## Chapter 15

## The Second Law of Thermodynamics



## Engines, Refrigerators, and their Efficiencies

- Engines must work using a cyclic process. Why?
- A useful engine must involve a temperature difference with one side at a high temperature and one at a low temperature.
- The efficiency for a closed loop:

$$
\begin{gathered}
Q=\Delta U+W \\
Q=W \\
Q_{\text {in }}-\left|Q_{\text {out }}\right|=W \\
Q_{\mathrm{H}}-\left|Q_{\mathrm{L}}\right|=W \\
\varepsilon=W / Q_{\mathrm{H}} \\
\varepsilon=\left(Q_{\mathrm{H}}-\left|Q_{\mathrm{L}}\right|\right) / Q_{\mathrm{H}}=1-\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}
\end{gathered}
$$

## Schematic diagram of energy transfer for a heat engine.

## High Temperature



$$
Q_{\mathrm{H}}=\left|Q_{\mathrm{L}}\right|+W
$$

$2^{\text {nd }}$ Law of Thermodynamics: Kelvin-Planck statement It is impossible for any cyclic device to transform a given amount of heat completely into work


$$
Q_{\mathrm{H}} \neq W
$$

There can be no $100 \%$ efficient engine.
$2^{\text {nd }}$ Law of Thermodynamics: Clausius statement
It is impossible for any cyclic device to transfer heat from a cold object to a hot object, with no other effect.


$$
Q_{\mathrm{H}} \neq\left|Q_{\mathrm{L}}\right|
$$

These statements were both empirically determined.

## Interactive Question

A heat engine that in each cycle does positive work and rejects heat, with no heat input, would violate:
A) The zeroth law of thermodynamics
B) The first law of thermodynamics
C) The second law of thermodynamics
D) Both the first and second laws of thermodynamics
E) None of the above

## Interactive Question

A heat engine absorbs heat from a reservoir and does an equivalent amount of work, with no other changes. This engine violates:
A) The zeroth law of thermodynamics
B) The first law of thermodynamics
C) The second law of thermodynamics
D) Both the first and second laws of thermodynamics
E) None of the above

## Interactive Question

A cyclic process that transfers heat from a high temperature reservoir to a low temperature reservoir with no other changes would violate:
A) The zeroth law of thermodynamics
B) The first law of thermodynamics
C) The second law of thermodynamics
D) Both the first and second laws of thermodynamics
E) None of the above

## Interactive Question

In the processes shown on the right, the total heat flow is:
A) Positive
B) Negative
C) Zero

D) Not determined

A heat engine runs according to the process shown below. Analyze this engine for a monatomic gas:
$P$ (atm)
Let's look at some general features of this graph, then develop a strategy for analyzing cyclic processes.

How would you physically carry out this process?

1. Sketch the process in a $P V$ diagram and make a table of $\Delta U, W$ and $Q$ for each segment in the cycle and for the entire process

- Use what is given and $\Delta U=Q-W$

2. If this isn't enough to complete the table:

- Find $T, P$, and $V$ at each vertex.
- If two are know, use the equation of state.
- If one is known, find a second by relating the values at adjacent vertices, knowing what is a constant (like $P V, P / T, V / T$, or $P V \gamma$ ).
- Use $\Delta U=N_{\mathrm{F}}(1 / 2) n R \Delta T$ where appropriate.

Analyze this engine process for a monatomic gas


|  | $\underline{\Delta U}$ | $\underline{W}$ | $\underline{Q}$ |
| :--- | :--- | :--- | :--- |
| (1) |  |  | 0 |
| (2) |  |  |  |
| (3) | 0 |  |  |
| Sign: 0 | + | + |  |
| Tot: |  |  |  |
|  |  |  |  |


| At corners: $\underline{P}$ | $\underline{V}$ | $\underline{T}$ |  |
| :--- | :--- | :--- | :--- |
| (a) | 1 | 500 | 303 K |
| (b) |  | 100 |  |
| (c) |  | 500 |  |



$$
\begin{aligned}
& P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma}=P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma} \\
& P_{\mathrm{b}}=P_{\mathrm{a}}\left(V_{\mathrm{a}} / V_{\mathrm{b}}\right)^{5 / 3}=1(5)^{5 / 3}=14.6 \text { atm }
\end{aligned}
$$

$$
\begin{aligned}
& P_{\mathrm{b}} V_{\mathrm{b}} / T_{\mathrm{b}}=P_{\mathrm{a}} V_{\mathrm{a}} / T_{\mathrm{a}} \\
& T_{\mathrm{b}}=T_{\mathrm{a}} P_{\mathrm{b}} V_{\mathrm{b}} / P_{\mathrm{a}} V_{\mathrm{a}} \\
& \quad=303(14.6) / 5=885 \mathrm{~K}
\end{aligned}
$$

$$
\begin{aligned}
& T_{\mathrm{c}} / V_{\mathrm{c}}=T_{\mathrm{b}} / V_{\mathrm{b}} \\
& T_{\mathrm{c}}=T_{\mathrm{b}} V_{\mathrm{c}} / V_{\mathrm{b}}
\end{aligned}
$$

$$
=885(5)=4420 \mathrm{~K}
$$

$$
n=P V / R T
$$

$$
=.0201 \mathrm{~mol}
$$

(Use Pa and $\mathrm{m}^{3}$ )

Analyze the following cyclic process for a monatomic gas

$\underline{\Delta U}$
W
(1) $(3 / 2) n R\left(T_{\mathrm{b}}-T_{\mathrm{a}}\right) \quad-\Delta U$
(2) $Q-W$
$P \Delta V$
(3) $Q$
0
$Q$
0
$C_{P}\left(T_{\mathrm{c}}-T_{\mathrm{b}}\right)$
$C_{V}\left(T_{\mathrm{a}}-T_{\mathrm{c}}\right)$

Analyze the following cyclic process for a monatomic gas


$$
\begin{aligned}
& C_{V}=(3 / 2) n R=0.2506 \\
& C_{P}=(5 / 2) n R=0.4177 \\
& \text { Use SI units }
\end{aligned}
$$

|  | $\underline{\Delta U}$ | $\underline{W}$ |
| :---: | :---: | :---: |
| (1) | 146 J | -146 J |
| (2) | 888 | 590 J |
| (3) | -1033 J | 0 |

Only good to 3 significant figures

$$
\begin{aligned}
& \underline{\Delta U} \\
& \text { W } \\
& -146 \text { J } \\
& 590 \text { J } \\
& 0 \\
& \begin{array}{c}
Q \\
0 \\
1478 \mathrm{~J} \\
-1033 \mathrm{~J}
\end{array} \\
& \Delta U_{\text {cycle }}=1 \quad W_{\text {cycle }}=444 \mathrm{~J} \quad Q_{\text {cycle }}=445 \mathrm{~J} \\
& \text { ("0") } \\
& \varepsilon=1-\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}=1-1033 / 1478=0.301
\end{aligned}
$$

Aside: We should also be able to get $\Delta U$ for (2) by using

$$
\begin{aligned}
\Delta U & =C_{V}\left(T_{\mathrm{c}}-T_{\mathrm{b}}\right)=(3 / 2) n R\left(T_{\mathrm{c}}-T_{\mathrm{b}}\right) \\
& =(3 / 2)(0.0201 \mathrm{~mol})(8.314 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{~K})(4420-885 \mathrm{~K}) \\
& =886 \mathrm{~J}
\end{aligned}
$$

(which is the same as 888 with round off errors)

Problem: What is the power output of the previous engine if it runs at 1200 rpm ?

## Carnot Cycle

(An engine using only "reversible" processes)

(1) Isothermal Expansion
(2) Adiabatic Expansion
(3) Isothermal Compression
(4) Adiabatic Compression

Only the Carnot engine can transfer all heat at constant temperature.
We want to calculated the efficiency of this engine:

$$
\varepsilon=1-\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}
$$

## Carnot Cycle



$$
\varepsilon=1-\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}
$$

For the isothermal paths:

$$
W=n R T \ln V_{\mathrm{f}} / V_{\mathrm{i}}
$$

$$
W=Q-\Delta U=Q-(3 / 2) n R \Delta T=Q
$$

$$
Q_{\mathrm{H}}=n R T_{\mathrm{H}} \ln \left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)
$$

$$
Q_{\mathrm{L}}=n R T_{\mathrm{C}} \ln \left(V_{\mathrm{d}} / V_{\mathrm{c}}\right)
$$

|  | $\underline{\Delta U}$ | $\frac{W}{l}$ | $\underline{Q}$ |
| :---: | :---: | :---: | :---: |
| (1) | 0 | $n R T_{\mathrm{H}} \ln \left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)$ | $n R T_{\mathrm{H}} \ln \left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)$ |
| (2) | $C_{V}\left(T_{\mathrm{c}}-T_{\mathrm{b}}\right)$ | $-\Delta U$ | 0 |
| (3) | 0 | $n R T_{\mathrm{L}} \ln \left(V_{\mathrm{d}} / V_{\mathrm{c}}\right)$ | $n R T_{\mathrm{L}} \ln \left(V_{\mathrm{d}} / V_{\mathrm{c}}\right)$ |
| (4) | $C_{V}\left(T_{\mathrm{a}}-T_{\mathrm{d}}\right)$ | $-\Delta U$ | 0 |

## Carnot Cycle



For the adiabatic paths:

$$
P_{\mathrm{c}} V_{\mathrm{c}}^{\gamma}=P_{\mathrm{b}} V_{\mathrm{b}} \gamma \quad P_{\mathrm{d}} V_{\mathrm{d}} \gamma=P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma}
$$

From the ideal gas law:
$P_{\mathrm{c}} V_{\mathrm{c}} / T_{\mathrm{c}}=P_{\mathrm{b}} V_{\mathrm{b}} / T_{\mathrm{b}} \quad P_{\mathrm{d}} V_{\mathrm{d}} / T_{\mathrm{d}}=P_{\mathrm{a}} V_{\mathrm{a}} / T_{\mathrm{a}}$ Notice that $T_{\mathrm{c}}=T_{\mathrm{d}}=T_{\mathrm{L}}$ and $T_{\mathrm{a}}=T_{\mathrm{b}}=T_{\mathrm{H}}$

Divide the top equations by the bottom equations:
$T_{\mathrm{L}} V_{\mathrm{c}}{ }^{\gamma-1}=T_{\mathrm{H}} V_{\mathrm{b}}{ }^{\gamma-1}$

$$
T_{\mathrm{L}} V_{\mathrm{d}}^{\gamma-1}=T_{\mathrm{H}} V_{\mathrm{a}}^{\gamma-1}
$$

Divide these two equations:

$$
\begin{aligned}
& \left(V_{\mathrm{c}} / V_{\mathrm{d}}\right)^{\gamma-1}=\left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)^{\gamma-1} \\
& \left(V_{\mathrm{c}} / V_{\mathrm{d}}\right)=\left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)^{2}
\end{aligned}
$$

From the isothermal processes:
$Q_{\mathrm{H}}=n R T_{\mathrm{H}} \ln \left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)$
$Q_{\mathrm{L}}=n R T_{\mathrm{L}} \ln \left(V_{\mathrm{d}} / V_{\mathrm{c}}\right) \Rightarrow\left|Q_{\mathrm{L}}\right|=n R T_{\mathrm{L}} \ln \left(V_{\mathrm{c}} / V_{\mathrm{d}}\right)$
$\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}=T_{\mathrm{L}} \ln \left(V_{\mathrm{c}} / V_{\mathrm{d}}\right) / T_{\mathrm{H}} \ln \left(V_{\mathrm{b}} / V_{\mathrm{a}}\right)=T_{\mathrm{L}} / T_{\mathrm{H}}$
$\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}=T_{\mathrm{L}} / T_{\mathrm{H}}$
$\varepsilon=1-\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}$
$\varepsilon=1-T_{\mathrm{L}} / T_{\mathrm{H}}$ for a Carnot cycle.
$P$
Carnot's Theorem:
The Carnot engine is the most efficient engine. Any reversible cycle can be approximated as a series of reversible Carnot cycles.

## Interactive Question

You are taking bids to have a heat engine built that will operate between $200^{\circ} \mathrm{C}$ and $30^{\circ} \mathrm{C}$. Different contractors claim the efficiency of their engines as:
A) $100 \%$
B) $80 \%$
C) $40 \%$
D) $30 \%$
E) $20 \%$

Which contractor would you accept the bid from?

## Interactive Question

Three students have designed an engine that operates between 300 K and 500 K . Which of these engines is possible?

Engine
1)
2)
3)

$$
\begin{aligned}
& Q_{\mathrm{in}} \\
& 250 \mathrm{~J} \\
& 250 \mathrm{~J} \\
& 250 \mathrm{~J}
\end{aligned}
$$

$$
\underset{-140 \mathrm{~J}}{Q_{\text {out }}}
$$

$$
\frac{W}{110 \mathrm{~J}}
$$

-170 J
90 J
-160 J 90 J
A) (1) only
B) (2) only
C) (3) only
D) More than one of them
E) None of them

Problem: Suppose 0.200 moles of an ideal diatomic gas ( $c_{V}=20.8 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ ) undergoes a Carnot cycle between temperatures of $227^{\circ} \mathrm{C}$ and $27^{\circ} \mathrm{C}$. The initial volume of the gas is $8.31 \times 10^{-4} \mathrm{~m}^{3}$ and during the high temperature isothermal expansion, the volume doubles. (a) Find the work done during the entire cycle. (b) Find the efficiency of the cycle.

Problem: A 100 hp car operates at $15 \%$ efficiency. Assume the engine's water temperature of $85^{\circ} \mathrm{C}$ is its low temperature and the intake temperature of $500^{\circ} \mathrm{C}$ is its high temperature. (a) How much does this efficiency differ from the maximum possible efficiency? (b) Estimate how much (b) power (in watts) goes into moving the car and (c) how much heat (in joules) is exhausted to the air in one hour.

Problem: The diesel cycle consists of (1) an adiabatic compression. (2) an isobaric expansion, (3) an adiabatic expansion, (4) an isochoric cooling
(A) Draw this cycle
(B) Fill in a rough outline of how you would determine $W$, $Q$ and $\Delta U$.
(C) Determine the efficiency in terms of the volumes.

## Refrigerators

## Coefficient of Performance:

$\mathrm{CP}=\left|Q_{\mathrm{L}}\right| / W$
From the first law, for a cyclic process, $\Delta U=0$
$Q=W$
$\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{L}}\right|=W$
$\mathrm{CP}=\left|Q_{\mathrm{L}}\right| /\left(\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{L}}\right|\right)$
A Carnot refrigerator is just a Carnot engine operating in

Low Temperature reverse. Only for a Carnot process, $\left|Q_{\mathrm{L}}\right| / Q_{\mathrm{H}}=T_{\mathrm{L}} / T_{\mathrm{H}}$ $\mathrm{CP}=T_{\mathrm{L}} /\left(T_{\mathrm{H}}-T_{\mathrm{L}}\right)$

Problem: An air conditioner operating between $93^{\circ} \mathrm{F}$ and $70^{\circ} \mathrm{F}$ is rated at $4000 \mathrm{Btu} / \mathrm{h}$ cooling capacity. Its coefficient of performance is $27 \%$ of that of a Carnot refrigerator operating between the same two temperatures. What horsepower is required of the air conditioner motor?
Note that $4000 \mathrm{Btu} / \mathrm{h}$ is not the mechanical work done by the air conditioner, but the available work (heat in).

## Proof of Carnot's Theorem

Assume there exists a reversible engine with a better efficiency $(\mathcal{\varepsilon})$ than the Carnot efficiency $(\mathcal{\varepsilon})$.

$$
\begin{gathered}
W^{\prime} / Q_{\mathrm{H}}^{\prime}=\varepsilon>\varepsilon=W / Q_{\mathrm{H}} \\
W^{\prime} / Q_{\mathrm{H}}^{\prime}>W / Q_{\mathrm{H}}
\end{gathered}
$$

Connect this engine to a Carnot engine running backwards as a Carnot refrigerator. The work output of the "better" engine is the work input to the Carnot refrigerator.

High Temperature ( $T_{\mathrm{H}}$ )


The Carnot engine is now working as a refrigerator between the same two temperatures ( $T_{\mathrm{C}}$ and $T_{\mathrm{H}}$ ). The engine on the right must be a reversible engine that will operate as a refrigerator between the same two temperatures. We know the Carnot engine can be reversible, and uses only two
temperatures, so the Carnot engine works on the right.

High Temperature, $\left(T_{\mathrm{H}}\right)$

$W^{\prime}| | Q_{\mathrm{H}}^{\prime}\left|>W /\left|Q_{\mathrm{H}}\right|\right.$ $|W| /\left|Q_{\mathrm{H}}^{\prime}\right|>|W| /\left|Q_{\mathrm{H}}\right|$ $\left|Q_{\mathrm{H}}^{\prime}\right|<\left|Q_{\mathrm{H}}\right|$

From the $1^{\text {st }}$ Law:

$$
\begin{aligned}
& W=\left|Q_{\mathrm{H}}^{\prime}\right|-\left|Q_{\mathrm{L}}^{\prime}\right| \\
& W=\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{L}}\right| \\
& \text { So: }
\end{aligned}
$$

$$
\left|Q_{\mathrm{H}}^{\prime}\right|-\left|Q_{\mathrm{L}}^{\prime}\right|=\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{L}}\right|
$$

$$
\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{H}}^{\prime}\right|=\left|Q_{\mathrm{L}}\right|-\left|Q_{\mathrm{L}}^{\prime}\right|
$$

$$
Q \equiv\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{H}}^{\prime}\right|=\left|Q_{\mathrm{L}}\right|-\left|Q_{\mathrm{L}}^{\prime}\right|>0
$$

$$
Q \equiv\left|Q_{\mathrm{H}}\right|-\left|Q_{\mathrm{H}}^{\prime}\right|=\left|Q_{\mathrm{L}}\right|-\left|Q_{\mathrm{L}}^{\prime}\right|>0
$$

This combined system works like a perfect refrigerator, which violates the 2nd law of thermodynamics.

## High Temperature

Low Temperature

The $2^{\text {nd }}$ law will not be violated if $\left|Q_{\mathrm{H}}^{\prime}\right| \geq\left|Q_{\mathrm{H}}\right|$ but that contradicts our original hypothesis that $\left|Q_{\mathrm{H}}^{\prime}\right|<\left|Q_{\mathrm{H}}\right|$.

Consequently, there is no reversible engine with a better efficiency than the Carnot engine, only possibly identical to it, with $\left|Q_{\mathrm{H}}\right|=\left|Q_{\mathrm{H}}^{\prime}\right|$, and $\left|Q_{\mathrm{L}}\right|=\left|Q_{\mathrm{L}}^{\prime}\right|$.

If the engine is not reversible, then it can only go on the left of the diagram


Using the same argument, we can show that $\left|Q_{\mathrm{H}}^{\prime}\right| \geq\left|Q_{\mathrm{H}}\right|$, but since the engine on the left can't be reversed, they can't be equal, so $\left|Q_{\mathrm{H}}^{\prime}\right|>\left|Q_{\mathrm{H}}\right|$, and the reversible engine has a greater efficiency

## Entropy

Consider a Carnot cycle
$\left|Q_{\mathrm{L}}\right| /\left|Q_{\mathrm{H}}\right|=T_{\mathrm{L}} / T_{\mathrm{H}}$
$-Q_{\mathrm{L}} / Q_{\mathrm{H}}=T_{\mathrm{L}} / T_{\mathrm{H}}$
$-Q_{\mathrm{L}} / T_{\mathrm{L}}=Q_{\mathrm{H}} / T_{\mathrm{H}}$
$Q_{\mathrm{L}} / T_{\mathrm{L}}+Q_{\mathrm{H}} / T_{\mathrm{H}}=0$
In general, $\sum_{\text {reversible cycle }} Q / T=0$
We define entropy $(S)$ as $S=d Q / T$
Although it is possible to define an absolute value for entropy, we will usually only be concerned with the change in entropy: $\Delta S=\int_{\mathrm{i}}^{\mathrm{f}} d Q / T$

For any reversible cycle $\int_{\text {cycle }} d Q / T=0$

For any process, the change in entropy is
$\Delta S=\int_{\mathrm{i}}^{\mathrm{f}} d Q / T$
$\Delta S$ may equal zero for an adiabatic process.
Let's now determine the change in entropy for a process at a constant temperature:
$\Delta S=\int_{\mathrm{i}}^{\mathrm{f}} d Q / T=(1 / T) \int_{\mathrm{i}}^{\mathrm{f}} d Q=Q / T$

## Entropy is a State Function

$$
\begin{aligned}
& d Q=d U+d W \\
& d Q=C_{\mathrm{V}} d T+P d V \\
& d Q / T=C_{\mathrm{V}} d T / T+P d V / T \\
& d Q / T=C_{\mathrm{V}} d T / T+n R d V / V \\
& \Delta S
\end{aligned}=\int_{\mathrm{i}}^{\mathrm{f}} d Q / T=C_{\mathrm{V}} \ln \left(T_{\mathrm{f}} / T_{\mathrm{i}}\right)+n R \ln \left(V_{\mathrm{f}} / V_{\mathrm{i}}\right),
$$

Since the right side only depends on state functions, the left side also must only depend on state functions. So entropy is a state function.

## Interactive Question

The change in entropy for a non-isolated system is zero for:
A) reversible adiabatic processes
B) reversible isothermal processes
C) reversible processes which no work is done
D) all of the above
E) all adiabatic processes

Problem: Two kilograms of water at $0^{\circ} \mathrm{C}$ is heated to $100^{\circ} \mathrm{C}$. What is the change in entropy?

Calculating entropy change when the heat input changes the temperature.

## Interactive Question

A hot object and a cold object are placed in thermal contact and the combination is isolated. They transfer heat until they reach a common temperature. What can you say about the change in entropy of the hot object $\left(\Delta S_{\mathrm{H}}\right)$, the cold object $\left(\Delta S_{\mathrm{C}}\right)$, and the total change in entropy $\left(\Delta S_{\mathrm{C}}\right)$.
A) $\Delta S_{\mathrm{H}}>0, \Delta S_{\mathrm{C}}>0, \Delta S_{\mathrm{T}}>0$
B) $\Delta S_{\mathrm{H}}<0, \Delta S_{\mathrm{C}}>0, \Delta S_{\mathrm{T}}>0$
C) $\Delta S_{\mathrm{H}}<0, \Delta S_{\mathrm{C}}>0, \Delta S_{\mathrm{T}}<0$
D) $\Delta S_{\mathrm{H}}>0, \Delta S_{\mathrm{C}}<0, \Delta S_{\mathrm{T}}>0$
E) $\Delta S_{\mathrm{H}}>0, \Delta S_{\mathrm{C}}<0, \Delta S_{\mathrm{T}}<0$

Problem: Two moles of an ideal gas undergo a free expansion to four times the initial volume. What is the change in entropy for this irreversible process?

Calculating entropy change when the heat input is used for doing work (an isothermal expansion) with no change in internal energy.

## Interactive Question

Consider four different methods of moving an ideal gas from one isotherm to another. Which has the greatest change in entropy?

E) None of the Above

## Interactive Question

A one kilogram block of ice at $0^{\circ}$ is placed on a stove. Assume the stove is large enough that its temperature does not change. Which of the following is correct?

$$
\begin{aligned}
& \text { A) } Q_{\text {ice }}=\left|Q_{\text {stove }}\right|, T_{\text {ice }}=T_{\text {stove }}, \Delta S_{\text {ice }}=\left|\Delta S_{\text {stove }}\right| \\
& \text { B) } Q_{\text {ice }}>\left|Q_{\text {stove }}\right|, T_{\text {ice }}=T_{\text {stove }}, \Delta \text { Sice }^{\text {ice }}\left|\Delta S_{\text {stove }}\right| \\
& \text { C) } Q_{\text {ice }}>\left|Q_{\text {stove }}\right| T_{\text {ice }}^{<T_{\text {stove }}, \Delta S_{\text {ice }}=\left|\Delta S_{\text {stove }}\right|} \\
& \text { D) } Q_{\text {ice }}=\left|Q_{\text {stove }}\right|, T_{\text {ice }}<T_{\text {stove }}, \Delta S_{\text {ice }}>\left|\Delta S_{\text {stovel }}\right| \\
& \text { E) } Q_{\text {ice }}=\left|Q_{\text {stove }}, T_{\text {ice }}<T_{\text {stove }}, \Delta S_{\text {ice }}<\left|\Delta S_{\text {stove }}\right|\right.
\end{aligned}
$$

Problem: A one kilogram block of ice at $0^{\circ}$ is placed on a stove. Assume the stove is large enough that its temperature does not change. How could the change in entropy be less than or equal to zero?

To determine the universal change in entropy in any irreversible process, we must include the system and the environment. The previous example is a specific case of a more general rule. For the (non-equilibrium) irreversible process to proceed, the change in entropy of the environment must be greater than the change in entropy of the system so that

$$
\text { For any irreversible process } \int d Q / T>0
$$

Another statement of the $2^{\text {nd }}$ Law of Thermodynamics. The entropy of an isolated system either stays the same (for any reversible process), or increases (for an irreversible process), $\Delta S \geq 0$.

The entropy of a system doesn't always increase. In fact, in our previous example, the entropy of the stove actually decreases. But the entropy of an isolated system must always increase. The universe is an isolated system so in any process, the entropy of the universe increases.

In any naturally occurring process, the total entropy increases, $\Delta S>0$.

## A Proof of Carnot's Theorem Using Entropy

Consider the entropy change of both the engine and the reservoirs (since the $2^{\text {nd }}$ law deals with entropy change of the universe) for the entire cycle of the engine. The entropy change of the reversible Carnot engine during one cycle is zero. The hot reservoir gives up heat and the cold reservoir absorbs heat.

$$
\begin{gathered}
\Delta S=\Delta S_{\mathrm{H}}+\Delta S_{\mathrm{C}}=-\left|Q_{\mathrm{H}}\right| / T_{\mathrm{H}}+\left|Q_{\mathrm{L}}\right| / T_{\mathrm{L}} \geq 0 \\
\left|Q_{\mathrm{L}} / / T_{\mathrm{L}} \geq\right| Q_{\mathrm{H}} / T_{\mathrm{H}} \\
T_{\mathrm{H}} / T_{\mathrm{L}} \geq\left|Q_{\mathrm{H}}\right| /\left|Q_{\mathrm{L}}\right| \\
T_{\mathrm{L}} / T_{\mathrm{H}} \leq\left|Q_{\mathrm{L}}\right| /\left|Q_{\mathrm{H}}\right| \\
\varepsilon=|W| /\left|Q_{\mathrm{H}}\right|=1-\left|Q_{\mathrm{L}}\right| /\left|Q_{\mathrm{H}}\right| \leq 1-T_{\mathrm{L}} / T_{\mathrm{H}}
\end{gathered}
$$

The Statistical View of Entropy

## Example: Roll Two Dice

| Ma |
| :--- |
| 2 |
| 3 |
| 4 |
| 5 |
| 5 |
| 6 |
| 7 |
| 8 |
| 9 |
| 10 |
| 11 |
| 12 |


| Num |  | Prob |
| :---: | :--- | :--- |
|  |  | $1 / 36$ |
| 2 |  | $1 / 18$ |
| 3 |  | $1 / 12$ |
| 4 |  | $1 / 9$ |
| 5 |  | $5 / 36$ |
| 6 |  | $1 / 6$ |
| 5 |  | $5 / 36$ |
| 4 |  | $1 / 9$ |
| 3 |  | $1 / 12$ |
| 2 |  | $1 / 18$ |
| 1 |  | $1 / 36$ |

All microstates are equally probable. All macrostates are not.

## Interactive Question

What is the probability of flipping a coin and getting 5 heads in a row?
A) $1 / 2$
B) $1 / 5$
C) $1 / 16$
D) $1 / 32$
E) $1 / 64$


A pendulum in an isolated box with 3 gas molecules and 11 units of energy. Why doesn't the pendulum start swinging on its own? We do know that energy is conserved.

$$
E_{\mathrm{tot}}=E_{\mathrm{gas}}+E_{\mathrm{pend}}
$$

Let's say the gas molecules are identical so microstates that differ only by rearranging the molecules are really the same. For instance, the microstate $(1,0,0)$ is identical to the microstate $(0,1,0)$.

The energy could be distributed in the gas in the following microstates.
E Microstates
$0 \quad(0,0,0)$
$1 \quad(1,0,0)$
$2(2,0,0)(1,1,0)$
$3(3,0,0)(2,1,0)(1,1,1)$
$4(4,0,0)(3,1,0)(2,2,0)(2,1,1)$
$5 \quad(5,0,0)(4,1,0)(3,2,0)(3,1,1)(2,2,1)$
$6 \quad(6,0,0)(5,1,0)(4,2,0)(4,1,1)(3,3,0)(3,2,1)(2,2,2)$
$7 \quad(7,0,0)(6,1,0)(5,2,0)(5,1,1)(4,3,0)(4,2,1)(3,3,2)(3,2,2)$
$8(8,0,0)(7,1,0)(6,2,0)(6,1,1)(5,3,0)(5,2,1)(4,4,0)(4,3,1)(4,2,2)$ $(3,2,2)$
$9(9,0,0)(8,1,0)(7,2,0)(7,1,1)(6,3,0)(6,2,1)(5,4,0)(5,3,1)(5,2,2)$ $(4,4,1)(4,3,2)(3,3,3)$
$10(10,0,0)(9,1,0)(8,2,0)(8,1,1)(7,3,0)(7,2,1)(6,4,0)(6,3,1)(6,2,2)$ $(5,5,0)(5,4,1)(5,3,2)(4,4,2)(4,3,3)$
$11(11,0,0)(10,1,0)(9,2,0)(9,1,1)(8,3,0)(8,2,1)(7,4,0)(7,3,1)(7,2,2)$ $(6,5,0)(6,4,1)(6,3,2)(5,5,1)(5,4,2)(5,3,3)(4,4,3)$


A pendulum in an isolated box with 3 gas molecules and 11 units of energy. Why doesn't the pendulum start swinging on its own? We do know that energy is conserved.

$$
E_{\mathrm{tot}}=E_{\mathrm{gas}}+E_{\mathrm{pend}}
$$

What is the most probable energy state?
$E_{\text {gas }}=11$
$E_{\text {pend }}=0$
The second law of thermodynamics is not about some new force or interaction, but just about probabilities. Systems migrate to the most probable macrostate, the one with the most microstates available.


A volume divided up into $N_{\mathrm{V}}$ regions. Here $N_{\mathrm{V}}$ is 3 .

1 molecule $(\mathrm{A}, 0,0)(0, \mathrm{~A}, 0)(0,0, \mathrm{~A})$
2 molecules (AB, 0,0 ) ( $0, \mathrm{AB}, 0$ ) ( $0,0, \mathrm{AB}$ ) ( $\mathrm{A}, \mathrm{B}, 0)(\mathrm{B}, \mathrm{A}, 0)$ $(\mathrm{A}, 0, \mathrm{~B})(\mathrm{B}, 0, \mathrm{~A})(0, \mathrm{~A}, \mathrm{~B})(0, \mathrm{~B}, \mathrm{~A})$
\# molecules
1
2
3
$N$
$\frac{3 \text { regions }}{3} \quad \frac{4 \text { regions }}{4}$
9
27
$3^{N}$

16
64

For $N$ molecules, the number of microstates $(\mathcal{W})$ is proportional to the volume to the $N$ th power. $\mathcal{W} \propto(\text { Volume })^{N}$

Let's see how a small isothermal expansion changes $\mathcal{W}$.
$\mathcal{W}_{\mathrm{f}} / \mathcal{W}_{\mathrm{i}}=\{(V+\Delta V) / V\}^{N}=(1+\Delta V / V)^{N}$
$\Delta Q=\Delta U+\Delta W=P \Delta V=(N k T) \Delta V / V$
$\mathcal{W}_{\mathrm{f}}^{\prime} \mathcal{W}_{\mathrm{i}}=(1+\Delta V / V)^{N}=\left\{(1+\Delta Q /(N k T)\}^{N}\right.$
When $N$ is very large, it is more convenient to use a smaller number by taking the natural logarithm. $\ln \mathcal{W}_{\mathrm{f}}-\ln \mathcal{W}_{\mathrm{i}}=\ln \left\{(1+\Delta Q /(N k T)\}^{N}=N \ln \{(1+\Delta Q /(N k T)\}\right.$ For small $x, \ln (1+x) \approx x$
$\ln \mathcal{W}_{\mathrm{f}}-\ln \mathcal{W}_{\mathrm{i}}=N \Delta Q /(N k T)$
$k \ln \mathcal{W}_{\mathrm{f}}-k \ln \mathcal{W}_{\mathrm{i}}=\Delta Q / T$
We have already seen that $\Delta S=\Delta Q / T$, so now we have another equivalent way of writing entropy:
$S=k \ln \mathcal{W}$
where $\mathcal{W}$ is the number of microstates!
$S=k \ln \mathscr{W}$
An increase in entropy is simply an increase in the number of microstates. The entropy always increases simply because a system will always migrate to the most probable state! There is nothing magic about entropy.

The Second Law of Thermodynamics: $\Delta S \geq 0$ For any real process: $\Delta S>0$

Problem: Two moles of an ideal gas undergo a free expansion to four times the initial volume. Find the change in entropy for this irreversible process using statistical means?

For $N$ identical objects with two possible configurations, one having $n_{1}$ objects and the other having $n_{2}$ objects, the number of microstates is given by:

$$
\mathcal{W}=N!/\left(n_{1}!n_{2}!\right)
$$

## Interactive Question

There are 25 identical molecules in a box that can be found on either the left side of the box or the right side of the box. How many total microstates are there?
A) 25
B) 50
C) 125
D) $3.36 \times 10^{7}$
E) $1.55 \times 10^{25}$

## Interactive Question

There are 25 identical molecules in a box. How many microstates are there with 10 molecules on one side of the box and 15 molecules on the other side of the box?
A) $1.03 \times 10^{23}$
B) $3.27 \times 10^{6}$
C) 150
D) 25
E) 5

Problem: (a) What is the probability that a coin is flipped 10 times and 10 heads come up?
(b) What is the change in entropy when you take 5 heads and 5 tails, and change them to 10 heads?

