Reversible & Irreversible Processes

- Example of a Reversible Process:
  - Cylinder must be pulled or pushed slowly enough (quasistatically) that the system remains in thermal equilibrium (isothermal).
- Change where system is always in thermal equilibrium: reversible process
- Change where system is not always in thermal equilibrium: irreversible process
  - Examples of irreversible processes:
    - Free expansion of a gas
    - Melting of ice in warmer liquid
    - Frictional heating
    - Anything that is real

All real processes are irreversible!

Heat Engine

- An engine is a device that cyclically transforms thermal energy (heat?) into mechanical energy (useful work).
  - Efficiency: Fraction of heat flow becomes mechanical work:
    \[ e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} \]
- A minimal version of an engine has two reservoirs at different temperatures \( T_H \) and \( T_L \), and follows a idealized reversible cycle known as the Carnot cycle.
  - Efficiency of the Carnot cycle
    \[ e_C = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \]
Heat Pumps, Refrigerators, and Air Conditioners

- Heat pumps, refrigerators, and air conditioners are engines run in reverse:
  - Refrigerator and air conditions remove heat from the cold reservoir and put it into the surroundings (hot reservoir), keeping the food/room cold.
  - A heat pump takes energy from the cold reservoir and puts it into a room or house (hot reservoir), thereby warming it.
  - In either case, energy must be added!
    - Work must be performed ON the system!

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Refrigerators and Air Conditioners

Schematic diagram of a refrigerator:

Schematic diagram of a room air conditioner:
Heat Pumps and Refrigerators

- Since the (idealized) Carnot engine is the most efficient heat engine, the Carnot refrigerator is the most efficient refrigerator.
  - Coefficient of Performance:
    \[ CP = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L} = \frac{T_L}{T_H - T_L} \]

- Heat Pumps work similarly but have a different objective, namely warm the house.
  - Coefficient of Performance:
    \[ CP = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} = \frac{T_H}{T_H - T_L} \]

The specifications of a freezer claim that it can remove 80 cal/s from the compartment at -20°C and release 94 cal/s into the room at 25°C while using 60 W of electrical energy to drive the compressor. Can you trust this statement?
The Second Law of Thermodynamics

There are many ways of expressing the second law of thermodynamics; here are two:

- The Clausius form: It is impossible to construct a cyclic engine whose only effect is to transfer thermal energy from a colder body to a hotter body.
  - Spontaneous heat flow always goes from the higher-temperature body to the lower-temperature one.
- The Kelvin form: It is impossible to construct a cyclic engine that converts thermal energy from a body into an equivalent amount of mechanical work without a further change in its surroundings.
  - Thermal energy cannot be entirely converted to work.
  - A 100% efficient engine is impossible.

Entropy and the Second Law

- Entropy is a measure of disorder.
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- Entropy is a measure of the energy unavailable to do work.
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Entropy and the Second Law

- In the Carnot cycle:
  \[ e_c = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H} \]

- Some arbitrary cycle
  - Divide into a number or Carnot cycles:
    - In the limit

Entropy and the Second Law

- But the Carnot cycle relies on 2 isothermal and 2 adiabatic processes.
  - Friction, Turbulence, etc.
  - For an irreversible cycle, there is less work done for the same amount of absorbed heat; therefore the entropy increases through the cycle:

- Definition of Entropy:
Entropy and the Second Law

- The entropy of an isolated system never decreases;
  - spontaneous (irreversible) processes always increase entropy.
- All the consequences of the second law of thermodynamics follow from the treatment of entropy as a measure of disorder.
  - Making engines that would convert mechanical energy entirely to work would require entropy to decrease in isolated system – can’t happen.
  - Many familiar processes increase entropy – shuffling cards, breaking eggs, and so on.
    - We never see these processes spontaneously happening in reverse – a movie played backwards looks silly. This directionality is referred to as the arrow of time.