement is the Clausius statement of the second law of thermodynamics. Let's apply our concept of entropy to it. Imagine tanks of hot and cold water separated by an insulating membrane. After you replace the membrane with a conducting membrane (one that allows heat to flow), the tanks will come to the same temperature: heat flows from the hot to the cold one. Consider one tiny time interval of this flow, before equilibrium is reached. A bit of heat, ΔQ flows from hot to cold. The entropy of the hot water falls by $\Delta Q/T_{\text{hot}}$ and the entropy of the cold water rises by $\Delta Q/T_{\text{cold}}$. But $T_{\text{hot}} > T_{\text{cold}}$ (heat flows from hot to cold!), so

$$\frac{\Delta Q}{T_{\text{cold}}} > \frac{\Delta Q}{T_{\text{hot}}},$$

and the combined entropy increases. In other words, whenever heat flows from hot to cold, entropy increases. And heat never flows from cold to hot, so

Entropy never decreases!

Statistics!

We defined entropy in terms of macroscopic quantities (heat and temperature). In Bill Allison's course (for those in Advanced Physics) or in the beautifully illustrated book by Atkins, *The Second Law*, you will learn that entropy has a microscopic, statistical interpretation. This interpretation was such a surprise to Boltzmann that he put it on his tombstone.

A clever little device

Here is a situation that connects the micro- and macroscopic interpretations of entropy. Imagine gas in a box. The box has two halves separated by a partition. The partition has a slider door (like on bottles of salt), and you in very tiny form open and close the door. As one of you pointed out when I was approximating everything away to compute $pV^\gamma = \text{const}$, gas molecules have a distribution of speeds. Some are fast, some are slow, and some are just average. When you see a fast molecule coming from the left side, you quickly open the door, let the molecule into the right side, and shut the door. When you see a slow molecule coming from the right side, you quickly open the door, let the molecule into the left side, and shut the door. The left side will steadily cool (lower average energy of the molecules) and the right side will steadily warm (higher average energy of the molecules), even though the total energy of the two sides will not change.

After the temperature gets sufficiently far apart, you connect them to a Carnot engine. The right side is the hot reservoir and the left side is the cold reservoir. You extract mechanical work from the system as heat flows from the hot reservoir to the cold. When the two reservoirs are at the same temperature (which is the initial temperature of the gas before you did your sliding door tricks), you take away the Carnot engine, do the sliding door tricks again, and then reconnect the engine to extract still more mechanical work…

What's wrong with this picture?

By the door tricks, you made heat flow from cold to hot; this change violates the second law (entropy never decreases). Using the Carnot engine, you also extract energy forever. This extraction violates the first law of thermodynamics (energy conservation). This sliding-door system indicates that the first law is somehow contained in the second law because it shows you how to take any system that can violate the second law and use it to violate the first law.

Macroscopically you can forbid these door tricks using the first and second laws. You can say, 'No, such a system cannot exist.' But that kind of legal barrier does not leave one entirely at ease. If it's wrong macroscopically, it should be wrong microscopically since macroscopic quantities arise from microscopic pictures. The microscopic picture should not give a different answer! Thermodynamics, after all, is supposed to be independent of the microscopic model. This generality is its great strength and also why it is so abstract and confusing if taught entirely independent of microscopic models. So, *how can you bring together the micro- and macroscopic pictures that this example tears asunder?*

References and further reading

Phase changes and vapour pressure.

Adkins, pp. 64–66, 81–83, and 110–111; or Baierlein, pp. 270–76 and (although a bit overloaded with equations) pp. 280–282.

Heat engines and entropy.

Adkins, pp. 104–110 and 114–116; or Baierlein, pp. 34–35 and 51–70.

The end

In this course I hope you've seen how physics surrounds us. On the one hand, physics has invented terrible weapons and served the powerful. On the other hand, physical principles explain so much of the world around us. The mass migrations of people looking for good farming land are an aspect of human culture resulting from $pV^\gamma =$ const. Wearing clothes is a consequence of

$$F = K\frac{\Delta T}{\Delta x}.$$

Our earth is the right temperature for life because of $F = \sigma T^4$. Who can say whether war or explanation and wonder will be the main result of physics. As physicists, you have a place in deciding.

> *Concern for man himself and his fate must always form the chief interest of all technical endeavours... Never forget this in the midst of your diagrams and equations.*
> –Albert Einstein