3.2: Introduction to the Second Law

Rudolph Clausius is kind enough in his 1879 work "The Mechanical Theory of Heat" (Clausius, 1879) to indicate where we have been in our discussion of thermodynamics, as well as where we are going.

> "The fundamental laws of the universe which correspond to the two fundamental theorems of the mechanical theory of heat:
> 1. The energy of the universe is constant.
> 2. The entropy of the universe tends to a maximum."
> — Rudolf Clausius, The Mechanical Theory Of Heat

The **second law of thermodynamics**, which introduces us to the topic of entropy, is amazing in how it constrains what we can experience and what we can do in the universe. As Sean M. Carroll, a CalTech Theoretical physicist, suggests in a 2010 interview with Wired Magazine (Biba, 2010),

> *I'm trying to understand how time works. And that's a huge question that has lots of different aspects to it. A lot of them go back to Einstein and spacetime and how we measure time using clocks. But the particular aspect of time that I'm interested in is the arrow of time: the fact that the past is different from the future. We remember the past but we don't remember the future. There are irreversible processes. There are things that happen, like you turn an egg into an omelet, but you can't turn an omelet into an egg.*

We, as observers of nature, are time travelers. And the constraints on what we can observe as we move through time step from the **second law of thermodynamics**. But more than just understanding what the second law says, we are interested in what sorts of processes are possible. And even more to the point, what sorts of processes are **spontaneous**.

A spontaneous process is one that will occur without external forces pushing it. A process can be spontaneous even if it happens very slowly. Unfortunately, Thermodynamics is silent on the topic of how fast processes will occur, but is provides us with a powerful toolbox for predicting which processes will be spontaneous. But in order to make these predictions, a new thermodynamic law and variable is needed since the first law (which defined ΔU and ΔH) is insufficient.

Consider the following processes:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$

with $\Delta H < 0$

$$NaHCO_3(s) \rightarrow Na + (aq) + HCO_3^-(aq)$$

with $\Delta H > 0$

Both reactions will occur spontaneously, but one is exothermic and the other endothermic. So while it is intuitive to think that an exothermic process will be spontaneous, there is clearly more to the picture than simply the release of energy as heat when it comes to making a process spontaneous. The Carnot cycle because a useful thought experiment to explore to help to answer the question of why a process is spontaneous.

Contributors

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