Thermodynamics
Second Law
Heat Engines

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Last time

- entropy (microscopic perspective)

Overview

- entropy (microscopic perspective)

- heat engines

- heat pumps (?)

Entropy in Thermodynamics

Consider the atmosphere, it is mostly Oxygen and Nitrogen.

Have you ever walked into a room and been unable to breathe because all of the oxygen in on the other side of the room?

As more oxygen molecules are added, the probability that there is oxygen is on both sides increases.

Macrostates and Microstates

A **macrostate** is something we can observe on a large scale.

The macrostates here could be:
- all oxygen on the left
- all oxygen on the right
- oxygen mixed throughout the room.

Macrostates and Microstates

A **microstate** is a state too small / complex to easily observe, but represents one way a macrostate can be achieved.

We want to consider the number of microstates for each macrostate.

The macrostates here could be:
- all oxygen on the left — 1 microstate
- all oxygen on the right — 1 microstate
- oxygen mixed throughout the room — 6 microstates

Suppose all of the microstates are equally likely. If so, even with only 3 molecules, we would expect to find the oxygen distributed throughout the room (75% probability).

$$S = -k_B \sum_i p_i \ln p_i$$

Entropy of the "all on the left" macrostate:

$$S_L = k_B \ln 1 = 0$$

Entropy of the "mixed" macrostate:

$$S_M = k_B \ln 6 \approx 1.8 k_B$$

The entropy of the "mixed" macrostate is higher!

Boltzmann's formula

The entropy of a macrostate can be written:

$$S = k_B \ln W$$

where W is the number of microstates for that macrostate, assuming all microstates are equally likely.

W is the number of *ways* the macrostate can occur.

Entropy and disorder

A macrostate that has very many microstates can be thought of as a disordered state.

If all the oxygen is on the left of the room, all the nitrogen on the right, the room is organized, or ordered.

But this is very unlikely!

Even if a room starts out ordered, you would expect it to become disordered right away, because a disordered room is more probable.

Entropy example

Imagine throwing two dice. The score of the dice will be the sum of the two numbers on the dice.

What score should you bet on seeing?

[1]Hewitt, 'Conceptual Physics', Problem 8, page 331.

Entropy example

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What is the number of microstates associated with that score?

What is the number of microstates associated a score of 2?

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Entropy example

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The macroscopic world is like a game in which there are $\sim 10^{23}$ dice, but you only ever see the (approximate) score, not the result on each dice.

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[1]Hewitt, 'Conceptual Physics', Problem 8, page 331.

Second Law of Thermodynamics

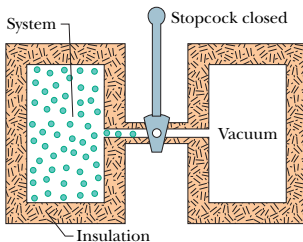This is another equivalent way to state the second law.

Heat must flow from hotter to colder because there are more ways to distribute energy evenly than to keep it in one place only.

$$\frac{\Delta S}{\Delta t} \geqslant 0$$

As time goes by, things tend to disorder.
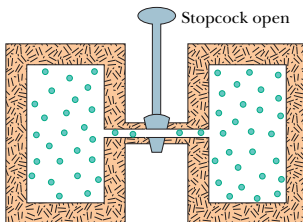
Second Law of Thermodynamics

ordered,
less probable,
low entropy

System — Stopcock closed

Vacuum

— Insulation

(a) Initial state i

Irreversible process

Stopcock open

disordered,
more probable,
high entropy

(b) Final state f

Example (Microscopic Entropy Analysis)

What is the entropy change during an adiabatic free expansion of an isolated gas of n moles going from volume V_i to volume V_f? (Note: such a process is not reversible.)

Two approaches: microscopic and macroscopic (seen earlier).

Now for **microscopic**. We need some way to count microstates of the gas.

Let's break up our volume, V, into a grid and say there are m different locations a gas particle could be in.[1] Let N be the number of particles and $m \gg N$.

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[1]Serway & Jewett, pg 671.

Example

Let V_m be the volume of one grid unit, so $m = V/V_m$.

How many ways can we place the particles? The first can be placed in any of $w = V/V_m$ places. For each of those positions, the second can be placed in w locations, giving w^2 ways in total.

For N, there are $w^N = \left(\frac{V}{V_m}\right)^N$ ways the particles can be arranged in the volume V.

This gives

$$S = Nk_B \ln \left(\frac{V}{V_m}\right)$$

Example

There are reasons to quibble over how we counted the microstates, but let us think what this gives us for the change in entropy.

We have a final volume V_f and an initial volume V_i:

$$\Delta S = Nk_B \ln \left(\frac{V_f}{V_m} \right) - Nk_B \ln \left(\frac{V_i}{V_m} \right)$$

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So,

$$\Delta S = Nk_B \ln \left(\frac{V_f}{V_i} \right)$$
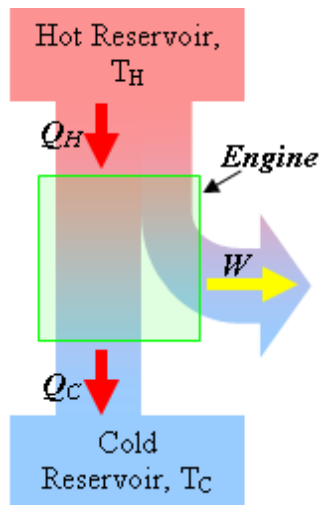
The same as for the macroscopic analysis!

Heat Engines

Steam engines and later incarnations of the engine run on a very simple principle: heat is transferred from a hot object to a colder object and mechanical work is done in the process.

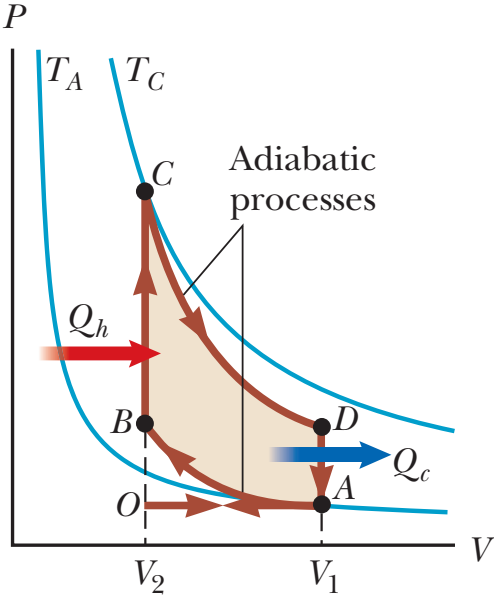Heat engines run in a cycle, returning their *working fluid* back to its initial state at the end of the cycle.

In practice, usually some chemical energy (burning fuel) is used to raise the temperature of one object, and the colder object remains at the ambient temperature.

Heat Engines

Example of a Heat Engine Cycle

Efficiency of a Heat Engine

The working fluid returns to its initial state, so in the entire cycle $\Delta E_{\text{int}} = 0$.

First law:

$$\Delta E_{\text{int}} = W + Q = 0$$

where W is the work done *on* the system.

This means

$$W_{\text{eng}} = Q_{\text{net}} = |Q_h| - |Q_c|$$

where W_{eng} is the work done *by* the engine (working fluid).

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We define the **efficiency** to be:

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

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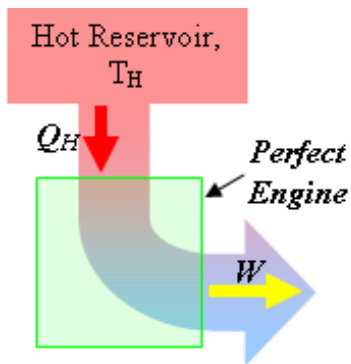
Ideally, we would like to have an efficiency of 1.

This would mean all heat that enters our fluid is converted to work.

Since we usually supply this heat through a chemical reaction, ideally all the energy from the reaction would become useful work.
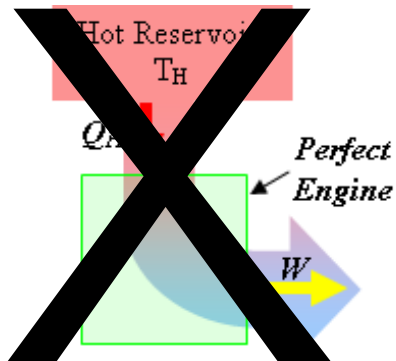
"Perfect" but Impossible Engine

It would be nice if all heat energy Q_h could be converted to work.

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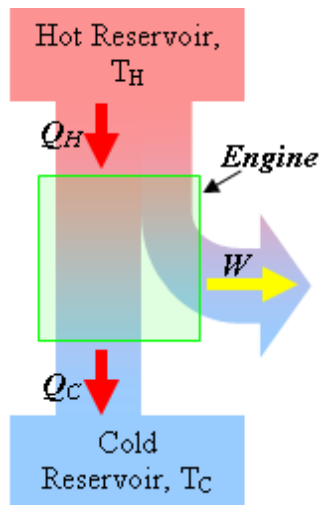But this is not possible.

We will see why shortly.

Second Law and Heat Engines

We can state the second law also as a fundamental limitation on heat engines.

Second Law of Thermodynamics (Heat Engine version)

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the input of energy by heat from a reservoir and the performance of an equal amount of work.
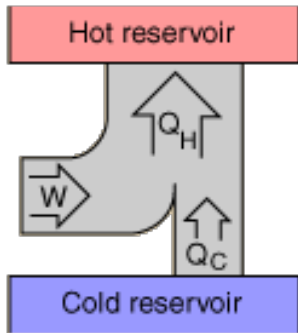
Heat Engines

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**.

Heat Pump Coefficient of Performance

The effectiveness of a heat pump isn't well represented with our previous definition of efficiency, since now the resource we are considering is work.

Instead we use the **Coefficient of Performance**, COP.

We can use heat pumps for two different purposes:

- to further heat an object (*eg.* a house) that is warmer than its surroundings
- to cool an object (*eg.* in a refrigerator) that is cooler than its surroundings

Each purpose has its own COP.

Heat Pump Coefficient of Performance

For cooling (refrigeration):

$$\text{COP (cooling)} = \frac{|Q_c|}{W}$$

Typical refrigerator COPs are around 5 or 6.

For heating:

$$\text{COP (heating)} = \frac{|Q_h|}{W}$$

Question

Quick Quiz 22.2[2] The energy entering an electric heater by electrical transmission can be converted to internal energy with an efficiency of 100%.

By what factor does the cost of heating your home change when you replace your electric heating system with an electric heat pump that has a COP of 4.00?

Assume the motor running the heat pump is 100% efficient.

(A) 4.00

(B) 2.00

(C) 0.500

(D) 0.250

[2]Serway & Jewett, page 658.

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Summary

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