Thermodynamics
Second Law
The Carnot Engine

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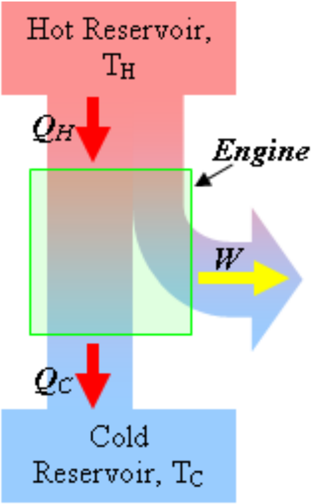
Last time

- entropy (microscopic perspective)
- heat engines
- heat pumps

Overview

- wrap up heat pumps
- Carnot engines
- efficiency of a Carnot engine
- entropy in a Carnot cycle (?)

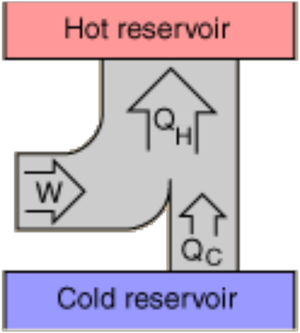
Heat Engines



[1]Diagram from http://www2.ignatius.edu/faculty/decarlo/

Heat Pump

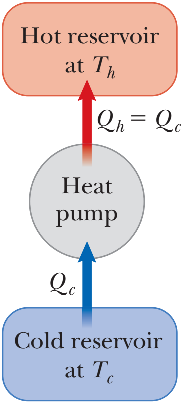
Refrigerators work by taking electrical energy, converting it to work, then pumping heat from a cold area to a hotter one.



This type of process, where work is converted into a heat transfer from a colder object to a hotter one is called a **heat pump**.

[1]Diagram from http://hyperphysics.phy-astr.gsu.edu

"Perfect" but Impossible Heat Pump



This heat pump (using no work) violates our first statement of the second law, since heat spontaneously goes from a cooler reservoir to a hotter one.

More formally, the Clausius statement of the second law:

Second Law of thermodynamics (Clausius)

It is impossible to construct a cyclical machine whose sole effect is to transfer energy continuously by heat from one object to another object at a higher temperature without the input of energy by work.

[1] Diagram from Serway and Jewett.

Question

Suppose you have a house with very excellent insulation. If you leave the door to your refrigerator open for the day, what happens to the temperature of your house?

(A) It increases.

(B) It decreases.

(C) It stays the same.

Carnot Engines

Sadi Carnot wanted to find the **fundamental limit of how efficient a heat engine could be**.

He imagined a theoretical engine (now called the Carnot engine) that was as efficient as possible.

He realized that no engine would be more efficient than a reversible one.

Only in a reversible process will no energy be lost to friction or turbulence in the fluid.

Carnot Engines

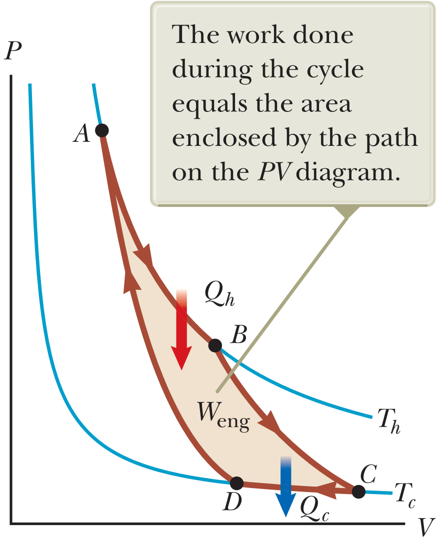
Carnot specified that his heat engine should use just two thermal reservoirs, each at constant temperature, T_h and T_c.

In order to be reversible, the heat must be exchanged in the cycle only when the engine fluid's temperature matches that of the reservoir with which it is in contact. $\Rightarrow$ Isothermal processes

The other parts of the cycle must be adiabatic ($Q = 0$).

(The Carnot engine is *the* reversible engine cycle you can operate between just two thermal reservoirs at constant temperature.)

The Carnot Cycle



Maximum Efficiency of an Engine

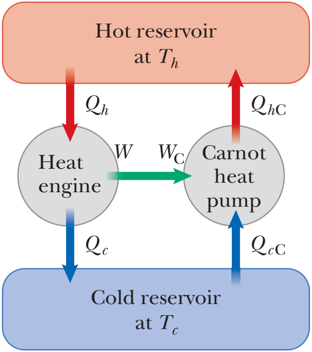
Assume a Carnot engine has efficiency e_C.

Now supoose it was possible to construct an engine (reversible or irreversible) that is even more efficient, with efficiency $e > e_C$.

Since the Carnot cycle is reversible, we could run the Carnot engine in reverse as a heat pump.

Maximum Efficiency of an Engine

Putting the imagined engine and the Carnot heat pump together:



Now, the work from the hypothetical engine drives the Carnot heat pump, so $W = W_C$

$$e > e_C \quad \Rightarrow \quad \frac{|W|}{|Q_h|} > \frac{|W_C|}{|Q_{hC}|}$$

Maximum Efficiency of an Engine

$$e > e_C \quad \Rightarrow \quad \frac{|W|}{|Q_h|} > \frac{|W|}{|Q_{hC}|}$$

This means

$$|Q_h| < |Q_{hC}|$$

We also know that $|W| = |Q_h| - |Q_c|$ (energy conservation). Since the works are equal:

$$\begin{aligned} W &= W_c \\ |Q_h| - |Q_c| &= |Q_{hC}| - |Q_{cC}| \end{aligned}$$

Rearranging:

$$|Q_{hC}| - |Q_h| = |Q_{cC}| - |Q_c|$$

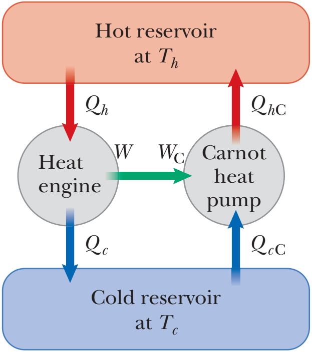
But the LHS is positive if $e > e_C$.

Heat arrives at the hot reservoir and leaves the cold one! $\Rightarrow$ Violates the Second Law.

Maximum Efficiency of an Engine

Putting the imagined engine and the Carnot heat pump together:

$$|Q_{hC}| - |Q_h| > 0$$



$\uparrow$ $Q_{h,\text{net}}$

$$|Q_{cC}| - |Q_c| > 0$$

$\uparrow$ $Q_{c,\text{net}}$

Violates the Second Law.

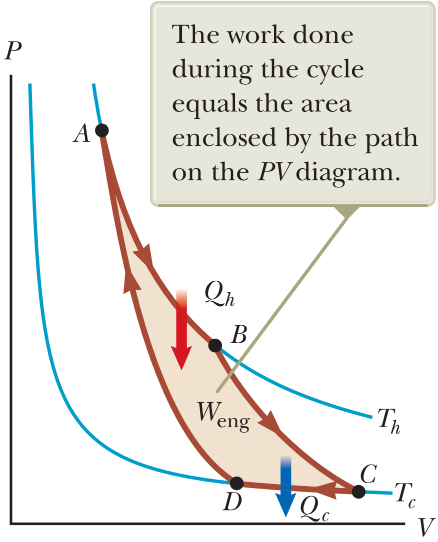
Carnot's Theorem

Carnot's Theorem

No real heat engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

But how efficient is a Carnot engine?

The Carnot Cycle



Efficiency of a Carnot Engine

First, we can relate the volumes at different parts of the cycle.

In the first adiabatic process:

$$T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1}$$

In the second adiabatic process:

$$T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1}$$

Taking a ratio, then the $\gamma - 1$ root:

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Efficiency of a Carnot Engine

First law: $\Delta E_{\text{int}} = Q + W = 0$ gives for the first isothermal process

$$|Q_h| = nRT_h \ln\left(\frac{V_B}{V_A}\right)$$

Second isothermal process:

$$|Q_c| = nRT_c \ln\left(\frac{V_C}{V_D}\right)$$

We will take a ratio of these to find the efficiency. Noting that $\frac{V_B}{V_A} = \frac{V_C}{V_D}$:

$$\frac{|Q_c|}{|Q_h|} = \frac{|T_c|}{|T_h|}$$

Efficiency of a Carnot Engine

Recall, efficiency of a heat engine:

$$e = 1 - \frac{|Q_c|}{|Q_h|}$$

Efficiency of a Carnot engine:

$$e = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$

(T is measured in Kelvin!)

This is the most efficient that any heat engine operating between two reservoirs at constant temperatures can be.

Third Law of Thermodynamics

3rd Law

As the temperature of a material approaches zero, the entropy approaches a constant value.

The constant value the entropy takes is very small. It is actually zero if the lowest energy state of the material is unique.

Another way to express the third law:

3rd Law - alternate

It is impossible to reach absolute zero using any procedure and only a finite number of steps.

Heat Engine question

Consider and ocean thermal energy conversion (OTEC) power plant that operates on a temperature difference between deep 4°C water and 25°C surface water. Show that the Carnot (ideal) efficiency of this plant would be about 7%.

[0] Hewitt, page 331, problem 2.

Clausius Equality

Clausius found that the entropy change around any reversible cycle (closed path) is zero.

This is called the Clausius Equality:

$$\Delta S = \oint \frac{dQ_r}{T} = 0$$

This follows directly from the fact that entropy is a state variable (though that was not obvious initially).

If a heat engine works in a cycle, the entropy change of the engine over the cycle is zero.

Entropy in the Carnot Cycle

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We can see this from an analysis also:

$$\Delta S = \int \frac{1}{T}\, \mathrm{d}Q_{\mathrm{r}}$$

In the reversible adiabatic processes

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In the reversible adiabatic processes $\Delta S = 0$.

In the reversible isothermal portions, T is constant so $\Delta S = \frac{Q}{T}$.

For the cycle

$$\Delta S_{\mathrm{eng}} = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}$$

Entropy in the Carnot Cycle

For the cycle

$$\Delta S_{\text{eng}} = \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}$$

We just found that

$$\frac{|Q_h|}{|Q_c|} = \frac{T_h}{T_c}$$

So

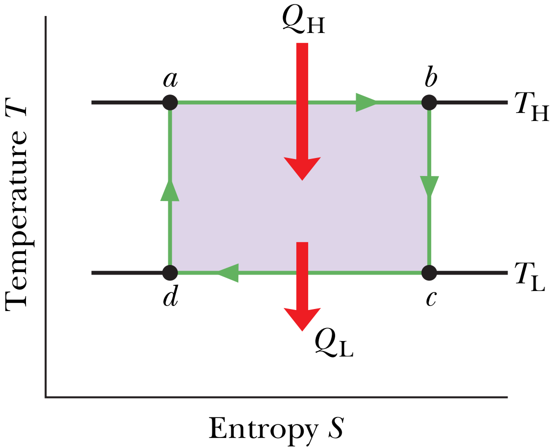
$$\frac{|Q_h|}{T_h} = \frac{|Q_c|}{T_c}$$

And for the cycle

$$\Delta S_{\text{eng}} = 0$$

Entropy in the Carnot Cycle

We can represent the Carnot Cycle on a *TS* diagram:



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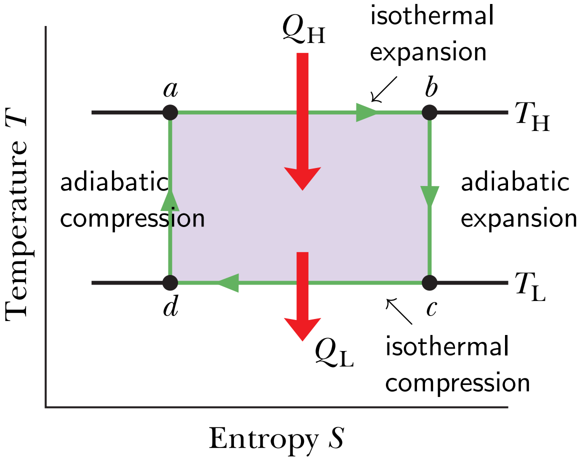

Entropy only changes during the isothermal processes.

Entropy in the Carnot Cycle

What is the energy change of the surroundings (the thermal reservoirs) for a Carnot engine?

Hot reservoir:

$$\Delta S_{\text{hot}} = -\frac{|Q_h|}{T_h}$$

Cold reservoir:

$$\Delta S_{\text{cold}} = +\frac{|Q_c|}{T_c}$$

However,

$$\frac{|Q_h|}{T_h} = \frac{|Q_c|}{T_c}$$

The total entropy change of the surroundings over the cycle:

$$\Delta S_{\text{surr}} = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = 0$$

Entropy in the Carnot Cycle

The total entropy change of the **engine + surroundings** over the cycle:

$$\Delta S_{\text{net}} = \Delta S_{\text{eng}} + \Delta S_{\text{surr}} = 0$$

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Remember that the engine only exchanges heat with its surroundings when they are at the same temperature. This is necessary for the processes to be reversible.

Entropy in the Carnot Cycle

The total entropy change of the **engine + surroundings** over the cycle:

$$\Delta S_{\text{net}} = \Delta S_{\text{eng}} + \Delta S_{\text{surr}} = 0$$

Remember that the engine only exchanges heat with its surroundings when they are at the same temperature. This is necessary for the processes to be reversible.

In any real, practical engine, some heat transfer occurs when the engine's working fluid is *not* at the same temperature as its surroundings. These are irreversible effects.

The surroundings *do not* quite return to their initial state $\Rightarrow$ entropy of the surroundings *increases*.

$$\Delta S_{\text{net}} > 0$$

Clausius Inequality

Since real engines always involve irreversible processes, the entropy of the **engine + surroundings** will increase:

$$\Delta S = \oint \frac{\mathrm{dQ_r}}{T} \geqslant 0$$

This is called the Clausius Inequality.

Entropy in an isolated system

This gives us another way to state the second law:

2nd Law

In an isolated system, entropy does not decrease. $\frac{dS}{dt} \geqslant 0$

In a non-isolated system (either closed or open) entropy can decrease, but only by increasing the entropy of the environment at least as much.

However, in an isolated system, such as when we include a heat engine and its thermal reservoirs in the system, the entropy cannot decrease.

Summary

- wrapped up heat pumps
- Carnot engines
- efficiency of a Carnot engine
- entropy in a Carnot cycle (?)

Homework

Serway & Jewett (additional problems you might like to look at):

- Ch 22, OQs: 1, 3, 7; CQs: 1; Probs: 20, 73