

# Chapter 5:: The 2nd law of thermodynamics

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# Entropy

## Abstract

Entropy is a measure of the degree of disorder/randomness in an arbitrary system. We can use this concept to discuss matters such as spontaneous and non spontaneous processes.

## Spontaneous & non spontaneous processes

A spontaneous change is one that occurs without a continuous input of energy from an outside system. A good example would be gravitational potential. We can increase the rate of a spontaneous process by introducing a catalyst to the system. **A spontaneous process is not always fast.**

Non spontaneous processes aren't impossible, but they require input of external energy or a **more spontaneous** reaction to proceed.

## Example

A good example of an impossible spontaneous process is a ball starting to bounce on a surface spontaneously. This would require all particles under it (approx  $6.02E23$  particles) to start vibrating in the same direction at the same time. The chance of this being possible is basically 0.

## Estimating spontaneity

The first law of thermodynamics accounts for energy in a system, but it does not predict the spontaneity of the energy transfer involved. We will use entropy to do this. A process is spontaneous if and only if  $\Delta S > 0$ .

## Entropy as a state function

Entropy is a measure of how dispersed the energy of a system is (in units of  $\frac{J}{K}$ ). We can start with this property::

$$\Delta S_{\Omega} = \Delta S_{\sigma} + \Delta S_{\bar{\sigma}}$$

Where  $\Omega$  is the universe,  $\sigma$  is an arbitrary system, and  $\bar{\sigma}$  is the surroundings. To calculate the absolute entropy of a system, the following formula is used::

$$S = k_b \ln(W) \implies \Delta S = k_b (\ln(W_0) - \ln(W_1))$$

Where  $k_b = 1.38E - 23 \frac{J}{K}$  is the boltzman constant, and  $W = 2^n$  is the number of possible arrangements of position and energy of all molecules in the system (microstates) for  $n \in \mathbb{N}$  particles. The macrostate with the **highest entropy** also has the **greatest dispersal of energy**.

## Multiplicity of energy

Assume we have a hypothetical solid system with four atoms and a total energy of  $E$ . How many ways can we distribute that energy among the 4 atoms? Clearly there are 4 ways to distribute 1 unit of energy among 4 atoms because the system is small. However, if there are  $N$  atoms, and total energy is  $qE$ , then the number of microstates is modelled by the following formula::

$$W(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}$$

## Bringing it all together

A hot and a cold bar, each made up of 4 atoms, are pushed together. What will happen? If the cold bar has 1 quantum of energy and the hot bar has 5 quanta of energy in the initial state, show that heat transfer is spontaneous by calculating  $\Delta S_{\Omega}$  for the process.

We can start by calculating the combinations of microstates for each process.

## Entropy at the molecular level

In any system, when  $T$  increases,  $S$  will also increase proportionally with it. This makes sense because the faster the particles move, the more disorder there is in the system overall.

## Statistical definition of entropy

We can model the change in entropy of a system between two states with the following formula::

$$\Delta S = S_2 - S_1 = k_b \ln\left(\frac{W_2}{W_1}\right)$$

This is possible since entropy is a state function.