

4.3: The Second Law of Thermodynamics

The Second Law of Thermodynamics states that the state of entropy of the entire universe, as an [isolated system](#), will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative.

Introduction

Why is it that when you leave an ice cube at room temperature, it begins to melt? Why do we get older and never younger? And, why is it whenever rooms are cleaned, they become messy again in the future? Certain things happen in one direction and not the other, this is called the "arrow of time" and it encompasses every area of science. The thermodynamic arrow of time (entropy) is the measurement of disorder within a system. Denoted as ΔS , the change of entropy suggests that time itself is asymmetric with respect to order of an isolated system, meaning: a system will become more disordered, as time increases.

Major players in developing the Second Law

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "father of thermodynamics," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- Rudolf Clausius was a German physicist, and he developed the Clausius statement, which says "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy.
- Constantin Carathéodory, a Greek mathematician, created his own statement of the second law arguing that "In the neighborhood of any initial state, there are states which **cannot** be approached arbitrarily close through adiabatic changes of state."

 Sadi Carnot.jpeg

Figure $[Math Processing Error]$: Sade Carnot(Louis-LéopoldBoilly public domain)

 Rudolf Clausius 01.jpg

Figure $[Math Processing Error]$: Rudolf Clausius (Theo Schafgans, public domain)

 William Thomson, 1st Baron Kelvin - Wikipedia

Figure $[Math Processing Error]$: Lord Kelvin (Smithsonian Institution, public domain)

 Caratheodory (cropped).jpg

Figure $[Math Processing Error]$: Constantin Carathéodory (Public Domain)

To understand why entropy increases and decreases, it is important to recognize that two changes in entropy have to be considered at all times. The entropy change of the surroundings and the entropy change of the system itself. Given the entropy change of the universe is equivalent to the sums of the changes in entropy of the system and surroundings:

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In an isothermal reversible expansion, the heat q absorbed by the system from the surroundings is

$[Math Processing Error]$

Since the heat absorbed by the system is the amount lost by the surroundings, $[Math Processing Error]$. Therefore, for a truly reversible process, the entropy change is

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If the process is irreversible however, the entropy change is

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If we put the two equations for ΔS_{univ} together for both types of processes, we are left with the second law of thermodynamics,

$$\Delta S_{\text{univ}} \geq 0$$

where ΔS_{univ} equals zero for a truly reversible process and is greater than zero for an irreversible process. In reality, however, truly reversible processes never happen (or will take an infinitely long time to happen), so it is safe to say all thermodynamic processes we encounter everyday are irreversible in the direction they occur.

The second law of thermodynamics can also be stated that "all **spontaneous** processes produce an **increase** in the entropy of the universe".

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