

Entropy: The greater the degree of randomness or disorder in a system, the greater its entropy.

Spontaneous Processes

Definition 1 (Spontaneous Processes). A *spontaneous* change is one that occurs *without* a continuous input of energy from outside the system.

It is easy to predict spontaneity in the physical world. Water flows and balls roll downhill spontaneously to reach lower a potential energy in the presence of gravity.

A *catalyst* can increase the *rate* of spontaneous processes. A catalyst, however, cannot do so for a non-spontaneous process. Non-spontaneous processes are not impossible, as they require the input of external energy or coupling to a more spontaneous reaction to proceed.

Consider a tennis ball bouncing. Would it make sense to draw the arrows in the other direction? Potential energy represents nondispersed energy, thermal energy represent dispersed energy. Each time the ball hits the floor, some of its kinetic energy K is dissipated among molecules in the floor, and the floor becomes warmer. Eventually, the ball comes to rest, i.e. all of its kinetic energy K transferred to the floor. This is the processes of inelastic collisions.

Question 1. *Can spontaneous processes occur in the opposite direction?*

For this process to occur, the ball needs to absorb sufficient energy from the floor. Thermal energy of the floor is random molecular motion. The amount of energy needed to raise the ball would require all molecules within the floor to line and vibrate in phase with another.

The answer to Question 1 is NO, as we are given the random nature of molecular motion. The magnitude of energy to have a ball at rest on the floor suddenly starts bouncing into air would be equivalent to having 6.0×10^{23} molecules aligned and vibrating in phase in the upward direction.

Calculating W for complex systems is too difficult. Entropy changes can be measured from changes of other thermodynamics quantities such as q (heat). Later on, we will see that

$$S = \frac{q_{rev}}{T}$$

A process occurs spontaneously in only one direction. The reverse cannot occur spontaneously under the same conditions. How do we know the direction of spontaneity of chemical reactions we are not familiar with? Why doesn't the coffee suck out all the energy out of the cold water?

Recall from the first law of thermodynamics:

- Accounts for energy.
- Does not predict of spontaneous energy transfer.

So we need the second law of thermodynamics, as this law relies on entropy!

Second Law of Thermodynamics

If we consider both the system and the system of the surroundings, we have the following.

Theorem 2 (Second Law of Thermodynamics). *All real processes occur spontaneously in the direction that increases the entropy of the universe.*

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur} > 0$$

Definition 3 (Entropy). Entropy is a thermodynamic quantity that is a measure of how dispersed the energy of a system is among the different possible ways that the system can contain energy.

$$S = k_B \ln \mathcal{W}$$

where

- \mathcal{W} is the number of possible arrangements of position and energy and molecules (microstates and unitless)
- k_B is the Boltzmann constant: 1.38×10^{-23} J/K

The units of S is

$$[S] = [k_B][\ln \mathcal{W}] = \text{J/K}$$

In the following system

- Closed: there is one way to arrange the position.
- Open: there are two ways to arrange the position.

The key to understanding entropy is to understand \mathcal{W} . How can the energy of a system be distributed in different ways while the total energy is kept constant?

- Kinetic Energy, K : translational, rotational, vibrational.
- Potential Energy, \mathcal{P} : intramolecular forces, intermolecular forces.

The quantity S is measured at a macrostate, i.e. gas with constant T , P , and V . The macrostate is the overall state of a system as defined by a given set of conditions.

Example 4. Consider the expansion of an ideal gas from a flask, through some tubing connecting it to an evacuated flask when a valve is opened.

1. When the valve is opened, the gas expands spontaneously.
2. The energy levels for each molecule move closer together and increase in number.
3. The number of microstates for the system increase and so does entropy.



When entropy increases during a chemical or physical process, then it has a positive value for the change:

$$\Delta S = S_2 - S_1$$

(spontaneous processes have a positive ΔS according to the second law of thermodynamics).

Entropy and Probability

A microstate is a single possible arrangement of position and kinetic energy of molecules. Entropy is a measure of how many microstates are associated with a particular macroscopic state.

$$S = k_B \ln \mathcal{W}$$

The macrostate with the highest entropy also has the greatest dispersal of energy.

- **Case 1:** When we have a closed system and we have one atom, then there is only one microstates.
 $\mathcal{W} = 1$
- **Case 2:** When we have an open system and we have one atom, then there are two microstates.
 $\mathcal{W} = 2^1 = 2$
- **Case 3:** When we have a closed system and we have two atoms, then there is only one microstates.
 $\mathcal{W} = 1$
- **Case 4:** When we have an open system and we have two atoms, then there are four microstates.
 $\mathcal{W} = 2^2 = 4$
- **Case 5:** When we have a closed system and we have three atoms, then there is one microstates.
 $\mathcal{W} = 1$.
- **Case 6:** When we have an open system and we have three atoms, then there are eight microstates.
 $\mathcal{W} = 2^3 = 8$.

Notice the pattern?

When the stopcock opens, the number of microstates is $\mathcal{W} = 2^n$, where n is the number of particles.

Question 2. *If we have a closed system where we want to arrange four atoms. How many microstates would you have if the stopcock is atoms? Open?*

Multiplicity and Energy

According to quantum mechanics, atoms in a crystal have energies, 0, E , $2E$,... How many different ways the total energy can be subdivided among all the atoms = \mathcal{W} ?

Example 5. Assume we have a solid system with four atoms and a total energy of E . How many different ways could you distribute that energy among the four different atoms?

If there are N atoms and the total energy is qE , then the number of microstates is given by

$$\mathcal{W}(N, q) = \frac{\Gamma(q + N)}{\Gamma(q + 1)\Gamma(N)} = \frac{\int_0^\infty x^{q+N-1} e^{-x} dx}{\int_0^\infty x^q e^{-x} dx \int_0^\infty x^{N-2} e^{-x} dx} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

For example,

$$\mathcal{W}(4, 1) = \frac{\Gamma(5)}{\Gamma(2)\Gamma(4)} = \frac{24}{6} = 4$$

A hot and a cold bar, each made up of four 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 ΔS_{uni} for the process.

When evaluating entropy change, ΔS will be related to the possible accessible microstates.

$$S = k_B \ln \mathcal{W} \Rightarrow \Delta S = k_B \ln(\mathcal{W}_2) - k_B \ln(\mathcal{W}_1)$$

If there are N atoms and the total energy is qE then the number of microstates is given by

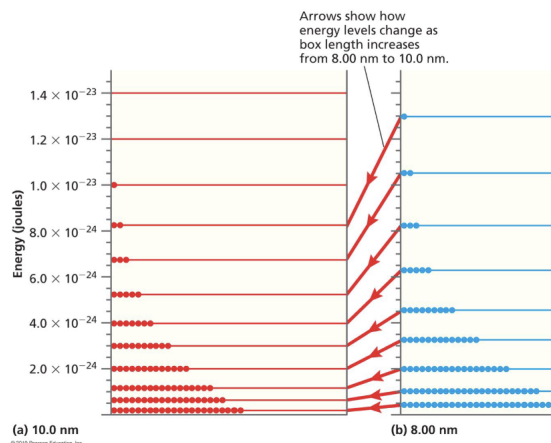
$$\mathcal{W}(N, q) = \frac{\Gamma(q + N)}{\Gamma(q + 1)\Gamma(N)} = \frac{\int_0^\infty x^{q+N-1} e^{-x} dx}{\int_0^\infty x^q e^{-x} dx \int_0^\infty x^{N-2} e^{-x} dx} = \frac{(q + N - 1)!}{q!(N - 1)!}$$

Question 3. *Determine the following values:*

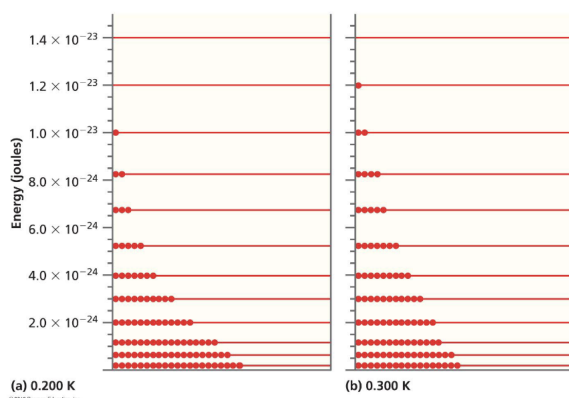
- In a cold system, initially, q and \mathcal{W} , if $N = 4$ and $E_T = 1E$
- In a cold system, final, q and \mathcal{W} , if $N = 4$ and $E_T = 3E$
- In a hot system, initially, q and \mathcal{W} if $N = 4$ and $E_T = 3E$
- In a hot system, final, q and \mathcal{W} if $N = 4$ and $E_T = 3E$

Entropy at the Molecular Level

Allowed energy levels for a He atom in a 1D-box. Box length is 10 nm in (a) and 8.00 nm in (b). The length of the chain of circles on each energy level gives the probability that each energy level is occupied. One circle corresponds to a probability of 0.01. The connecting lines between the boxes show how the energy levels change as the box length increases from 8.00 nm to 10.0 nm.



Probabilities for a He atom of occupying the allowed energy levels in a one dimensional box. Energy levels are for (a) 0.200 K and (b) 0.300 K. Box lengths are 10 nm. The length of the chain of circles on each energy level is proportional to the probability that each energy level is occupied. One circle corresponds to a probability of 0.01.



Statistical Definition of Entropy

Consider two systems where the volume V_1 is half the volume of V_2 .

- For a cylinder containing He atoms the probability of finding any one atom in volume V_2 is one, i.e.

$$\Pr(V_2 = 1) = 1$$

- The probability of finding one He atom in volume V_1 is 0.5, or

$$\Pr(V_1 = 1) = \frac{1}{2}$$

- The probability of finding two He atoms in V_1 is 0.5×0.5 or 0.25, i.e.

$$\Pr(V_1 = 2) = \frac{1}{4}$$

We can generalize:

$$\Pr(V = x) = \mathcal{W} = \left(\frac{1}{2}\right)^N \quad N \in \mathbb{N}$$

so as N increases, the probability of finding all atoms in V_1 decreases.

Consider the cases where the

- Initial State (Least Probable): all the atoms are compressed in V_1
- Final State (Most Probable): all the atoms are evenly distributed over entire V_2 .

spontaneous change occurs from state of low probability occurring to a state of maximum probability.

We can now express enthalpy as being proportional to probability:

$$S = k_B \mathcal{W}$$

but this equation is incorrect! Say we have that as W increases to W^2 , S increases to $2S$.

$$S = k_B \ln \mathcal{W}$$

and so if

$$S_1 = k_B \ln \mathcal{W}_1 \Rightarrow S_2 = k_B \ln \mathcal{W}_2$$

Question 4. What is the probability of gas expanding from V_1 to V_2 , in an isothermal expansion.

Let $\mathcal{W}_1 = (CV_1)^N$ and $\mathcal{W}_2 = (CV_2)^N$. Then

$$\Delta S = S_2 - S_1 = k_B \ln \left(\frac{(CV_2)^N}{(CV_1)^N} \right) = k_B \ln \left[\left(\frac{V_2}{V_1} \right)^N \right]$$

and so

$$\Delta S = \frac{N}{N_A} R \ln \left(\frac{V_2}{V_1} \right) = nR \ln \left(\frac{V_2}{V_1} \right)$$

Remark 6. This equation holds for an *isothermal expansion*, as entropy is affected by the changes in temperature. Entropy is a state function, so it does not matter how the expansion happened.

Example 7. Calculate the change in entropy when the volume of 85.0 g of CO initially at 298 K and 1.00 bar increases by a factor of three in an isothermal reversible expansion. $V_1 \rightarrow 3V_1$

Solution:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = \frac{85}{28} (8.314) \ln(3) = 27.7 \text{ J/K}$$

Now estimate the probability that the gas will contract spontaneously from the final volume to the initial volume.

$$\Delta S = k_B \ln \left(\frac{W_1}{W_2} \right)$$

and so

$$-27.7 = (1.381 \times 10^{-3}) \ln \left(\frac{W_1}{W_2} \right) \Rightarrow \frac{W_1}{W_2} = e^{-2.09 \times 10^{24}}$$