Thermodynamics
Second Law
Entropy

Lana Sheridan

De Anza College

May 13, 2020

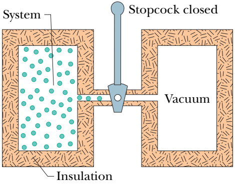
Last time

- entropy (macroscopic perspective)

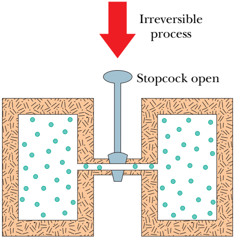
Overview

- entropy (microscopic perspective)

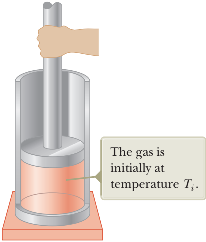
Irreversible & Reversible Processes Example



(a) Initial state i

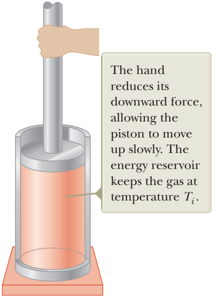


(b) Final state f



The gas is initially at temperature T_i.

Energy reservoir at T_i



The hand reduces its downward force, allowing the piston to move up slowly. The energy reservoir keeps the gas at temperature T_i.

Energy reservoir at T_i

Example (Macroscopic 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.)

Example (Macroscopic 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.)

In an adiabatic free expansion $Q = 0$, and since its isolated, $W = 0$, and therefore $\Delta E_{\text{int}} = 0$ and $T_f = T_i$.

$$\Delta S = nC_v \ln \left(\frac{T_f}{T_i} \right) + nR \ln \left(\frac{V_f}{V_i} \right)$$

Example (Macroscopic 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.)

In an adiabatic free expansion $Q = 0$, and since its isolated, $W = 0$, and therefore $\Delta E_{\text{int}} = 0$ and $T_f = T_i$.

$$\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

using $\ln 1 = 0$ becomes

$$\underline{\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)}$$

Example

Exercise for you:

What is the entropy change the same *n* moles of gas (a diatomic gas around room temperatures) in an constant volume process, with temperature going T_i to T_f?

What is the entropy change when the pressure is constant and the volume goes V_i to V_f?

Question

Quick Quiz 22.5[1] An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths. Path A is at constant pressure, and path B is at constant volume. What is the relation between the entropy changes of the gas for these paths?

(A) $\Delta S_A > \Delta S_B$

(B) $\Delta S_A = \Delta S_B$

(C) $\Delta S_A < \Delta S_B$

---

[1] Serway & Jewett, page 673.

Question

Quick Quiz 22.5[1] An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths. Path A is at constant pressure, and path B is at constant volume. What is the relation between the entropy changes of the gas for these paths?

(A) $\Delta S_A > \Delta S_B \longleftarrow$

(B) $\Delta S_A = \Delta S_B$

(C) $\Delta S_A < \Delta S_B$

---

[1] Serway & Jewett, page 673.

Entropy Microscopically

So far, we have seen that entropy is measuring something about how energy is distributed in our system. However, that's not the only thing entropy can represent.

Entropy Microscopically

So far, we have seen that entropy is measuring something about how energy is distributed in our system. However, that's not the only thing entropy can represent.

Entropy is a measure of disorder in a system.

It can also be used as a measure of information content.

Intriguingly, entropy was introduced separately in physics and then later in information theory. The fact that these two measures were the same was observed by John von Neumann.

Entropy

According to Claude Shannon, who developed Shannon entropy, or information entropy:

"I thought of calling it 'information', but the word was overly used, so I decided to call it 'uncertainty'. [...] Von Neumann told me, 'You should call it entropy, for two reasons. In the first place your uncertainty function has been used in statistical mechanics under that name, so it already has a name. In the second place, and more important, nobody knows what entropy really is, so in a debate you will always have the advantage.' "

So what is entropy?

Consider the Yo. app (valued at $5-10 million in 2014).

You (originally) could only use it to send the message "yo."

If you get a message on the app, you can guess what it will say.

So what is entropy?

Consider the Yo. app (valued at $5-10 million in 2014).

You (originally) could only use it to send the message “yo.”

If you get a message on the app, you can guess what it will say.

The message has no information content, and it is perfectly ordered, there is no uncertainty.

The message is a physical system that can only be in one state.

So what is entropy?

But what if the message is only sent with 50% probability?

"If you get the message, let's meet for drinks, if not, I'm still in a meeting and can't join you."

So what is entropy?

But what if the message is only sent with 50% probability?

"If you get the message, let's meet for drinks, if not, I'm still in a meeting and can't join you."

Now you learn something when you get the message.

The information content is 1 bit.

So what is entropy?

But what if the message is only sent with 50% probability?

“If you get the message, let’s ‘meet’ (on Zoom) for drinks, if not, I’m still in a meeting and can’t join you.”

Now you learn something when you get the message.

The information content is 1 bit.

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

For the fully-determined message “yo”:

$$\begin{aligned} H(m) &= -1 \log 1 - 0 \log 0 \\ &= 0 \text{ bits} \end{aligned}$$

So what is entropy?

(Shannon) Entropy of a message m:

$$H(m) = -\sum_i p_i \log p_i$$

where p_i is the probability of receiving message i.

For the fully-determined message “yo”:

$$\begin{aligned} H(m) &= -1 \log 1 - 0 \log 0 \\ &= 0 \text{ bits} \end{aligned}$$

For the “yo”-or-no message:

$$\begin{aligned} H(m) &= -\frac{1}{2} \log \frac{1}{2} - \frac{1}{2} \log \frac{1}{2} \\ &= \log 2 \\ &= 1 \text{ bit} \end{aligned}$$

Entropy in Thermodynamics

In physics, we express entropy a little differently:

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

p_i is the probability of being in the ith microstate, given you are in a known macrostate.

k_B is called the Boltzmann constant.

$$k_B = 1.38 \times 10^{-23} \text{J K}^{-1}$$

Notice that this changes the units of entropy to J / K.

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?

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?

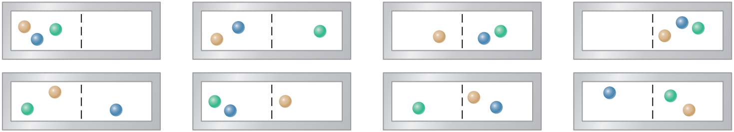
As more oxygen molecules are added, the probability that there is oxygen is on both sides increases.

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.



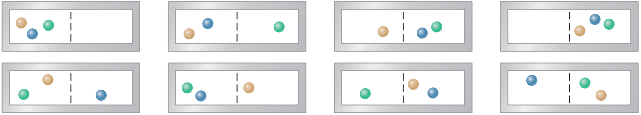
Macrostates and Microstates

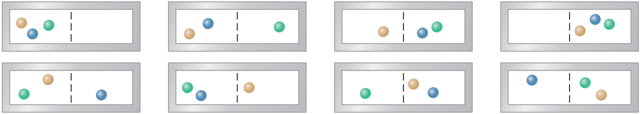
A **microstate** is a state too small / complex to easily observe, but represents one way a macrostate can be achieved.

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.

Summary

- entropy (microscopic perspective)