First Law: During any process, the energy of the universe is constant.

\[ dU_{\text{universe}} = dU_{\text{sys}} + dU_{\text{surroundings}} = ZERO \]

Any energy transfer between system and surroundings is accomplished via work or transfer of heat.

\[ dU = dq + dw \]

The first law tells whether a process is possible or impossible.

Examples:
Possible: I can evaporate 1 ml of H\textsubscript{2}O with a red hot skillet
Impossible: I can boil the Gulf of Mexico with one match
Example 1: Gas in a box

Remove the partition

Gas expands to fill volume
- Observed

Gas remains in partitioned section
- Not Observed

The two configurations have the same energy. We gain no stability by choosing 1 or 2. Both are possible! Why is only 1 observed?

First law is happy with either outcome!
Bouncing Ball

Bounces up -- Not Observed
During Collision, Energy of Ball is Converted into Thermal Motion of Atoms
Suppose we place a hot body next to a cold body.

The First Law allows either situation. But heat transfer is only observed from a hot body to a cold body.

The essence of these examples is that just because a process is possible does not mean that it is spontaneous.
Spontaneity

What is meant by spontaneous?

- **A SPONTANEOUS** process is one that occurs naturally (needs no external source of work).
- **A NON-SPONTANEOUS** process is a possible process (allowed by the 1\textsuperscript{st} Law), BUT an external source of work is required to drive it.

The 1\textsuperscript{st} Law requires a process to be possible, but says nothing about the spontaneity of the process.

Spontaneity **REQUIRES** us to formulate the 2\textsuperscript{nd} Law. You are likely already familiar with the 2\textsuperscript{nd} Law in at least one of several forms.
1. Clausius: The **ENTROPY** of the universe increases during **EVERY** process.
2. Murphy: Anything that can possibly go wrong **WILL** go wrong
3. Bumper Sticker: $h!t$ Happens

We essentially employ the Clausius version:

The entropy of the universe increases during every spontaneous process

\[ \Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surroundings}} \]
That is OK, but we know that a non-spontaneous process is possible. How does one occur?

a. Actually, they do not happen
b. Occasional violations of the 2\textsuperscript{nd} Law are weakly allowed.
c. A non-spontaneous process only occurs when coupled to a spontaneous process in a way that $\Delta s_{\text{universe}} > 0$.
d. The 2\textsuperscript{nd} Law only applies to true spontaneous processes.
Entropy
A measure of molecular disorder

Second Law uses Entropy, $S$, to identify spontaneous change.

Restatement of Second Law:

The entropy of the universe tends always towards a maximum
($\Delta S_{universe} > 0$ for a spontaneous process)
Statistical Definition of Entropy

\[ S = k_B \ln W \]

\( k_B \) is \( k \), the gas constant per molecule
\( B = \text{Boltzmann, a great scientist} \)

\( W \) is number of different ways in which the energy of the system can be arranged by redistributing the atoms or molecules among the available energy and position microstates.

We are going to develop this concept further, as I believe it to be much more intuitive than the standard thermodynamic development. However the statistical view was really only placed on a firm footing after the development of quantum mechanics.
S describes the extent to which energy is dispersed chaotically to surroundings and can be characterized by measuring the quantity of energy that is transferred to surroundings as heat.

\[ dS_{\text{surr}} = \frac{dq_{\text{surr}}}{T} \]

Large changes in entropy occur when much heat is dissipated to surroundings at low temperature.
The Second Law deals with whether a chemical or physical change can take place spontaneously.

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.
Heat is Never Completely Converted into Work

Some Heat Dissipated to Surroundings

Not 100% Conversion
To calculate the entropy change in the surroundings when 1.0 mole of $H_2O(l)$ is formed from its elements under standard conditions at 25°C (298.15 K), we start with the chemical reaction:

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O (l)$$

The standard enthalpy of formation, $\Delta_f H^\circ$, is given as $-286$ kJ/mol.

The solution involves calculating the entropy change in the surroundings, $\Delta S_{surr}$, using the formula:

$$\Delta S_{surr} = \frac{dQ_{surr}}{T} = \frac{(+286 \text{ kJ/mol})}{298 \text{ K}}$$

This results in:

$$\Delta S_{surr} = +0.960 \text{ kJ/mol K} = 960 \text{ J/K}$$

No shocking new insights here!
Heat Engine with Overall Spontaneous Process

Heat withdrawn from hot reservoir. Entropy decreases by \( q_h/T_h \).

If \( T_c < T_h \), entropy change can be positive even if \( q_c < q_h \). The difference \( q_h - q_c \) can be withdrawn as work.

Heat added to cold sink. Entropy increases by \( q_c/T_c \).

No shocking new insights here either!
The 2\textsuperscript{nd} Law involves something called entropy.

Entropy, $S$, is a \textbf{STATE} Function, like $U$ and $H$. Its meaning, however, is really difficult to really understand.

The text follows the traditional (historical) route in describing entropy in terms of macroscopic thermodynamics and then defined entropy microscopically. We will take the opposite approach.
Entropy

Ludwig Eduordo Boltzmann

\[ S = k_B \ln \Omega \]