

## Second Law of Thermodynamics

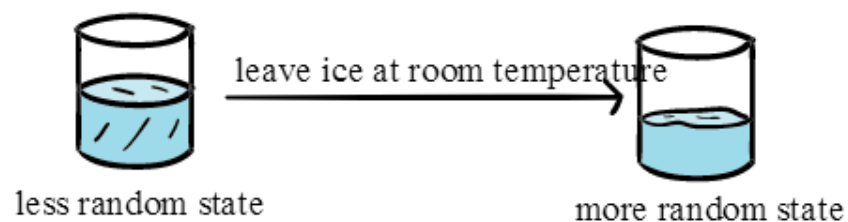
This law states “The total change in entropy of a system plus its surroundings will always increase for a spontaneous process”

Entropy is defined as the “measure of disorder or randomness of a system”. Every system wants to achieve a state of maximum disorder or randomness. A commonly observed daily life example of something constantly moving towards a state of randomness is a ‘kid’s room’. Every time mom cleans up the room, within minutes the room looks like this



This is the natural state in which a kid’s room wants to exist ☺

Another commonly encountered entropy driven process is the melting of ice into water. This happens spontaneously as soon as ice is left at room temperature. Ice is a solid with an ordered crystalline structure as compared to water, which is a liquid in which molecules are more disordered and randomly distributed. All natural processes tend to proceed in a direction which leads to a state that has more random distribution of matter and energy.



All of these processes take place spontaneously, meaning that once they start, they will proceed to the end if there is no external intervention. You will never witness the reverse of this process, in which water converts back to ice at room temperature. In other words, it would be inconceivable that this process could be reversed without tampering with the external conditions (you will have to put water in the freezer to force it to form ice). So what determines the direction in which a process will go under a given set of conditions? Now you know the answer - all these processes are driven by entropy.

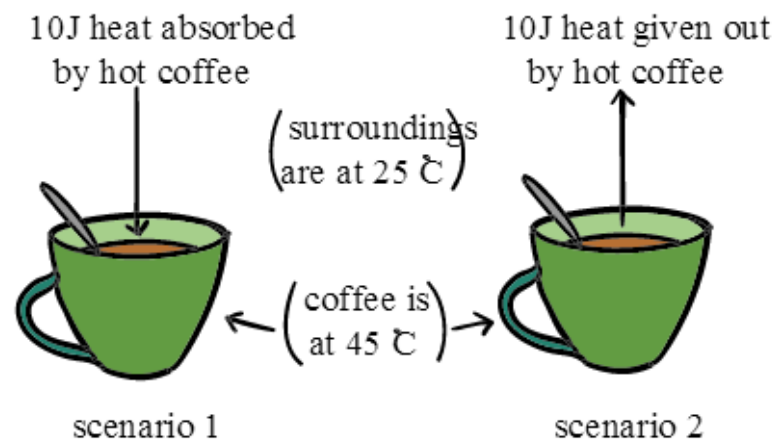
## Why is the second law of thermodynamics so important?

Second law of thermodynamics is very important because it talks about entropy and as we have discussed, '*entropy dictates whether or not a process or a reaction is going to be spontaneous*'.

I want you to realize that any natural process happening around you is driven by entropy!!

Let's take a daily life example:

We drink coffee every day. What happens to our cup of hot coffee in say 10 minutes? The coffee starts getting cold, or in thermodynamic terms you will tell me that the hot coffee gives out heat to the surroundings and in turn the coffee cools down. You are 100% correct, but the thing you might not have realized is that this very obvious daily life phenomenon is governed by "entropy". Let's try to prove this mathematically. As shown below, the following two scenarios are possible



The temperature of the surroundings and the coffee are 25 °C and 45 °C respectively.

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**Scenario 1:** 10 J of heat is absorbed (from the surroundings) by coffee, so surroundings lose 10 J and the system (coffee) gains 10 J. Thus,  $Q_{system} = +10$  J and  $Q_{surroundings} = -10$  J

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= Q_{system} / T_{system} + Q_{surroundings} / T_{surroundings}$$

$$= 10 / (45 + 273) + (-10) / (25 + 273) \text{ [temperatures are to be converted into Kelvin]}$$

$$= -0.0021 \text{ Joules/ Kelvin}$$

This violates the second law of thermodynamics ( $\Delta S_{universe}$  should be greater than zero), so the above process cannot occur spontaneously.

**Scenario 2:** 10 J of heat is released (to the surroundings) by hot coffee, so surroundings gain 10 J and system (coffee) loses 10 J. Thus,  $Q_{system} = -10$  J and  $Q_{surroundings} = +10$  J

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= Q_{system} / T_{system} + Q_{surroundings} / T_{surroundings}$$

$$= -10 / (45 + 273) + 10 / (25 + 273) \text{ [temperatures have to be converted into Kelvin]}$$

$$= +0.0021 \text{ Joules/ Kelvin}$$

This obeys the second law of thermodynamics ( $\Delta S_{universe} > 0$ ), so the above process occurs spontaneously.

In the case of a cup of coffee this was pretty intuitive. But this is not true for chemical reactions. Just by looking at a chemical reaction, we cannot predict if it will take place spontaneously or not. So, calculating the entropy change for that particular reaction becomes important.