Entropy and Probability

(A statistical view)

Entropy ~ a measure of the disorder of a system.

A state of high order = low probability
A state of low order = high probability

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.

We will illustrate the concepts by considering the free expansion of a gas from volume \( V_i \) to volume \( V_f \).

The gas always expands to fill the available space. It never spontaneously compresses itself back into the original volume.
First, two definitions:

**Microstate:** a description of a system that specifies the properties (position and/or momentum, etc.) of each individual particle.

**Macrostate:** a more generalized description of the system; it can be in terms of macroscopic quantities, such as P and V, or it can be in terms of the number of particles whose properties fall within a given range.

In general, each *macrostate* contains a large number of *microstates*.

**An example:** Imagine a gas consisting of just 2 molecules. We want to consider whether the molecules are in the left or right half of the container.
There are 3 macrostates: both molecules on the left, both on the right, and one on each side.

There are 4 microstates: LL, RR, LR, RL.

How about 3 molecules? Now we have: LLL, (LLR, LRL, RLL), (LRR, RLR, RRL), RRR

(all L)  (2 L, 1 R)  (2 R, 1 L)  (all R)

i.e. 8 microstates, 4 macrostates

How about 4 molecules? Now there are 16 microstates and 5 macrostates

(all L) (3L, 1R) (2L, 2R) (1L, 3R) (all R)

1 4 6 4 1

number of microstates
In general:

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\[
W_{N,n} = \frac{N!}{N! \ (N-n)!}
\]

i.e. \(W_{6,2} = \frac{6!}{2! \ 4!} = 15\)

“multiplicity”

This table was generated using the formula for # of permutations for picking \(n\) items from \(N\) total:

\[
W_{N,n} = \frac{N!}{N! \ (N-n)!}
\]

i.e. \(W_{6,2} = \frac{6!}{2! \ 4!} = 15\)
**Fundamental Assumption of Statistical Mechanics:** All microstates are equally probable.

Thus, we can calculate the likelihood of finding a given arrangement of molecules in the container.

E.g. for 10 molecules:
Conclusion: Events such as the spontaneous compression of a gas (or spontaneous conduction of heat from a cold body to a hot body) are not impossible, but they are so improbable that they never occur.
We can relate the number of microstates $W$ of a system to its entropy $S$ by considering the probability of a gas to spontaneously compress itself into a smaller volume.

If the original volume is $V_i$, then the probability of finding $N$ molecules in a smaller volume $V_f$ is

$\text{Probability} = \frac{W_f}{W_i} = \left(\frac{V_f}{V_i}\right)^N$

$\ln(W_f/W_i) = N \ln(V_f/V_i) = n N_A \ln(V_f/V_i)$

We have seen for a free expansion that

$\Delta S = n R \ln(V_f/V_i)$,

so

$\Delta S = \left(\frac{R}{N_A}\right) \ln(W_f/W_i) = k \ln(W_f/W_i)$

or

$S_f - S_i = k \ln(W_f) - k \ln(W_i)$
Thus, we arrive at an equation, first deduced by Ludwig Boltzmann, relating the entropy of a system to the number of microstates:

\[ S = k \ln(W) \]

He was so pleased with this relation that he asked for it to be engraved on his tombstone.