Lecture 9
(Entropy and the Second Law of Thermodynamics)

Physics 161-01 Spring 2012

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The Carnot Cycle

- In 1824, the French Engineer Nicolas Léonard Sadi Carnot developed a hypothetical engine cycle that would maximize the efficiency.

- In order to do this, each step of the cycle had to be kept **reversible**.

- Remember what that means – no heat exchanged except when the temperatures between the two bodies are the same.

- Also remember that this cannot be accomplished, but it is a reasonable approximation when the process is slow enough that thermal equilibrium is maintained.

The Carnot Cycle

- So, there are four steps in the Carnot cycle:
  - Isothermal expansion at temperature T_H (heat added but at constant temperature, so reversible).
  - Adiabatic expansion and cooling to temperature T_C (no heat added, so reversible).
  - Isothermal compression at temperature T_C (heat taken out, but at constant temperature, so reversible).
  - Adiabatic compression and heating to temperature T_H (no heat exchanged, so reversible).
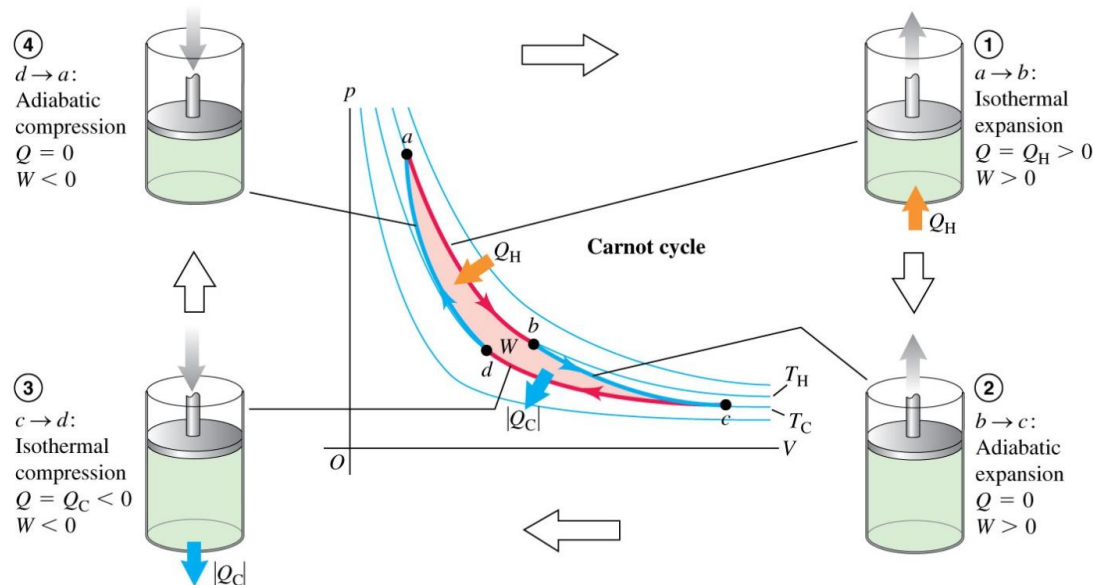
Carnot Engine Efficiency

- Let's go through the derivation of the Carnot efficiency:

  - For the isothermal expansion from a to b: $Q_H = W_{ab} = nRT_H \ln\dfrac{V_b}{V_a}$

  - For the isothermal compression from c to d: $Q_C = W_{cd} = -nRT_C \ln\dfrac{V_c}{V_d}$

  - For the adiabatic expansion from b to c: $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$

  - For the adiabatic compression from d back to a: $T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$

  - Dividing these last two: $\dfrac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \dfrac{V_c^{\gamma-1}}{V_d^{\gamma-1}} \implies \dfrac{V_b}{V_a} = \dfrac{V_c}{V_d}$

  - Which, substituting into the first two and using the definition of the efficiency, gives: $\dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H} \implies e = 1 - \dfrac{T_C}{T_H}$

Example 20.2 **Analyzing a Carnot engine I**

A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is its efficiency?

SOLUTION

IDENTIFY and SET UP: This problem involves a Carnot engine, so we can use the ideas of this section and those of Section 20.2 (which apply to heat engines of all kinds). Figure 20.14 shows the energy-flow diagram. We have $Q_H = 2000$ J, $T_H = 500$ K, and $T_C = 350$ K. We use Eq. (20.13) to find Q_C, and then use the first law of thermodynamics as given by Eq. (20.2) to find W. We find the efficiency e from T_C and T_H using Eq. (20.14).

EXECUTE: From Eq. (20.13),

$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} = -1400 \text{ J}$$

Then from Eq. (20.2), the work done is

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) = 600 \text{ J}$$
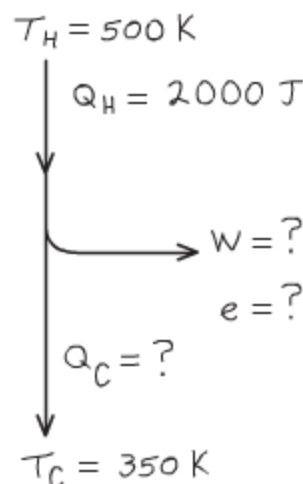
From Eq. (20.14), the thermal efficiency is

$$e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$

EVALUATE: The negative sign of Q_C is correct: It shows that 1400 J of heat flows *out* of the engine and into the cold reservoir. We can check our result for e by using the basic definition of thermal efficiency, Eq. (20.3):

$$e = \frac{W}{Q_H} = \frac{600 \text{ J}}{2000 \text{ J}} = 0.30 = 30\%$$

20.14 Our sketch for this problem.

$T_H = 500$ K

$Q_H = 2000$ J

$W = ?$

$e = ?$

$Q_C = ?$

$T_C = 350$ K

Example 20.3 | **Analyzing a Carnot engine II**

Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle between 227°C and 27°C, starting at $p_a = 10.0 \times 10^5$ Pa at point a in the pV-diagram of Fig. 20.13. The volume doubles during the isothermal expansion step $a \rightarrow b$. (a) Find the pressure and volume at points a, b, c, and d. (b) Find Q, W, and ΔU for each step and for the entire cycle. (c) Find the efficiency directly from the results of part (b), and compare with the value calculated from Eq. (20.14).

IDENTIFY and SET UP: This problem involves the properties of the Carnot cycle and those of an ideal gas. We are given the number of moles n and the pressure and temperature at point a (which is at the higher of the two reservoir temperatures); we can find the volume at a using the ideal-gas equation $pV = nRT$. We then find the pressure and volume at points b, c, and d from the known doubling of volume in step $a \rightarrow b$, from equations given in this section, and from $pV = nRT$. In each step we use Eqs. (20.10) and (20.11) to find the heat flow and work done and Eq. (19.13) to find the internal energy change.

EXECUTE: (a) With $T_H = (227 + 273.15)$ K $= 500$ K and $T_C = (27 + 273.15)$ K $= 300$ K, $pV = nRT$ yields

$$V_a = \frac{nRT_H}{p_a} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})}{10.0 \times 10^5 \text{ Pa}}$$

$$= 8.31 \times 10^{-4} \text{ m}^3$$

The volume doubles during the isothermal expansion $a \rightarrow b$:

$$V_b = 2V_a = 2(8.31 \times 10^{-4} \text{ m}^3) = 16.6 \times 10^{-4} \text{ m}^3$$

Because the expansion $a \rightarrow b$ is isothermal, $p_a V_a = p_b V_b$, so

$$p_b = \frac{p_a V_a}{V_b} = 5.00 \times 10^5 \text{ Pa}$$

For the adiabatic expansion $b \rightarrow c$, we use the equation $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$ that follows Eq. (20.12) as well as the ideal-gas equation:

$$V_c = V_b \left(\frac{T_H}{T_C}\right)^{1/(\gamma-1)} = (16.6 \times 10^{-4} \text{ m}^3)\left(\frac{500 \text{ K}}{300 \text{ K}}\right)^{2.5}$$

$$= 59.6 \times 10^{-4} \text{ m}^3$$

$$p_c = \frac{nRT_C}{V_c} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{59.6 \times 10^{-4} \text{ m}^3}$$

$$= 0.837 \times 10^5 \text{ Pa}$$

For the adiabatic compression $d \rightarrow a$ we have $T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1}$ and so

$$V_d = V_a \left(\frac{T_H}{T_C}\right)^{1/(\gamma-1)} = (8.31 \times 10^{-4} \text{ m}^3)\left(\frac{500 \text{ K}}{300 \text{ K}}\right)^{2.5}$$

$$= 29.8 \times 10^{-4} \text{ m}^3$$

$$p_d = \frac{nRT_C}{V_d} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{29.8 \times 10^{-4} \text{ m}^3}$$

$$= 1.67 \times 10^5 \text{ Pa}$$

(b) For the isothermal expansion $a \rightarrow b$, $\Delta U_{ab} = 0$. From Eq. (20.10),

$$W_{ab} = Q_H = nRT_H \ln\frac{V_b}{V_a}$$

$$= (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})(\ln 2) = 576 \text{ J}$$

For the adiabatic expansion $b \rightarrow c$, $Q_{bc} = 0$. From the first law of thermodynamics, $\Delta U_{bc} = Q_{bc} - W_{bc} = -W_{bc}$; the work W_{bc} done by the gas in this adiabatic expansion equals the negative of the change in internal energy of the gas. From Eq. (19.13) we have $\Delta U = nC_V \Delta T$, where $\Delta T = T_C - T_H$. Using $C_V = 20.8$ J/mol $\cdot$ K for an ideal diatomic gas, we find

$$W_{bc} = -\Delta U_{bc} = -nC_V(T_C - T_H) = nC_V(T_H - T_C)$$

$$= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K}) = 832 \text{ J}$$

For the isothermal compression $c \rightarrow d$, $\Delta U_{cd} = 0$; Eq. (20.11) gives

$$W_{cd} = Q_C = nRT_C \ln\frac{V_d}{V_c}$$

$$= (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})\left(\ln\frac{29.8 \times 10^{-4} \text{ m}^3}{59.6 \times 10^{-4} \text{ m}^3}\right)$$

$$= -346 \text{ J}$$

For the adiabatic compression $d \rightarrow a$, $Q_{da} = 0$ and

$$W_{da} = -\Delta U_{da} = -nC_V(T_H - T_C) = nC_V(T_C - T_H)$$

$$= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 500 \text{ K}) = -832 \text{ J}$$

We can tabulate these results as follows:

Process	Q	W	ΔU
$a \rightarrow b$	576 J	576 J	0
$b \rightarrow c$	0	832 J	-832 J
$c \rightarrow d$	-346 J	-346 J	0
$d \rightarrow a$	0	-832 J	832 J
Total	230 J	230 J	0

(c) From the above table, $Q_H = 576$ J and the total work is 230 J. Thus

$$e = \frac{W}{Q_H} = \frac{230 \text{ J}}{576 \text{ J}} = 0.40 = 40\%$$

We can compare this to the result from Eq. (20.14),

$$e = \frac{T_H - T_C}{T_H} = \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} = 0.40 = 40\%$$

EVALUATE: The table in part (b) shows that for the entire cycle $Q = W$ and $\Delta U = 0$, just as we would expect: In a complete cycle, the *net* heat input is used to do work, and there is zero net change in the internal energy of the system. Note also that the quantities of work in the two adiabatic processes are negatives of each other. Can you show from the analysis leading to Eq. (20.13) that this must *always* be the case in a Carnot cycle?

CPS 9-1

A Carnot engine takes heat in from a reservoir at 400 K and discards heat to a reservoir at 300 K.

If the engine does 12,000 J of work per cycle, how much heat does it take in per cycle?

A. 48,000 J

B. 24,000 J

C. 16,000 J

D. 9000 J

E. none of the above

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Entropy

- "Any method involving the notion of entropy, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension." - Willard Gibbs, *Graphical Methods in the Thermodynamics of Fluids* (1873)
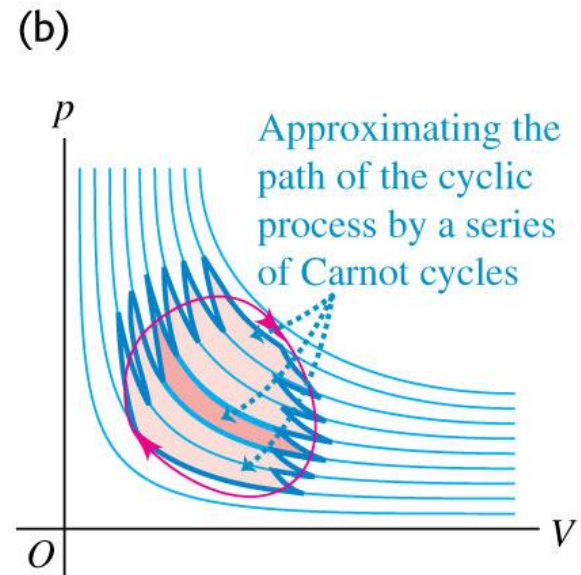
Entropy

- Let us start our discussion of entropy by looking at one of the last steps in our derivation of the Carnot efficiency: $\dfrac{Q_C}{Q_H} = -\dfrac{T_C}{T_H} \implies \dfrac{Q_C}{T_C} + \dfrac{Q_H}{T_H} = 0$

- Now, if we define a variable S, such that: $dS = \dfrac{dQ}{T}$

- Then, we can see that over the entire Carnot cycle, the variable S, which we now refer to as the entropy, returns to the same value. In other words the change in entropy adds to zero over the entire cycle.

Entropy as a State Variable

- Now, perhaps that is just some artifact of the Carnot cycle, but, using calculus, we can show that over any cycle, the entropy returns to its original value.

- Therefore, entropy is a state variable! It can describe the state of a system (like the temperature, volume, pressure, etc.)
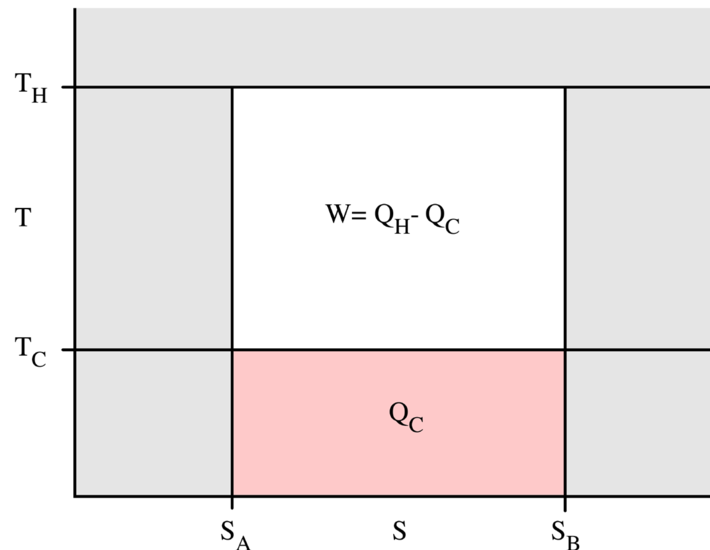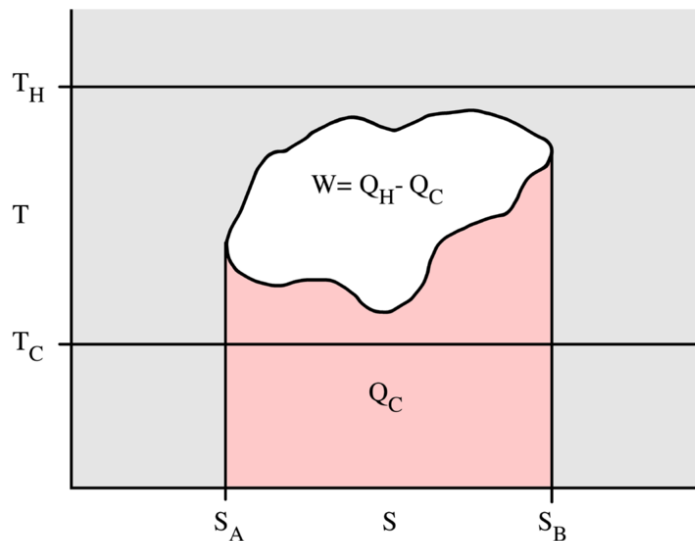
$$dS = \frac{dQ}{T}$$

(b)

Approximating the path of the cyclic process by a series of Carnot cycles

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Carnot Cycle and Entropy

- Let us re-examine the Carnot efficiency using the state variables S and T:

$$dS = \frac{dQ}{T} \Rightarrow$$

$$dQ = TdS \Rightarrow$$

$$Q = \int_a^b TdS$$

Carnot Cycle, Entropy, and the 2nd Law

- So, there can be no engine that works between two temperatures that has a greater efficiency than a Carnot cycle working between the same two temperatures.

Entropy and the 2nd Law

- So, somehow entropy is strongly related to the 2nd Law of Thermodynamics.
- Let's examine now an infinitesimal isothermal expansion:
  - Since dU = 0, then $$dQ = dW = pdV = \frac{nRT}{V}dV \Rightarrow$$

  $$\frac{dV}{V} = \frac{dQ}{nRT} \propto S$$

  - Now, it turns out that the incremental fractional volume increase (for added heat) is directly related to the increase in *disorder* of the gas.
  - Since there is more space to occupy, there are more ways which the *molecules* can exist where the *gas* has the same state.

Entropy and the 2nd Law

- The second law of thermodynamics can be stated in terms of entropy: No process is possible in which the total entropy of an isolated system decreases.

- The term "isolated system" here is crucial. The entropy of some object can decrease, if it is in contact with another object whose entropy increases just as much or more.

- It is certainly possible for something to have more order than it did at some point in the past, but it just means that something else, in contact with it now has less order.

- Consider cooking macaroni in a microwave:

The Arrow of Time

- You can slide a book across a table where it stops due to energy lost from friction.
  - But, have you ever seen a book start sliding taking energy from the thermal energy of the table?
- You could start out with all of the air in this room in one half and vacuum in the other half, separated by a partition. Then remove the partition and the air would fill the room.
  - But, you wouldn't expect for a room filled with air to spontaneously separate into half filled and half empty.
- Neither of these scenarios are prohibited by the conservation laws or by the first law of thermodynamics.
- Why don't many things that happen spontaneously in nature also happen in reverse?

Macroscopic and Microscopic States

- In order to understand this apparent direction in time, let's look at a simpler problem: a coin toss.
- Let's say we have one coin. For simplicity, it is motionless and can only be in one place. Its "state", which we now specify as its "macro-state" is defined as whether it is a heads or a tails.
- How many ways can you make each macro-state? Only one for each state.
- So, if we toss a single coin in the air, what is the probability that it will land in each macro-state?

$$P\left(1\text{H}\right) = \frac{\#\,\text{microstates}\left(1\text{H}\right)}{\sum \text{microstates}} = \frac{1}{1+1} = \frac{1}{2}$$

Macroscopic and Microscopic States

- Now, lets do the same with four coins.
- There are five different macro-states, but for each macro-state, there is a different number of ways to make it. For two tails and two heads, there are six ways to make it.
- So, if we toss four coins in the air, what is the probability that they will come up all heads?

$$P(4\text{H}) = \frac{\#\,\text{microstates}(4\text{H})}{\sum \text{microstates}} = \frac{1}{1+4+6+4+1} = \frac{1}{16}$$

- What is the probability that they will come up two heads and two tails?

$$P(2\text{H}2\text{T}) = \frac{\#\,\text{microstates}(2\text{H}2\text{T})}{\sum \text{microstates}} = \frac{6}{1+4+6+4+1} = \frac{6}{16} = \frac{3}{8}$$

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One head, three tails	
Four tails	

Disorder and Entropy

- Notice that the total number of micro-states is just 2^N, where N is the number of coins.
- So, for 100 coins, there are 2^{100} micro-states and the possibility of throwing 100 heads is 1 in 1,267,650,600,228,229,401,496,703,205,376!
- Now, the number of molecules in this room is approximately 1×10^{29}. Consider the macro-states as being if (heads) if a molecule is in one half of the room and (tails) if it is in the other half. What is the probability that on a random sampling of the molecules position, we find them all in one half of the room?
- So, this tendency towards disorder is just a consequence of the probability of finding a particular macro-state given the statistics of the micro-states which make it up!
- This is the underlying nature of entropy, and the underlying nature of the direction of time.

Calculating Entropy

- One can calculate the entropy, first expressed by Ludwig Boltzmann, as:

$$S = k \log w$$

- Where k is the Boltzmann constant and w is the number of micro-states.

- Or, since only the difference in entropies are ever used in calculations:

$$\Delta S = k \log \frac{w_2}{w_1}$$