The Second Law of Thermodynamics

Disclaimer: The Second Law of Thermodynamics is unlike any law you have learned before because it has at least three different and equivalent expressions. It also has the added drawback that the best explanation (the entropy one) is the most complicated.

1 Topics Covered

- The Direction of Processes and The Second Law of Thermodynamics:
  - Irreversible Processes: Most processes in nature are irreversible, i.e., they only proceed in one direction. But how do we determine which directions are allowed and which are forbidden?
  - Second Law of Thermodynamics (Version 1): Heat will never spontaneously flow from a colder object to a hotter object.
  - Reversible Processes: We can imagine an idealized process that is reversible, i.e., a process whose direction can be reversed by infinitesimal changes in the conditions of the process. The only way that this is possible is if the system is very close to thermal equilibrium during the process.

- Heat Engines and the Second Law of Thermodynamics:
  - Heat Engine: A heat engine converts heat into mechanical energy. It takes heat ($Q_H$) from a heat source as input, converts some of it to work ($W$), and sends the rest to a cold reservoir ($Q_C$).
  - Efficiency: The efficiency of a machine is the ratio of output to cost. For a heat engine, the output is work and the cost is the heat input. So $\varepsilon = W/Q_H = 1 - |Q_C|/|Q_H|$.
  - The Second Law of Thermodynamics (Version 2): The thermal efficiency of a heat engine is always less than 1. In other words, a heat engine cannot convert heat entirely to work.
  - Carnot Efficiency: The maximum thermal efficiency for a heat engine operating between a heat source at temperature $T_H$ and a cold reservoir at temperature $T_C$ is $\varepsilon_{\text{max}} = 1 - T_C/T_H$.

- Entropy and the Second Law of Thermodynamics:
  - Macrostate/Microstate: The macrostate of a thermodynamic can be described by state variables like $P$, $V$, and $T$. Each macrostate has many microstates, which must be described by the positions and velocities of each particle in the system.
  - Probability: Probability tells us that if all microstates are equally likely, the system is most likely to be in the macrostate with the largest number of corresponding microstates.
  - Entropy: Let $w_M$ be the number of microstates associated with macrostate $M$. If the system is in macrostate $M$, define the entropy of the system to be $S = k_B \ln w_M$.
  - The Second Law of Thermodynamics (Version 3): Entropy never decreases, i.e., for any process, $\Delta S \geq 0$. (This is a consequence of probability.)
  - Entropy Change for Non-Constant Temperature: Break the process into tiny constant temperature reversible processes to find that $\Delta S = mc \ln (T_2/T_1)$.
2 Problems

1. Consider a system that consists of four quarters, each of which can be either heads (H) or tails (T).
   (a) Write down all possible microstates of the system. There should $2^4 = 16$ of them. To get you started, one possible state is HHHH.
   (b) Write down all possible macrostates of the system. For example, one of them is “one quarter shows heads and the other three show tails.”
   (c) Calculate the entropy associated with each macrostate.
   (d) If you flip four fair coins, what macrostate do you expect to see?
   (e) If you start with four heads and then shake up the coins, what do you expect to happen? Does this agree with the second law?
   (f) People sometimes say that entropy measures the “disorder” of a system. Why do you think they say this?

2. Suppose that in one cycle, a car engine takes 10000 J of heat from a heat source at temperature $T_H = 5000 \text{ K}$ and passes 8000 J of heat to a cold reservoir at temperature $T_C = 300 \text{ K}$.
   (a) How much mechanical work does the engine deliver during each cycle?
   (b) What is the efficiency of this engine?
   (c) What would be the efficiency of a Carnot engine operating between the same temperatures?
   (d) If each cycle takes 0.01 s to complete, what is the power output of the engine?

3. You have an ice cube of mass $m = 2 \text{ kg}$ that is at 0°C.
   (a) If the ice melts during a reversible process, what is the change in its entropy? (The latent heat of melting for water is $L = 3.34 \times 10^5 \text{ J/kg}$.)
   (b) If the resulting water is subsequently heated from 0°C to 50°C, what is its change in entropy? (The specific heat for water is 4186 J/kgK.)

4. If an ideal gas undergoes an isothermal process, is it reversible or irreversible?

5. An ideal gas undergoes an adiabatic expansion. What is its change in entropy?

6. A refrigerator is a machine that moves heat from a cold reservoir to a hot reservoir by taking mechanical work as its input. What do you think the efficiency of a refrigerator is? What do you think the maximum efficiency for a refrigerator is?