3.2: The Second Law

The second law of thermodynamics is a statement of what we know by direct experience. It is not something that is derived from more fundamental principles, even though a better understanding of this law has emerged over time. There are several ways to state the second law, the most common ones being the Kelvin statement and the Clausius statement.

> K: Kelvin statement of the second law: There exists no thermodynamics process whose sole effect is to extract an amount of heat from a source and convert it entirely to work.
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> C: Clausius statement of the second law: There exists no thermodynamics process whose sole effect is to extract an amount of heat from a colder source and deliver it to a hotter source.

The keyword here is “sole". Consider the expansion of a gas and consequent conversion of heat into work. Complete conversion can be achieved but this is not the sole effect, for the state of the system has been changed. The second law does not forbid such a process.

The two statements are equivalent. This can be seen by showing that $\tilde{K} \Rightarrow \tilde{C}$ and $\tilde{C} \Rightarrow \tilde{K}$, where the tildes denote the negation of the statements.

First consider $\tilde{K} \Rightarrow \tilde{C}$. Consider two heat reservoirs at temperatures T_L and T_H, with $T_H > T_L$. Since K is false, we can extract a certain amount of heat from the colder reservoir (at T_L) and convert it entirely to work. Then, we can use this work to deliver a certain amount of heat to the hotter reservoir. For example, work can be converted to heat by processes like friction. So we can have some mechanism like this to heat up the hotter source further. The net result of this operation is to extract a certain amount of heat from a colder source and deliver it to a hotter source, thus contradicting C. Thus $\tilde{K} \Rightarrow \tilde{C}$.

Now consider $\tilde{C} \Rightarrow \tilde{K}$. Since C is presumed false, we can extract an amount of heat, say Q_2, from the colder reservoir (at T_L) and deliver it to the hotter source. Then we can have a thermodynamic engine take this amount of heat Q_2 from the hotter reservoir and do a certain amount of work $W = Q_2 - Q_1$ delivering an amount of heat Q_1 to the colder reservoir. The net result of this cycle is to take the net amount of heat $Q_2 - Q_1$ from the reservoir at T_L and convert it entirely to work. This shows that $\tilde{C} \Rightarrow \tilde{K}$.

The two statements $\tilde{K} \Rightarrow \tilde{C}$ and $\tilde{C} \Rightarrow \tilde{K}$ show the equivalence of the Kelvin and Clausius statements of the second law.

The second law is a statement of experience. Most of the thermodynamic results can be derived from a finer description of materials, in terms of molecules, atoms, etc. However, to date, there is no clear derivation of the second law. Many derivations, such as Boltzmann’s $\mathcal{H}$-theorem, or descriptions in terms of information, have been suggested, which are important in their own ways, but all of them have some additional assumptions built-in. This is not to say that they are not useful. The assumptions made have a more fundamental nature and do clarify many aspects of the second law.