Reese Ch. 15, Part A1
(pp. 667-677)

- Motivation for the Second Law
- Heat Engines and the Second Law
- The Carnot Engine and its Efficiency
- Absolute Zero
- Refrigerators and the Second Law

Motivation for the Second Law

- Conservation laws forbid certain things.
  - Conservation of electric charge
  - Conservation of momentum
  - Conservation of angular momentum
  - Conservation of energy
- However, we can also describe various hypothetical processes that are consistent with all known conservation laws, and yet have never been observed.

Heat Engines and the Second Law: I

- It is possible (even easy) to "turn work completely into heat."
- The function of a heat engine is the reverse: to employ heat to perform useful work.
- The efficiency ε of a cyclic heat engine is defined as the ratio of work done to high-temperature heat invested:

$$\boxed{\varepsilon \equiv \frac{W_{by}}{Q_H}}$$

Heat Engines and the Second Law: II

- One version of the Second Law of Thermodynamics states that:

  "It is impossible to construct a perfect heat engine."
- This means that the efficiency $\varepsilon < 1$ for any cyclic heat engine.
- We shall encounter two other ways of stating the Second Law.

The Carnot Engine and its Efficiency:I

In 1824, Sadi Carnot considered a very particular engine cycle involving an ideal gas as the "working fluid." This Carnot engine has two great virtues:

1. It is relatively easy to calculate its efficiency.
2. More importantly, it turns out that the Carnot efficiency is the greatest possible efficiency for any engine cycle utilizing given temperatures (T_H and T_C) for the "heat source" and the "heat sink."

The Carnot Engine and its Efficiency: II

In the Carnot engine, a fixed quantity of ideal gas follows the following four-stage cycle:

- Isothermal expansion at temperature T_H
- Adiabatic expansion until $T=T_C$
- Isothermal compression at temperature T_C
- Adiabatic compression until $T=T_H$ & $V = V_{init}$

NOTE: To get a true cycle requires careful choice of the endpoints of the isothermal stages.

The Carnot Engine and its Efficiency: III

- Using the definition of efficiency, the first law of thermodynamics, and the ideal gas law, it is not difficult to show that the efficiency of the Carnot engine is $$\boxed{\varepsilon_{Carnot} = 1 - \frac{T_C}{T_H}}$$
- NOTE: Although the value of ε is most easily calculated for a Carnot cycle that uses an ideal-gas working fluid, the same efficiency applies to ANY working fluid that cycles using these four stages.

Absolute Zero

- From the expression for the Carnot efficiency, we can see that if we could use a heat sink at 0 K, we would have a perfect heat engine. Since the Second Law rules out perfect engines, we conclude that it is impossible to achieve a temperature of 0 K. This is often referred to as the Third Law of Thermodynamics.

Refrigerators and the Second Law: I

- Energy spontaneously moves from hot material to cold material.
- The purpose of a refrigerator is to accomplish the reverse: the transfer of energy from a cold reservoir to a hot one.
- A cyclic refrigerator accomplishes this with a "working fluid" that completes a closed cycle.
- The coefficient of performance of a refrigerator is

$$\boxed{K \equiv \frac{|Q_C|}{|W_{by}|} = \frac{|Q_C|}{W_{on}}}$$

Refrigerators and the Second Law: II

- A perfect refrigerator would transfer energy from cold matter to hot matter without the input of work.
- "Perfect refrigerators do not exist." (This is an alternative version of the Second Law.)
- A Carnot engine can be reversed and used as a Carnot refrigerator. Its coefficient of performance is

$$\boxed{K_{Carnot} = \frac{T_C}{T_H - T_C}}$$

Reese Ch. 15, Part A2 (pp. 677-689)

- Carnot Efficiency as the Upper Limit for the Efficiency of a Real Heat Engine
- Coefficient of Performance of a Carnot Refrigerator as the Upper Limit for the Coefficient of Performance of a Real Refrigerator
- The Concept of Entropy
- Entropy and the Second Law
- Application: The Direction of Heat Flow

Carnot Efficiency as the Upper Limit for the Efficiency of Real Heat Engines

- A Carnot engine is reversible.
- Suppose that a "super engine" exists, with $\varepsilon > \varepsilon_C$. Then use it to run a Carnot refrigerator of just the correct size.
- Bundle the two inside a box and *bingo*, you have a perfect refrigerator, in contradiction to the 2nd Law.
- Therefore there can be no engine with $\varepsilon > \varepsilon_C$.

Carnot Coefficient of Performance as the Upper Limit for COP's of Real Refrigerators

- Suppose that a "super refrigerator" exists, with $K>K_C$.
- Run this "super refrigerator" with a Carnot engine of just the correct size.
- Bundle the two inside a box and *bingo*, you again have a perfect refrigerator, in contradiction to the 2^{nd} Law.
- Therefore there can be no refrigerator with $K>K_C$.

Entropy: I

- CARNOT ENGINE: When the working fluid proceeds clockwise around a Carnot cycle, it receives $|Q_H|$ via heat transfer during the hot isothermal expansion and expels $|Q_C|$ during the cold isothermal compression.
- CARNOT REFRIGERATOR: When the working fluid proceeds counterclockwise around a Carnot cycle, it receives $|Q_C|$ via heat transfer during the cold isothermal expansion and expels $|Q_H|$ during the hot isothermal compression.
- In each case, the quantity $\oint \frac{\delta Q}{T}$ equals zero!

Entropy: II

- By judicious combination of enough Carnot cycles (large and small), we can mimic essentially any closed path in the PV plane. Thus if we calculate $\oint \frac{\delta Q}{T}$ around ANY closed path in the PV plane, we get 0.
- In mechanics, when we encountered forces for which the work done around ANY closed path is 0, we were able to define a function of position called the "potential energy," such that

$$\boxed{(PE_2)-(PE_1) = -\int_{\substack{anypath\\ from 1 to 2}} \delta W}$$

Entropy: III

- Similarly, here we can define a quantity called the entropy (S) for which $\boxed{\Delta S \equiv S_2 - S_1 \equiv \int_{\substack{anypath\\ from 1 to 2}} \frac{\delta Q}{T}}$

NOTES:

- S is a function of the thermodynamic equilibrium state. It appears that we could use any state as a reference state, for which S=0, but we'll see later that there is a natural choice.
- In analogy with $\boxed{\delta W_{by} = PdV}$, we have $\boxed{\delta Q = TdS.}$
- Inward heat transfer ("heat gain") increases a system's entropy; outward heat transfer ("heat loss") decreases it.

Important Examples of Entropy Changes

(Table 15.1 shows additional examples.)

- Ideal gas taken from state 1 to state 2:

$$\boxed{\Delta S = nc_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)}$$

- Melting or boiling: $\boxed{\Delta S = \frac{mL}{T}}$
- Free expansion of an ideal gas: (This one deserves care!) $\boxed{\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)}$

Entropy and the Second Law

- The most general statement of the second law is that the entropy of any isolated thermodynamic system cannot decrease with time: $\boxed{\Delta S_{\substack{isolated \\ system}} \geq 0}$
- N.B.: A *nonisolated* system CAN show decreasing S.
- Although it's merely one application of the second law, notice that since (by definition?!) the universe is an isolated system: $\boxed{\Delta S_{universe} \geq 0}$

Application: Direction of Heat Flow

- If energy were to move from a cold reservoir to a hot one via heat transfer, that would cause the entropy of the universe to increase.
- Thus spontaneous heat transfer from hotter to colder regions can be thought of as a consequence of the Second Law.