Lecture 16: Entropy II

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Entropy theory, on the other hand, is not concerned with the probability of succession in a series of items but with the overall distribution of kinds of items in a given arrangement.

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Introduction

- **We ended the last lecture with two definitions of the entropy, the macroscopic definition we got from the Carnot cycle $\Delta S = Q/T$ and the microscopic one that comes from Boltzmann's law $S = k_B \ln \Omega$.**

- **In this lecture, I want to pick up where the Carnot cycle left off, and look at the macroscopic definition of entropy a little more closely, and see how it fits into the second law.**

A general result for all reversible cycles

- First, I want to show that the results we arrived at for the Carnot cycle can be extended to *any* reversible cycle.

Some of you may have spotted this possibility when I showed the *T*-*V* diagram while talking about absolute thermodynamic temperature. There we had engine 1 and refrigerator 2 (which brought in our 'standard' temperature reservoir) give the net effect of engine 3.

In other words, engine 3 = engine 1 + refrigerator 2 = engine 1 – engine 2.

But we could equally well see this in another way – as a reversible engine 1 being 'approximated' by smaller reversible engines 2 and 3, or in other words, engine 1 = engine 2 + engine 3.

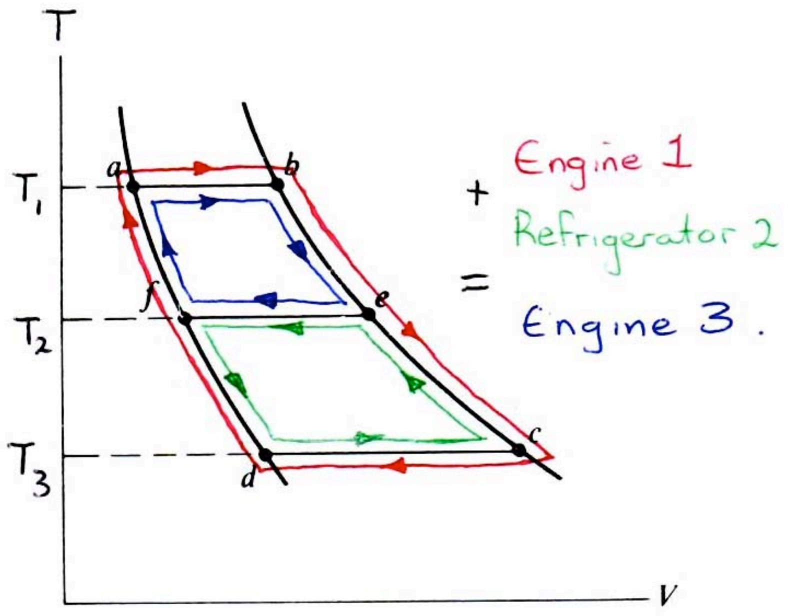


Fig. 5–2 Carnot cycles represented in the T–*V* plane. Curves *a-f-d* and *b-e-c* are reversible adiabatics.

A general result for all reversible cycles

- We can generalise this idea further, and as shown below, and approximate any arbitrary reversible cyclic process by some finite number of Carnot cycles.

The heavy zig-zag line is our approximation to the arbitrary (oval-shaped) reversible process, and while it might look a bit rough, it should be clear that (just like with the trapezoidal rule in integration) if we 'add' more smaller Carnot cycles we will get an increasingly better approximation to the arbitrary process.

Note that we go around each Carnot cycle the same way, so those adiabatic portions of the cycles that coincide are traversed twice in opposite directions and will thus cancel out.

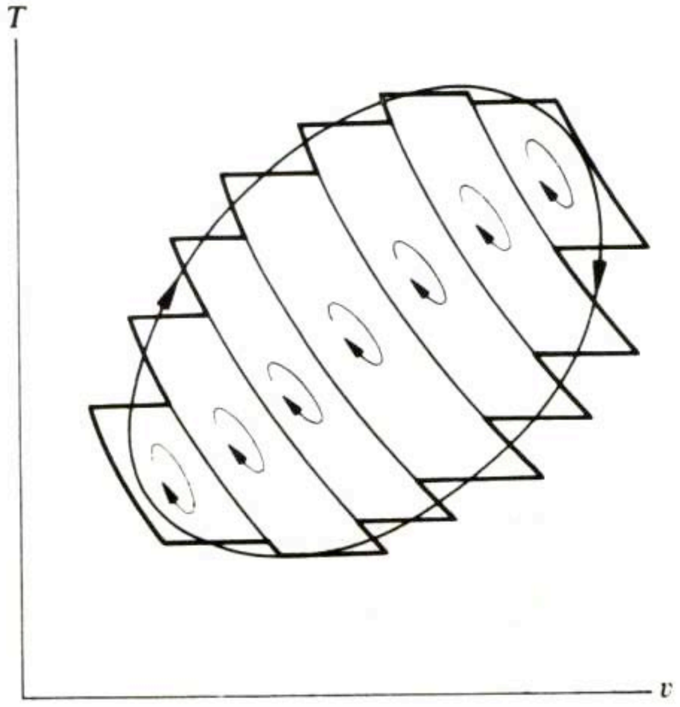


Fig. 5–3 Any arbitrary reversible cyclic process can be approximated by a number of small Carnot cycles.

Adding up Carnot cycles

- **Let's consider this mathematically now. You'll remember for a Carnot cycle that:**

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c} \qquad \textbf{(14.13)}$$

We can instead rewrite this as:

$$\frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0 \qquad \textbf{(16.1)}$$

which is equivalent to saying that the entropy S of the engine is constant (i.e., isentropic) because the entropy coming into our engine $\Delta S_{\text{in}} = Q_h/T_h$ is equal to the entropy leaving our engine $\Delta S_{\text{out}} = Q_c/T_c$.

Adding up Carnot cycles

To prove we can add cycles together, let's begin with the simplest possible case, shown right. Here we consider adding cycles 1 and 2 to get cycle 3. For engine1, we would have:

$$\frac{Q_{1h}}{T_2} = \frac{Q_{1c}}{T_1} \quad \text{or} \quad \frac{Q_{1h}}{T_2} - \frac{Q_{1c}}{T_1} = 0 \qquad \textbf{(16.2)}$$

For engine 2, we would have:

$$\frac{Q_{2h}}{T_2} = \frac{Q_{2c}}{T_1} \quad \text{or} \quad \frac{Q_{2h}}{T_2} - \frac{Q_{2c}}{T_1} = 0 \qquad \textbf{(16.3)}$$

And if we consider engine 3 on its own:

$$\frac{Q_{3h}}{T_2} = \frac{Q_{3c}}{T_1} \quad \text{or} \quad \frac{Q_{3h}}{T_2} - \frac{Q_{3c}}{T_1} = 0 \qquad \textbf{(16.4)}$$

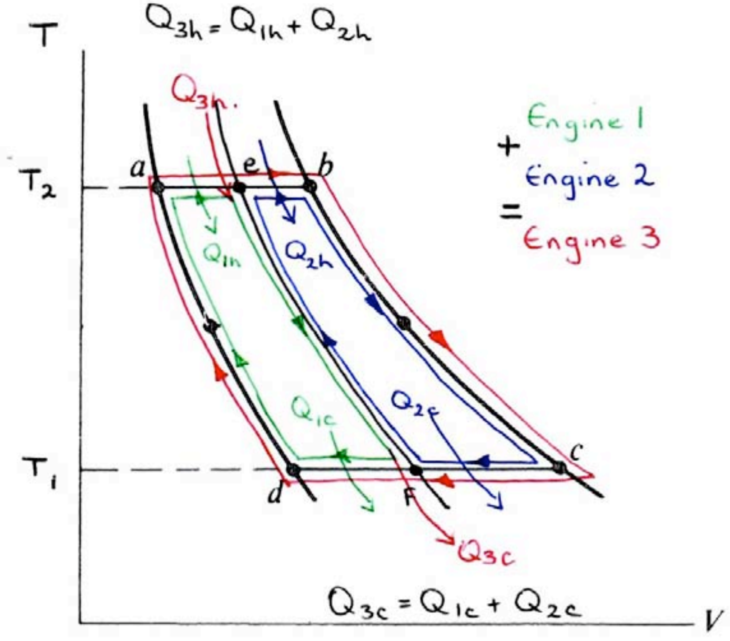


Fig. 5–2 Carnot cycles represented in the T–V plane. Curves a-d, e-F & b-c are reversible adiabatics.

The sum of engine 1 and 2, should give Eqn. 16.4, so lets work that out…

The Clausius equality

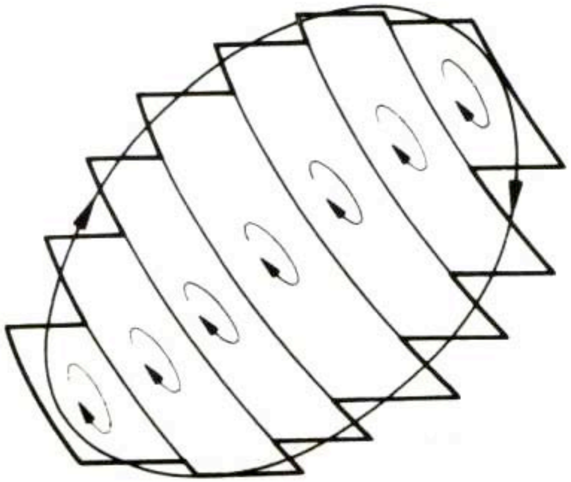
If we now combine cycles 1 and 2, we get:

$$\frac{Q_{1h}}{T_2}-\frac{Q_{1c}}{T_1}+\frac{Q_{2h}}{T_2}-\frac{Q_{2c}}{T_1}=\frac{Q_{1h}+Q_{2h}}{T_2}-\frac{Q_{1c}+Q_{2c}}{T_1}=\frac{Q_{3h}}{T_2}-\frac{Q_{3c}}{T_1}=0 \qquad \textbf{(16.5)}$$

Eqn. 16-5 gives the same answer as Eqn 16-4, showing that we can add up the Carnot cycles to make some arbitrary reversible cycle, as shown below.

You'll also notice that we can add up all the little contributions of Q/T, and just as we do in integration, we arrive at:

$$\sum_i \frac{Q_i}{T_i}=0 \qquad \text{or} \qquad \oint \frac{dQ_r}{T}=0 \qquad \textbf{(16.6)}$$



where the *r* in *Q*$_r$ is a reminder that this holds only for reversible processes.

Eqn. 16-6 is called the Clausius equality – a general result for *all* reversible cyclic processes.

Entropy

Let’s think a moment about what Eqn. 16-6 really means.

$$\sum_i \frac{Q_i}{T_i} = 0 \qquad \text{or} \qquad \oint \frac{dQ_r}{T} = 0 \tag{16.6}$$

The heat flow dQ_r into the system at any point is divided by the temperature T of the system at that point, and if these quotients are summed over the entire closed cycle, the sum equals zero.

Note that dQ_r is sometimes positive and sometimes negative, but T is positive always, so over a complete cycle the negative dQ_r/T contributions cancel out the positive ones, just like we saw in Eqns. 16-1, 16-2, 16-3 and 16-5.

Since the integral of any exact differential around a closed path is zero (a differential that has the same value for all processes between initial and final states, two examples are dV and dU – keep these in mind, you will soon see something significant regarding these), we can see from Eqn. 16-6 that dQ_r/T is an exact differential.

Entropy

We can therefore define a property of the system *S* whose value depends only on the state of the system (in other words, we've discovered yet another state variable to join *U*, *P*, *V* and *T*. In contrast, *W* and *Q* aren't state variables they're transfer variables), and whose differential is:

$$dS = \frac{dQ_r}{T} \tag{16.7}$$

We've now discovered the entropy *S*, exactly as Clausius first defined it in 1865. He called it entropy, after the greek word meaning 'transformation' and because it sounds like energy, since he noticed that in reversible processes entropy was conserved much like energy is. Combining Eqns 16-6 and 16-7, we get:

$$\oint dS = 0 \tag{16.8}$$

which means that, for a reversible cycle at least, the change in entropy *dS* is zero (same as *dU* and *dV* around a closed cycle).

Entropy

Another property of an exact differential (as you should all know from your real analysis course) is that its integral between any two points (not forming a closed cycle) depends only on the two points and not on the path between them. Hence for any path between states *a* and *b* we can write:

$$\int_a^b dS = S_b - S_a \qquad \textbf{(16.9)}$$

Hence entropy *S* is a state variable of a system, it has units J/K and it’s an extensive property (which means if I double the mass or number of particles in the system the entropy also doubles. In contrast, temperature is an intensive variable).

For the moment, it is important to realise that entropy is a relative variable not an absolute variable – hence the absolute value of the entropy has no real meaning (ditto for energy, really) all that matters are relative values.

Just to recap…

Now here comes a really nice bit of physics, because now we can link up a trail of ‘second laws’ that we’ve been creating in the last few lectures.

Just to recap, we have:

1. **Kelvin-Planck statement:** You can’t have a 100% efficient engine where Q_h all gets converted to W and $Q_c = 0$.

2. **Clausius statement:** You can’t have a 100% (COP = 1) efficient fridge where Q_c gets transmitted from the cold reservoir to the hot reservoir without an input of work.

3. We logically proved that the Kelvin-Planck and Clausius statements are equivalent.

4. **Carnot statement:** No real (irreversible) heat engine operating between two energy reservoirs can be more efficient than a Carnot (reversible) engine operating between the same two reservoirs.

5. We also logically proved that the Carnot statement is equivalent to KP and C.

6. Finally, last lecture we looked at entropy from a microscopic perspective and found that any spontaneous process heads toward a state with the highest entropy.

Linking it all together

We are now ready to unify all these things – in other words, build the bridge from Carnot's theorem across to the entropic statement of the second law and the principle of increasing entropy, to complete the puzzle. So let's start from Carnot's theorem, which states that:

$$e \leq e_C \qquad \textbf{(16.10)}$$

the equality only holding for a reversible process. Now $e = 1 - Q_c/Q_h$, and while the same result holds for e_C, there we can use our final result in Eqn. 14-10 to say $e_C = 1 - T_c/T_h$, so:

$$1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h} \qquad \textbf{(16.11)}$$

$$-\frac{Q_c}{Q_h} \leq -\frac{T_c}{T_h} \qquad \textbf{(16.12)}$$

$$\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \qquad \textbf{(16.13)}$$

Linking it all together

$$\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \tag{16.13}$$

Just a quick reality check on Eqn. 16-13: If we make Q_h equal to that of a Carnot engine operating between the same two reservoirs at T_c and T_h, then W would be less than the Carnot engine and Q_c more, which gives the result in Eqn. 16-13.

Likewise if we make Q_c equal to that of a Carnot engine, then both W and Q_h will be less than for the Carnot engine ($e = 1 - Q_c/Q_h$) and again we get Eqn. 16-13.

If we now multiply both sides of Eqn. 16-13 by Q_h/T_c, then:

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \quad \text{or} \quad \Delta S_{out} \geq \Delta S_{in} \tag{16.14}$$

Possibility 1

$$\frac{Q_c}{T_c} \ge \frac{Q_h}{T_h} \qquad \text{or} \qquad \Delta S_{out} \ge \Delta S_{in} \qquad \textbf{(16.14)}$$

In Eqn 16-14 we have two changes in entropy ΔS and we’re comparing them. We need to be very careful about what they relate to, there are two clear possibilities:

The system alone: Here we have $\Delta S_{in} = Q_h/T_h$ coming in from the hot reservoir and $\Delta S_{out} = Q_c/T_c$ leaving to the cold reservoir. Eqn. 16-14 says that $\Delta S_{out} \ge \Delta S_{in}$ and so as we did earlier with Eqn. 16-1:

$$\Delta S_{total} = \Delta S_{in} - \Delta S_{out} = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \le 0 \qquad \textbf{(16.15)}$$

An important question is, does this violate the second law because ΔS isn’t greater than zero?

Well no, the second law deals with the universe as we’ll see below. What’s happening here is that the engine is putting out more entropy than it’s bringing in and this is reflected by a net entropy change for the engine as a system that’s less than zero. This happens quite frequently.

Possibility 2

$$\frac{Q_c}{T_c} \ge \frac{Q_h}{T_h} \qquad \text{or} \qquad \Delta S_{out} \ge \Delta S_{in} \tag{16.14}$$

In Eqn 16-14 we have two changes in entropy ΔS and we're comparing them. We need to be very careful about what they relate to, there are two clear possibilities:

The system and surroundings: If we consider the system and surroundings together (i.e., the universe) then the total entropy will be the sum of the entropies of the two separate parts – system and surroundings. Lets consider what happens to each separately.

First, we transfer some entropy $\Delta S_{in} = Q_h/T_h$ from the surroundings to the system, so the entropy of the surroundings falls and the entropy of the system increases.

Second, we transfer some entropy $\Delta S_{out} = Q_c/T_c$ back from the system to the surroundings again.

But as we know from Eqn 16-14, $\Delta S_{out} \ge \Delta S_{in}$, so the total entropy of the universe will increase by $\Delta S = \Delta S_{out} - \Delta S_{in} \ge 0$, exactly as we'd expect from the second law.

The Clausius inequality

- **What does this mean physically?**

As a net process, all we've done is pass entropy from surroundings to system and back again, but somehow the surroundings' 'loan of some entropy' to the system has grown (or at best remained constant) while it was in the system's hands. In a sense, Schroeder puts it quite nicely in his book when he says:

> ***"In this context, I like to imagine entropy as a fluid that flows around with heat and that can be created but never destroyed."***

We can apply this result directly to Eqn 21-6, and so we get:

$$\sum_i \frac{Q_i}{T_i} \geq 0 \qquad \text{or} \qquad \oint \frac{dQ}{T} = \oint dS \geq 0 \qquad \textbf{(16.16)}$$

Eqn. 16-16 is called the Clausius inequality, and guess what? It's just the mathematical version of the principle of increase in entropy, because it says that any irreversible engine will lead to an increase in the total entropy of the universe, and at best entropy is conserved, but most importantly, entropy isn't going to decrease.

This is a nice result, we've now hooked all the versions of the 2nd law together.

Summary

- **Any arbitrary reversible cycle can be approximated as the sum of a finite number of small Carnot cycles.**

- **This fact leads to the Clausius equality for any reversible cycle, namely that $\Sigma\, Q/T = 0$ or the integral of dS over a closed reversible cycle equals zero.**

- **The Clausius equality leads to the definition of entropy, which is a state variable like volume and internal energy and an exact differential (i.e., dependent only on initial and final values and not on the path).**

- **Carnot's theorem leads to what is known as the Clausius inequality, $\Sigma\, Q/T \geq 0$ or $\Delta S \geq 0$, where the equality holds for reversible processes and > holds for irreversible processes. This is equivalent to the principle of increasing entropy and is yet another statement of the 2nd law.**

- **Irreversible processes lead to the creation of new entropy, and are often hard to deal with due to inhomogeneities and are best approximated as inefficient reversible processes.**

In the next lecture we will look at the ramifications of the second law in two of thermodynamics' most interesting problems – the arrow of time and Maxwell's demon.