Chapter 4 - Second Law of Thermodynamics

"The motive power of heat is independent of the agents employed to realize it."

-Nicolas Léonard Sadi Carnot

David J. Starling
Penn State Hazleton
Fall 2013

Entropy

An irreversible process is a process that cannot occur spontaneously in the opposite direction.

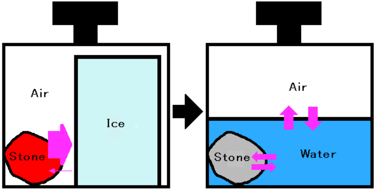

Figure 2

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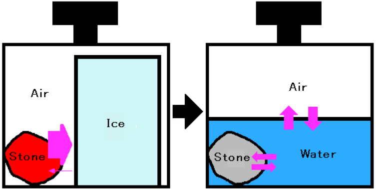

Figure 2

Examples:

- the warming of your hands by a hot cup of tea;
- the breaking of a glass;
- the hatching of an egg.

Entropy

What makes these processes **irreversible**? *It's not the energy—energy is still conserved!*

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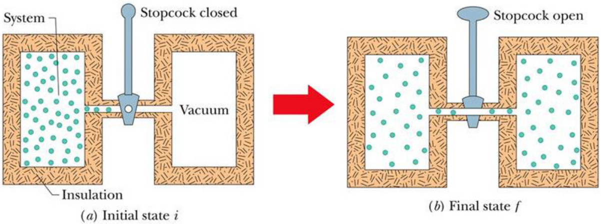
The order of the object has changed. The object is more **disordered**.

Entropy

The disorder of system is a state property, just like pressure and temperature, that depends only on the current state and not how it got there.



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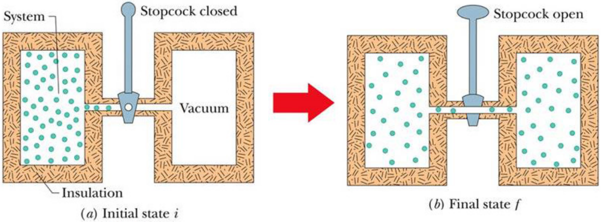

The measure of disorder is known as **entropy**.

Entropy

The definition of the change in entropy of a closed system from one state to another is:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} \quad (1)$$

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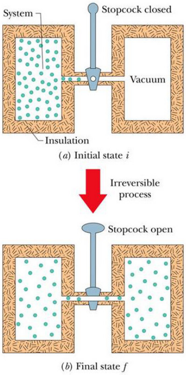
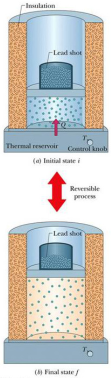
And remember: it doesn't matter *how* the system gets from one state the next.

- For a reversible process: $\Delta S = 0$
- For an irreversible process: $\Delta S > 0$

Entropy

To calculate the change in entropy of a closed system, sometimes we can play a trick.





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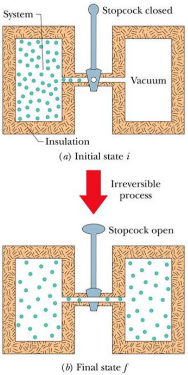
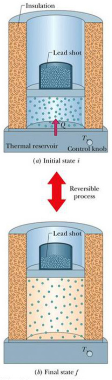
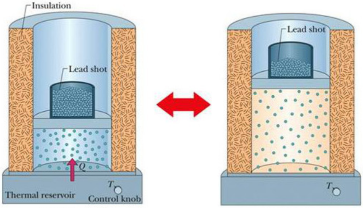




Calculate the integral for the reversible process—it's much easier!

Entropy

Consider the same initial and final volumes and moles, with a constant temperature. Then,



(a) Initial state i (b) Final state f

Entropy

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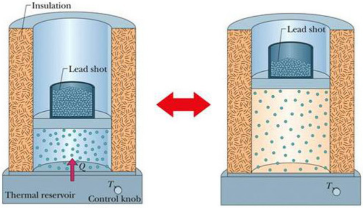
$$\begin{aligned}\Delta S &= \int_i^f \frac{dQ}{T} \\ &= \frac{1}{T}\int_i^f dQ \\ &= \frac{Q}{T} \text{ (isothermal process)}\end{aligned}$$



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In a closed system, the entropy always increases for an irreversible process, and remains the same for a reversible process.

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This is the **Second Law of Thermodynamics.**
Entropy always increases or stays the same in any process.

Entropy

A box with five adiabatic sides contains an ideal gas with an initial temperature T_0. The sixth side is placed in contact with a reservoir with a constant temperature $T_2 > T_0$. Why must the entropy change of the universe always be increasing as the box warms?

(a) Entropy will always be increasing since the work done on the gas in the box is negative.

(b) Entropy will always be increasing since the temperature of the box is always $\leq T_2$.

(c) Entropy will always be increasing since this process is reversible.

(d) Entropy will always be increasing since the temperature of the box is always greater than absolute zero.

(e) Entropy will always be increasing since in any process entropy increases.

Engines

An engine is a device that extracts heat from the environment and converts it to work.

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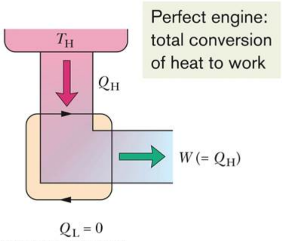
- Every engine needs a working substance (water/steam, air, gasoline)
- The working substance moves in a **cycle** composed of **strokes**

Engines

How much work W can be done with a given amount of heat Q_H?



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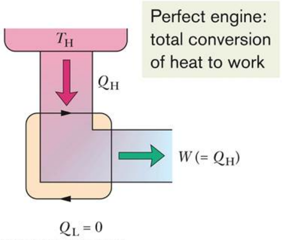

- An **ideal engine** is one that does not suffer from waste (friction, turbulence).
- A **perfect engine** is one that converts 100% of its heat to work.

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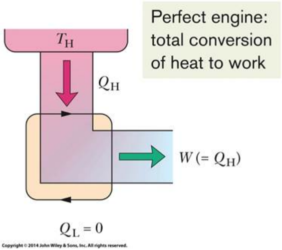

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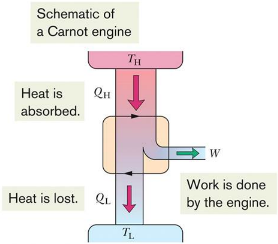
Is this possible?

Engines

Let's look at the Carnot engine and compute its efficiency.



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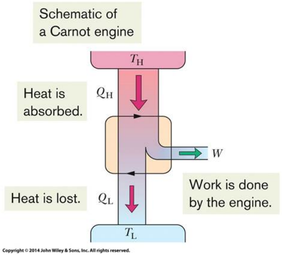

- Heat is absorbed by the working substance
- Some energy is converted to work, some is dumped as waste

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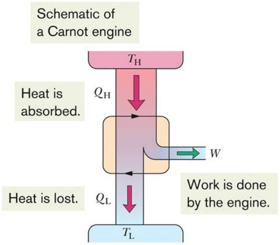

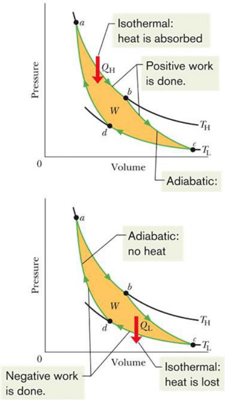

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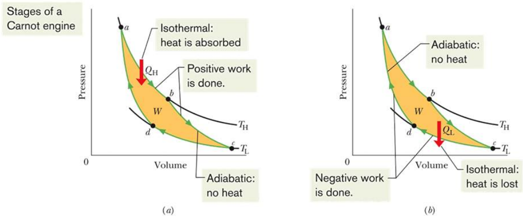
- Measuring the heat transfer can be tricky
- Let’s analyze the cycle and try to compute this ratio

Engines

Compute the change in entropy for a full cycle:



$$\Delta S = \Delta S_{a\to b} + \Delta S_{b\to c} + \Delta S_{c\to d} + \Delta S_{d\to a}$$

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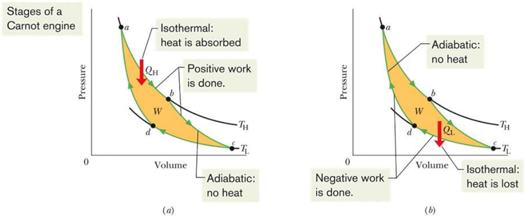

$$\begin{aligned} \Delta S &= \Delta S_{a\to b} + \Delta S_{b\to c} + \Delta S_{c\to d} + \Delta S_{d\to a} \\ &= \Delta S_H + \Delta S_L \end{aligned}$$

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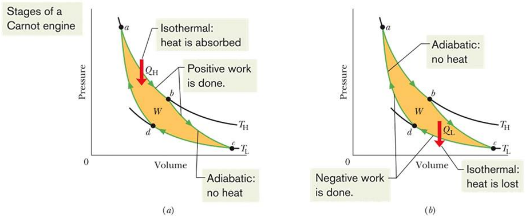

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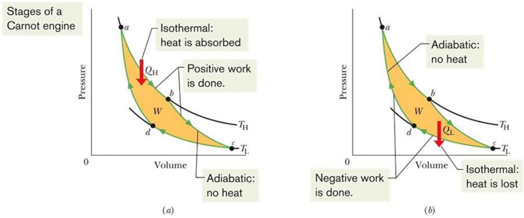

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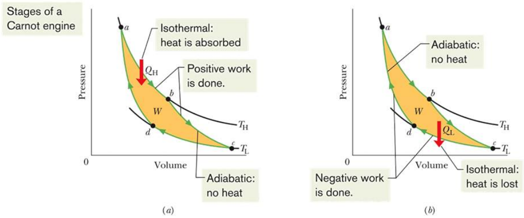
Compute the change in entropy for a full cycle:



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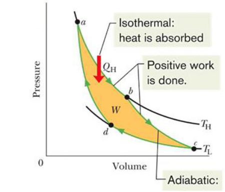
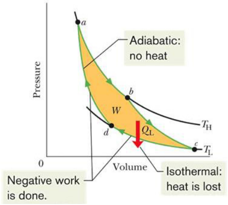
&= \frac{|Q_H|}{T_H} - \frac{|Q_L|}{T_L} \\
&= 0 \\
\frac{|Q_L|}{|Q_H|} &= \frac{T_L}{T_H}
\end{aligned}
$$

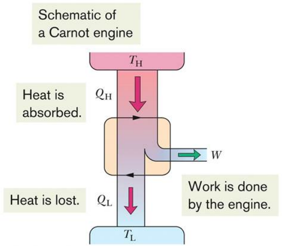
Engines

The efficiency of the Carnot engine depends only on the temperatures of the hot and cold reservoirs.

$$\epsilon = 1 - \frac{T_L}{T_H} \quad (3)$$







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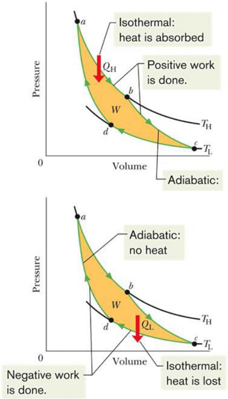
The Carnot engine is an ideal engine in that its efficiency is as high as possible.



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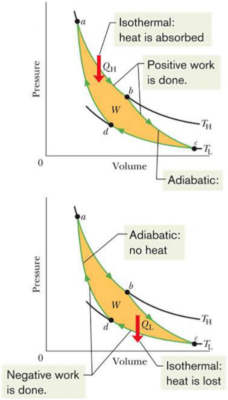
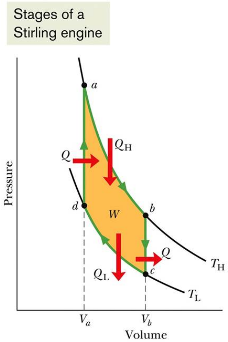


- Isothermal expansion and compression (constant T)
- Adiabatic expansion and compression ($Q = 0$)

Engines

The Stirling engine has lower efficiency but is more practical.



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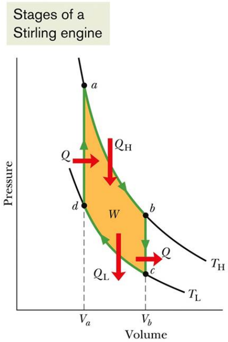


- Isothermal expansion and compression (constant T)
- Constant volume heating/cooling ($Q \neq 0$)

Engines

During the power stroke of an internal combustion engine, the air-fuel mixture is ignited and the expanding hot gases push on the piston. Assuming the engine exhibits the highest efficiency possible, which of the following statements concerning the exhaust gas must be true to avoid violating the second law of thermodynamics?

(a) The exhaust gas must be hotter than the outside air temperature.

(b) The exhaust gas must be at the same pressure as the outside air.

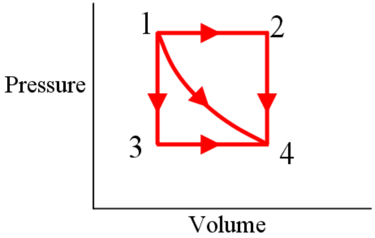
(c) The exhaust gas must be cooled to the same temperature as the outside air.

(d) The exhaust gas must be cooled below the temperature of the outside air.

(e) Real engines will always violate the second law of thermodynamics.

Engines

Consider the various paths shown on the pressure-volume graph. By following which of these paths, does the system do the most work?



(a) 1 to 2 to 4

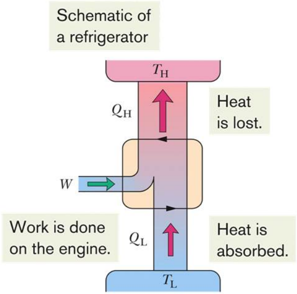
(b) 1 to 4

(c) 1 to 3 to 4

(d) Each of these paths results in the same amount of work done.

Refrigerators

An ideal refrigerator operates in reverse of an engine.



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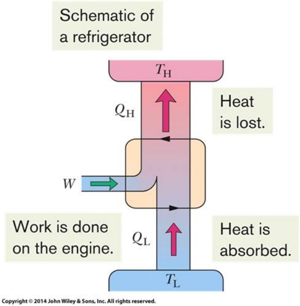

We put in work which draws heat from the cold reservoir and dumps it into the hot reservoir.

Refrigerators

The coefficient of performance is defined in a similar way as before:

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_L|}{|W|}$$

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We can simplify this further by using $\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$:

$$K = \frac{T_L}{T_H - T_L}$$

Refrigerators

You are repairing a window-style air conditioner in a closed workroom. You succeed in getting it to work, but are called away soon after you turn it on. Unfortunately, you are unable to return for several hours to turn it off. Assuming that it was running as efficiently as possible while you were away, how has the temperature of the workroom changed in your absence?

(a) The room is somewhat cooler than before I left.

(b) The room is slightly cooler than before I left.

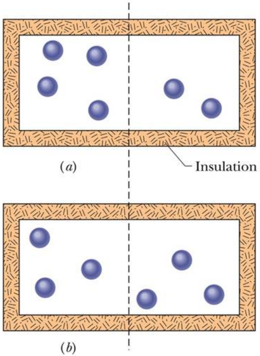
(c) The temperature of the room has not changed.

(d) The room is warmer than before I left.

(e) The air near the ceiling will be very warm, but the air around the air conditioner will be very cool.

Statistics of Entropy

Entropy can be calculated by considering the possible arrangements of atoms/molecules in a given system.



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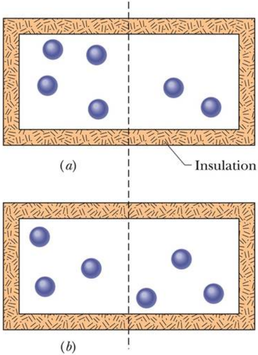

If we have six molecules in a box, what are their possible **combinations**?

Statistics of Entropy

In mathematics, the number of combinations of N things taken k at a time can be computed as:

$$\binom{N}{k} = \frac{N!}{k!(N-k)!} \tag{4}$$

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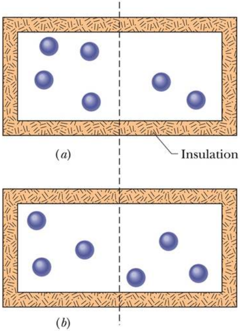
For example: given three fruit (apple, orange, banana), how many combinations of two can be made?

- apple + orange, apple + banana, orange + banana $= 3$
- $\binom{3}{2} = 3!/[2!(3-2)!] = 3 \times 2 \times 1/(2 \times 1 \times 1) = 3.$

Statistics of Entropy

Given a box of 6 particles, how many configurations are there if we split them left/right?



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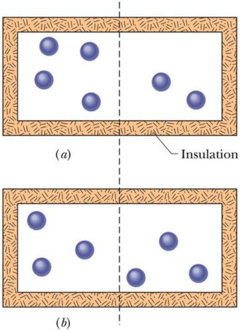

Seven: 6-0, 5-1, 4-2, 3-3, 2-4, 1-5, 0-6.

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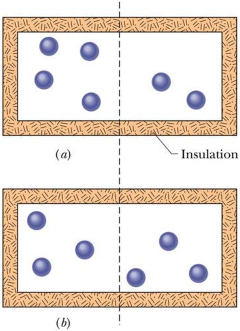
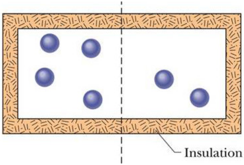


Seven: 6-0, 5-1, 4-2, 3-3, 2-4, 1-5, 0-6.
Each of these configurations can be done in one or more ways.

Statistics of Entropy

For the configuration shown (4-2), how many combinations are there?



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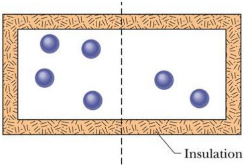

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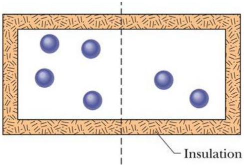

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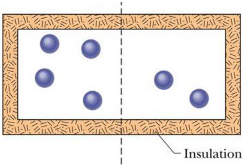

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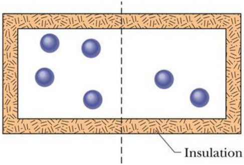
- W is called the **multiplicity** of the 4-2 configuration.
- Each of the 15 combinations is called a **microstate**

Statistics of Entropy

For the configuration shown (4-2), how many combinations are there?



- $W = \binom{6}{2} = 6!/2!4! = 6 \times 5/2 = 15$
- W is called the **multiplicity** of the 4-2 configuration.
- Each of the 15 combinations is called a **microstate**
- The configuration (4-2) is known as the **macrostate**

Statistics of Entropy

We can list a number of important features:

- The more evenly distributed the configuration, the higher the multiplicity.
- The more microstates for a configuration, the more likely that configuration.
- The lower the multiplicity, the lower the entropy
- The higher the multiplicity, the higher the entropy

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Table 20-1 Six Molecules in a Box

Configuration Label	n_1	n_2	Multiplicity W (number of microstates)	Calculation of W (Eq. 20-20)	Entropy 10^{-23} J/K (Eq. 20-21)
I	6	0	1	$6!/(6!\ 0!) = 1$	0
II	5	1	6	$6!/(5!\ 1!) = 6$	2.47
III	4	2	15	$6!/(4!\ 2!) = 15$	3.74
IV	3	3	20	$6!/(3!\ 3!) = 20$	4.13
V	2	4	15	$6!/(2!\ 4!) = 15$	3.74
VI	1	5	6	$6!/(1!\ 5!) = 6$	2.47
VII	0	6	1	$6!/(0!\ 6!) = 1$	0
			Total = 64		

Statistics of Entropy

To obtain the entropy of a system, we use the famous Boltzmann entropy equation:

$$S = k \ln W \tag{5}$$

with $k = 1.381 \times 10^{-23}$ J/K the Boltzmann constant.

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Statistics of Entropy

If the multiplicity is very large, we can compute S with Stirling's approximation,

$$\ln N! \approx N \ln N - N. \tag{6}$$

(different Stirling from the engine guy)

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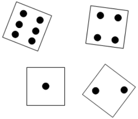
Statistics of Entropy

In the system shown,



(a) the number on a die corresponds to a microstate, and the numbers on all the dice (1, 2, 4, 6) correspond to the macrostate;

(b) the number on a die corresponds to a microstate, and the sum of the numbers on all the dice corresponds to the macrostate;

(c) the numbers on all the dice correspond to a microstate, and the sum of the numbers on all the dice corresponds to the macrostate;

(d) the sum of the numbers on all the dice corresponds to a microstate, and the numbers on all the dice correspond to the macrostate.