PHYS 1P22/92 Prof. Barak Shoshany Spring 2024

15. Thermodynamics

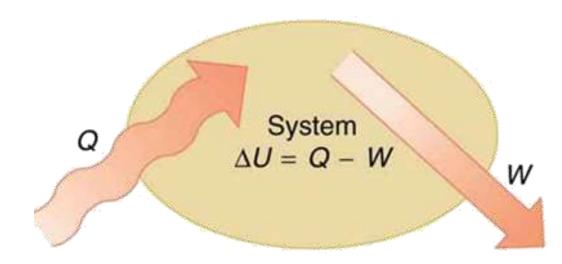
15.1 The First Law of Thermodynamics

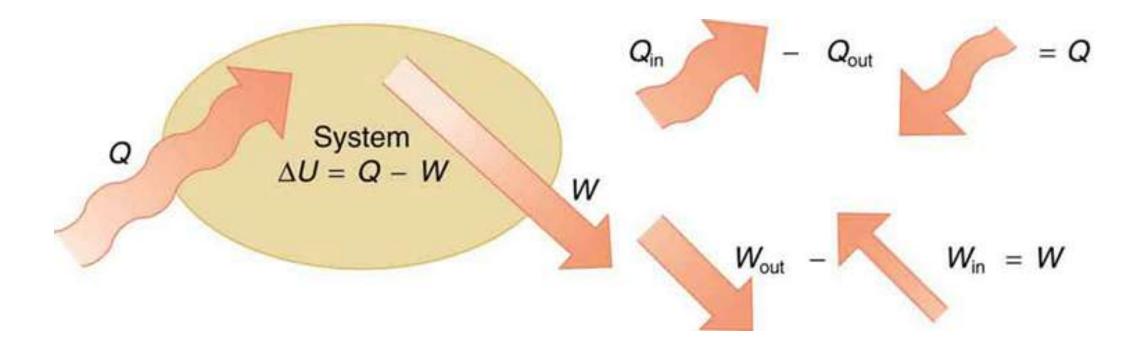
The First Law of Thermodynamics

• Closed system, can exchange heat and work but not matter.

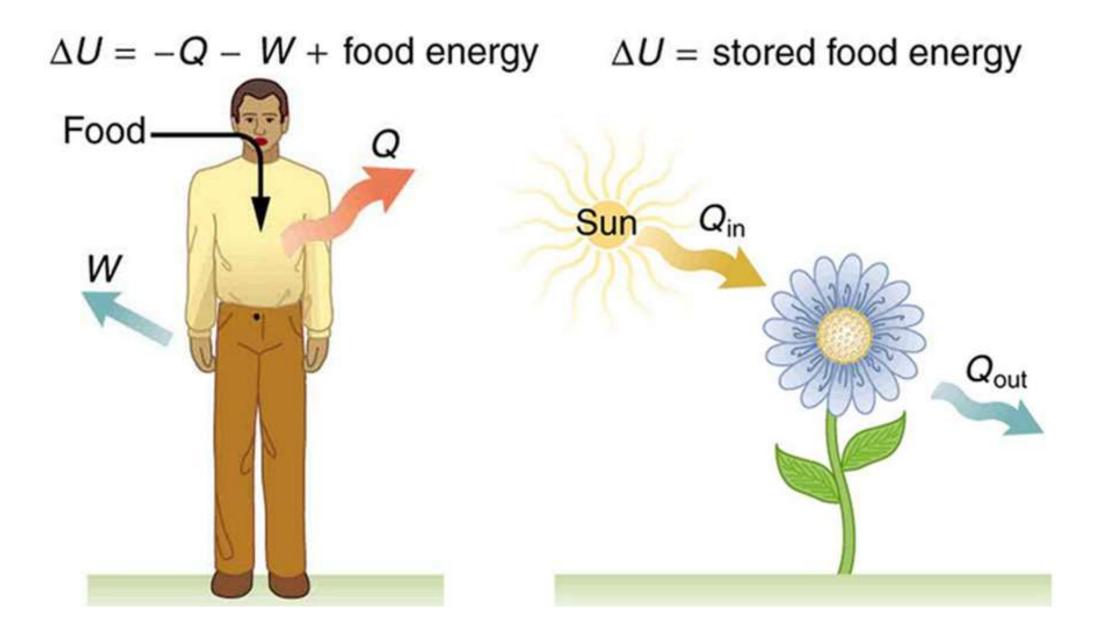
 $\Delta U = Q - W$

- U = internal energy.
- ΔU = change in internal energy.
- *Q* = net heat transferred **into** the system.
 - $Q \equiv |Q_{\rm in}| |Q_{\rm out}|$
- *W* = net work done **by** the system.
 - $W \equiv |W_{\rm by}| |W_{\rm on}|$
- Just conservation of energy...





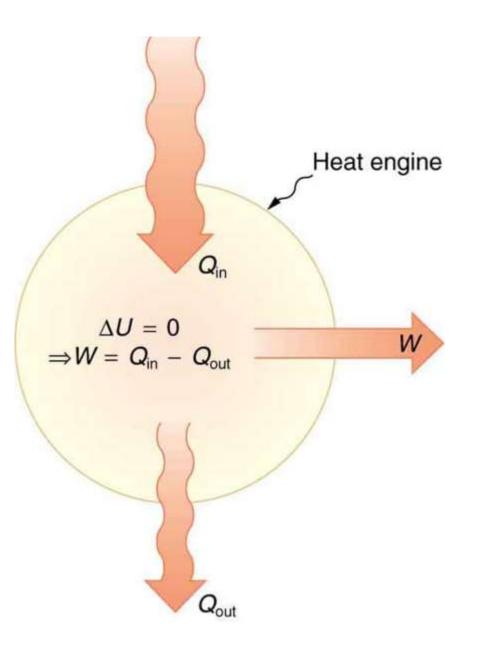
Note: The 2nd edition of the textbook uses ΔE_{int} instead of ΔU . However, the correct notation is ΔU .



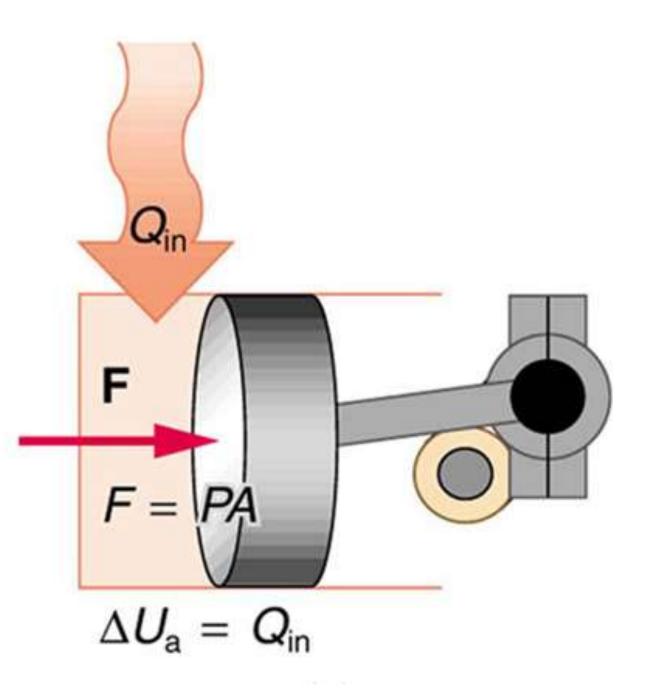
15.2 The First Law of Thermodynamics and Some Simple Processes

Schematic representation of a heat engine.

It is impossible to devise a system where $Q_{out} = 0$.



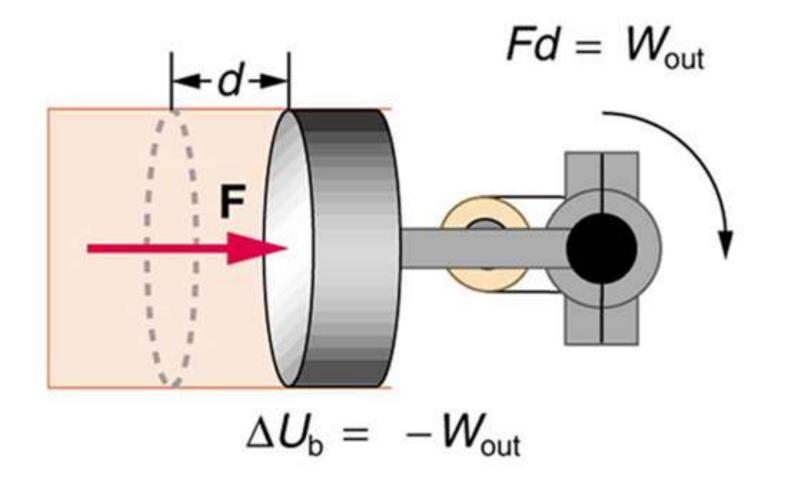
Heat transfer to the gas in a cylinder increases the internal energy of the gas, creating higher pressure and temperature.



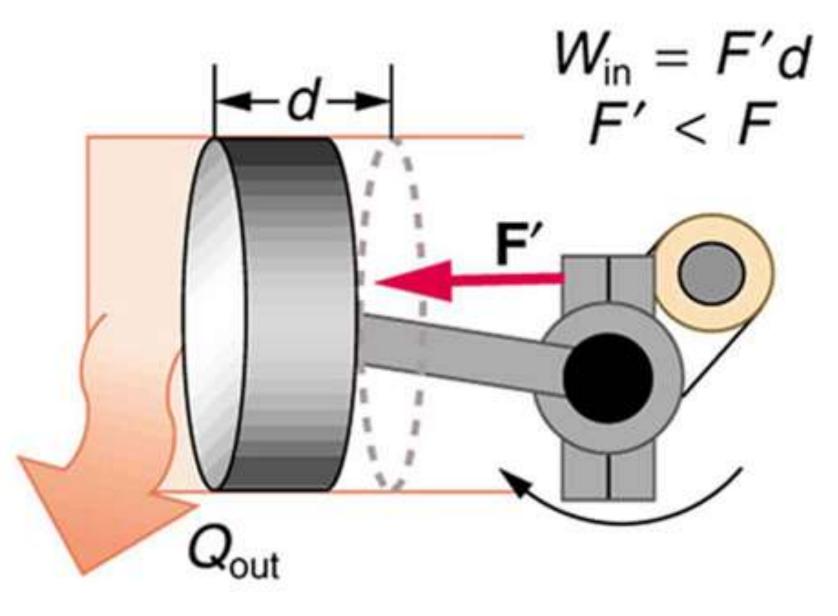
The force exerted on the cylinder does work.

Gas pressure and temperature decrease when it expands.

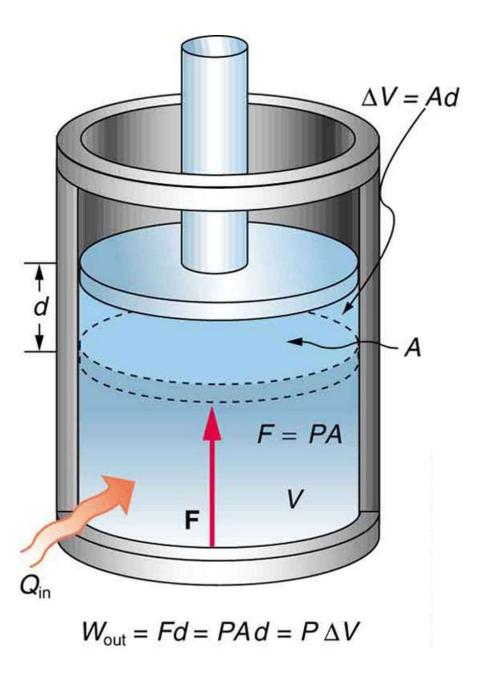
The gas's internal energy has been decreased by doing work.



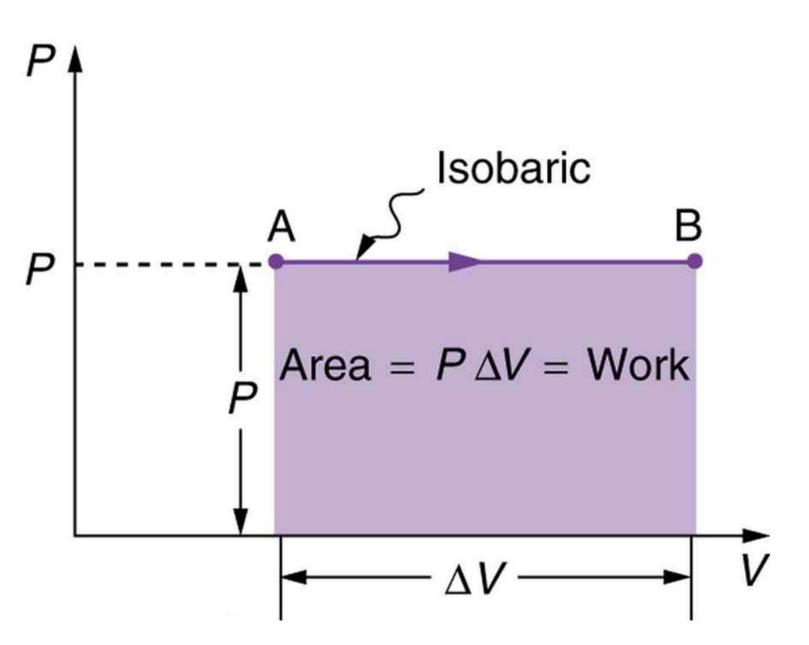
Heat transfer to the environment further reduces pressure in the gas so that the piston can be more easily returned to its starting position.



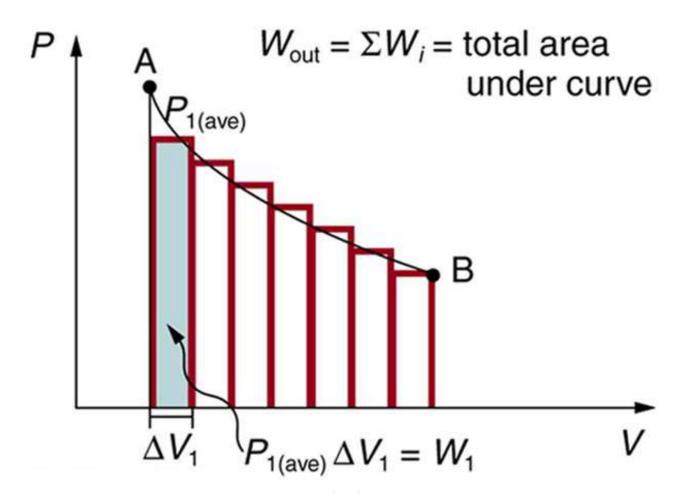
An isobaric (constant pressure) expansion of a gas requires heat transfer to keep the pressure constant.

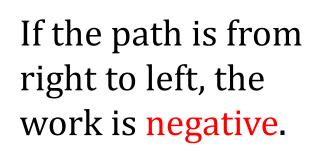


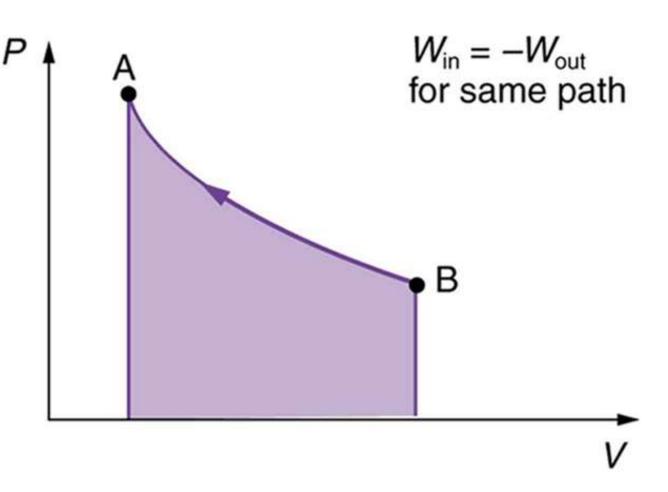
A *PV* diagram for an isobaric process. The area under the curve equals the work done by the gas.



If the pressure is not constant, we need to use calculus to calculate the total area under the curve using an integral.





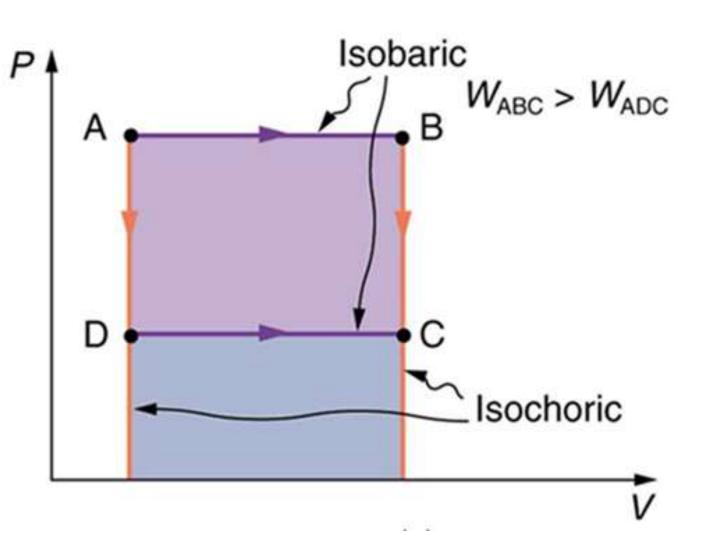


The horizontal lines are **isobaric: constant pressure.**

The vertical lines are **isochoric: constant volume.**

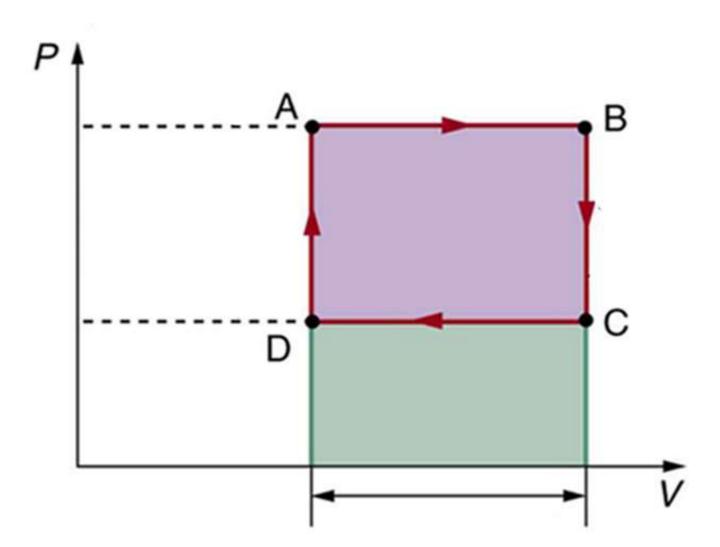
The work done in going from A to C depends on the path.

 $W_{ABC} > W_{ADC}$ because ABC is at higher pressure.



The total work done in the cyclical process ABCDA is the area inside the loop.

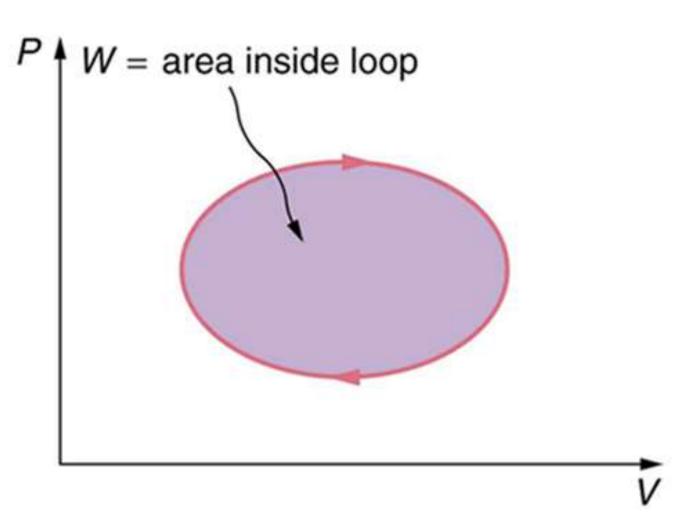
The negative area below CD cancels out.



The area inside any closed loop is the work done in the cyclical process.

If the loop is clockwise, *W* is positive = work done on the outside environment.

If the loop is **counterclockwise**, *W* is **negative** = work done to the system.



The upper curve is an isothermal process $(\Delta T = 0 \text{ or constant } T)$. The lower curve is an adiabatic process (Q = 0).

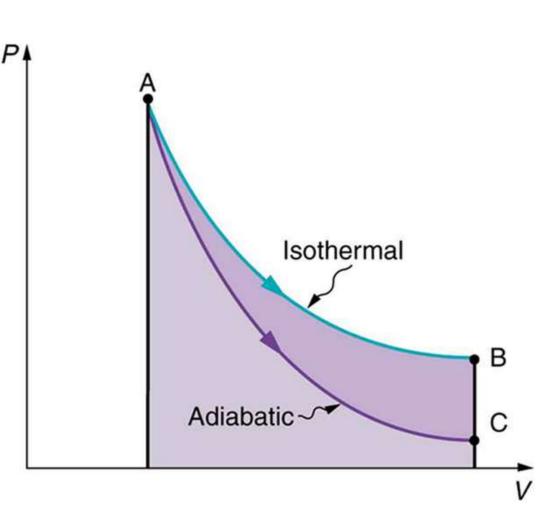
For the isothermal process:

$$U = N \cdot \frac{1}{2}m\bar{v}^2 = \frac{3}{2}Nk_BT$$

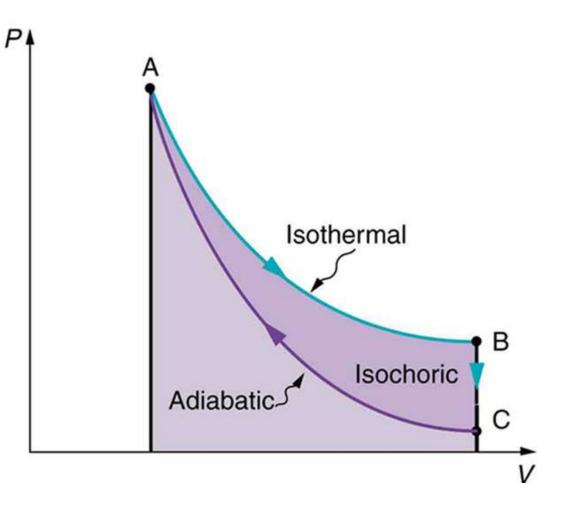
So if *T* is constant:

$$\Delta U = Q - W = 0 \implies Q = W$$

The adiabatic process converts some internal energy to work ($\Delta U = -W$), so *T* must decrease, therefore *P* also decreases ($PV = Nk_BT$). The isothermal process does more work.



The cycle ABCA produces a net work output.



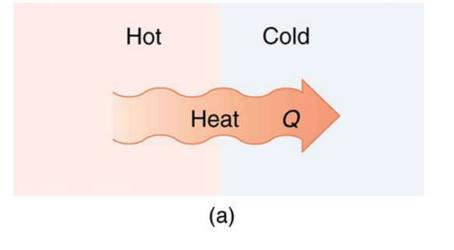
Pop Quiz:

Term	Meaning	Defining Eq.	Work
Isobaric			
Isochoric			
Isothermal			
Adiabatic			

Answers:

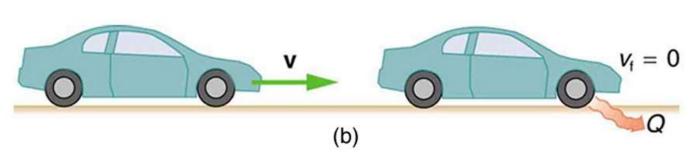
Term	Meaning	Defining Eq.	Work
Isobaric	Constant pressure	$\Delta P = 0$	$W = P\Delta V$
Isochoric	Constant volume	$\Delta V = 0$	W = 0
Isothermal	Constant temperature	$\Delta T = \Delta U = 0$	W = Q
Adiabatic	No heat transfer	Q = 0	$W = -\Delta U$

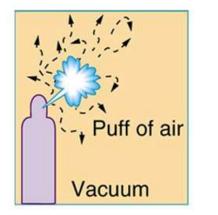
15.3 Heat Engines and Their Efficiency

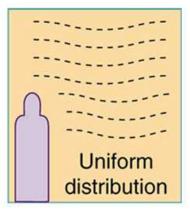


Examples of irreversible (1-way) processes:

- a. Heat transfer: hot \Rightarrow cold.
- b. Brakes: kinetic energy \Rightarrow heat.
- c. Gas expands to fill a container.



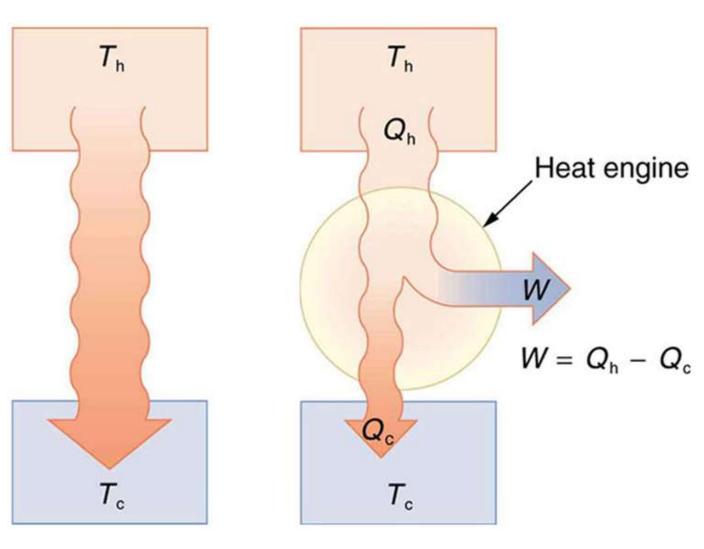




The Second Law of Thermodynamics (first version)

Heat flows spontaneously from a hot system to a cold system, but not in the other direction.

- Top (T_h) : Hot reservoir $(T_h > T_c)$.
- Bottom (*T*_c): Cold reservoir.
- Left: 2nd law of thermodynamics, heat flows from hot to cold.
- Right: Heat engine (circle) uses part of the heat transfer to do work *W*.
- $Q_{\rm h}$ = heat transfer **out of** the hot reservoir.
- Q_c = heat transfer **into** the cold reservoir.



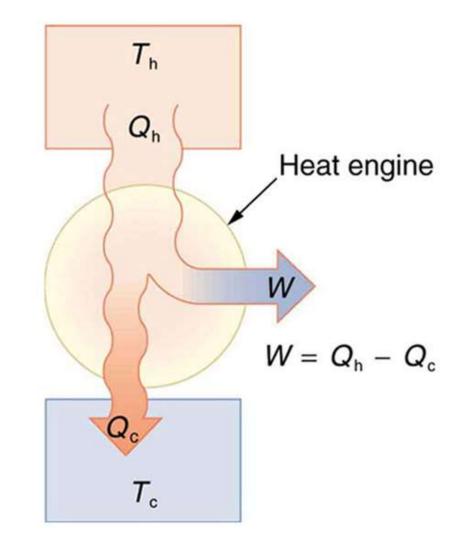
The Second Law of Thermodynamics (second version)

Heat engines are not perfect. That is, heat cannot be completely converted to work in a cyclical process. Efficiency η (Greek eta) = ratio of work output to energy input:

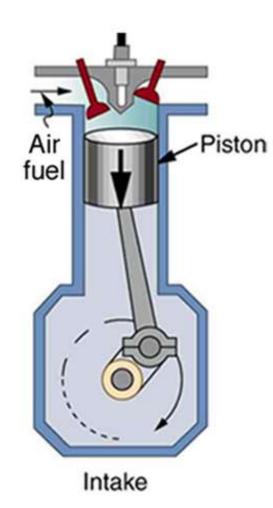
$$\eta \equiv \frac{W}{Q_{\rm h}} = \frac{Q_{\rm h} - Q_{\rm c}}{Q_{\rm h}} = 1 - \frac{Q_{\rm c}}{Q_{\rm h}}$$

•
$$\eta = 1 = 100\%$$
 if $Q_c = 0$ (or $Q_h = \infty$).

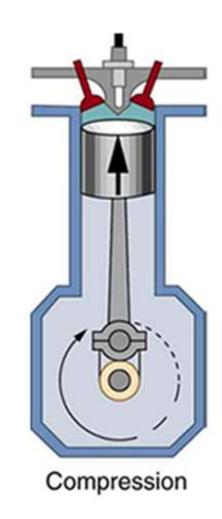
• But we will prove soon that this is not possible.



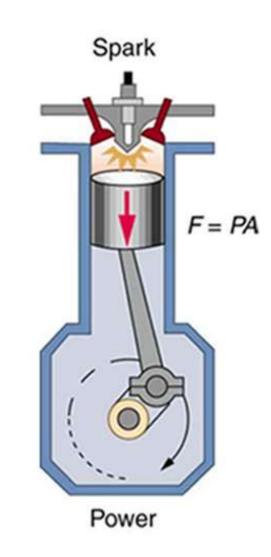
- Otto cycle: an idealized thermodynamic cycle that describes the functioning of engines like the four-stroke internal combustion engine.
- Step 1: Air is mixed with fuel during the intake stroke.



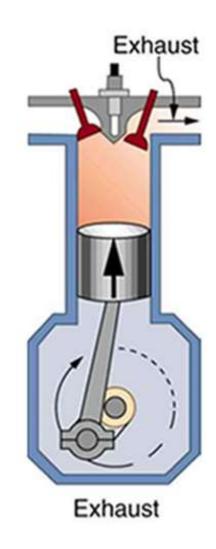
• Step 2: During the compression stroke, the air-fuel mixture is rapidly compressed in a nearly adiabatic process, as the piston rises with the valves closed. Work is done on the gas.



- Step 3: The power stroke has two distinct parts.
- First, the air-fuel mixture is ignited, converting chemical potential energy into thermal energy, increasing pressure.
- Then the piston descends, and the gas does work by exerting a force through a distance in a nearly adiabatic process.

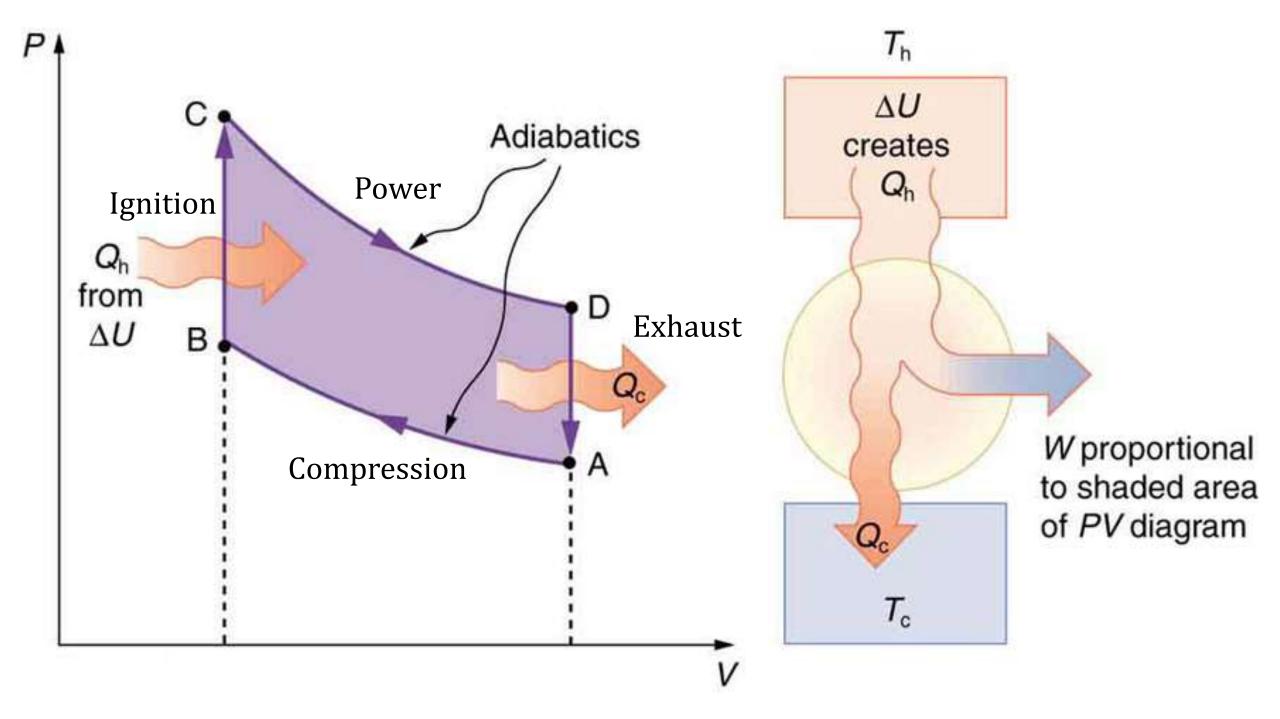


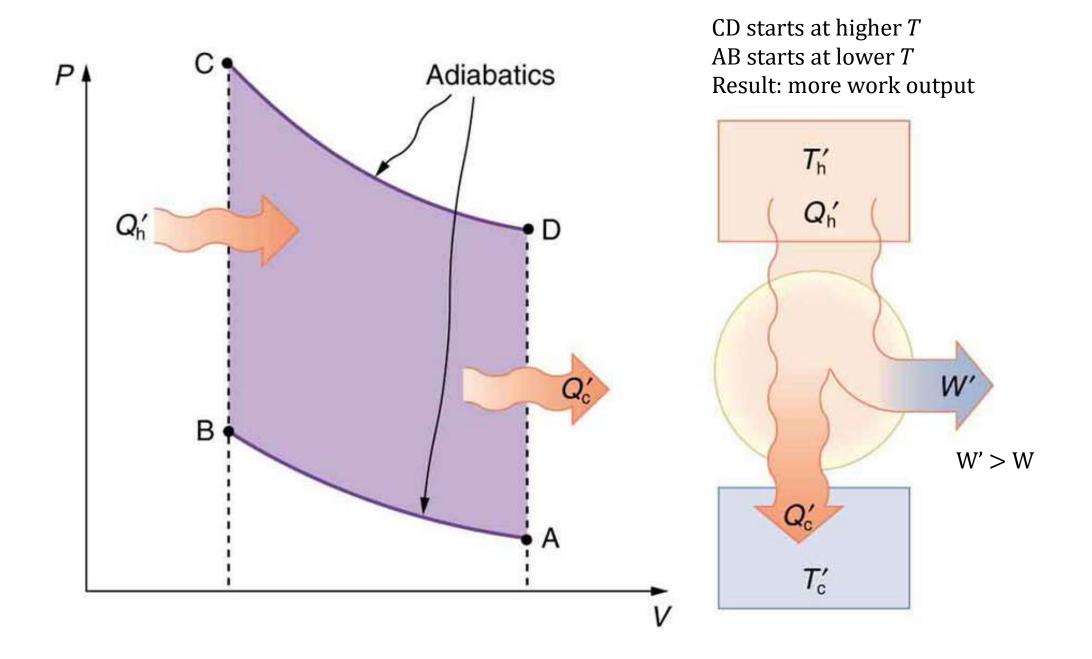
• Step 4: The exhaust stroke expels the hot gas to prepare for another cycle.





https://youtu.be/Pu7g3uIG6Zo





15.4 Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated

The drinking bird: "perpetual motion"?

- Head gets wet
- Water evaporates
- Head cools
- Pressure lowers in head
- Fluid rises
- Center of gravity changes
- Bird tips forward
- Pressure equalizes
- Fluid flows back down
- Bird tips back up
- Repeat...

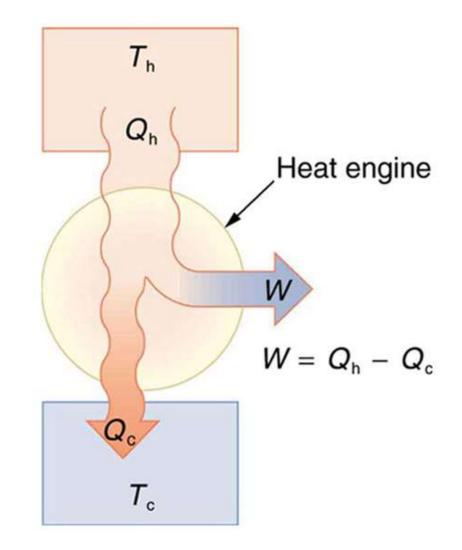


• Recall the definition of efficiency η :

$$\eta \equiv \frac{W}{Q_{\rm h}} = \frac{Q_{\rm h} - Q_{\rm c}}{Q_{\rm h}} = 1 - \frac{Q_{\rm c}}{Q_{\rm h}}$$

•
$$\eta = 1 = 100\%$$
 if $Q_c = 0$ (or $Q_h = \infty$).

- Cannot be achieved.
- What is the maximum possible efficiency?
- Carnot cycle: the most efficient (cyclical) process possible. Theoretical only.
- Carnot engine: an engine using the Carnot cycle.

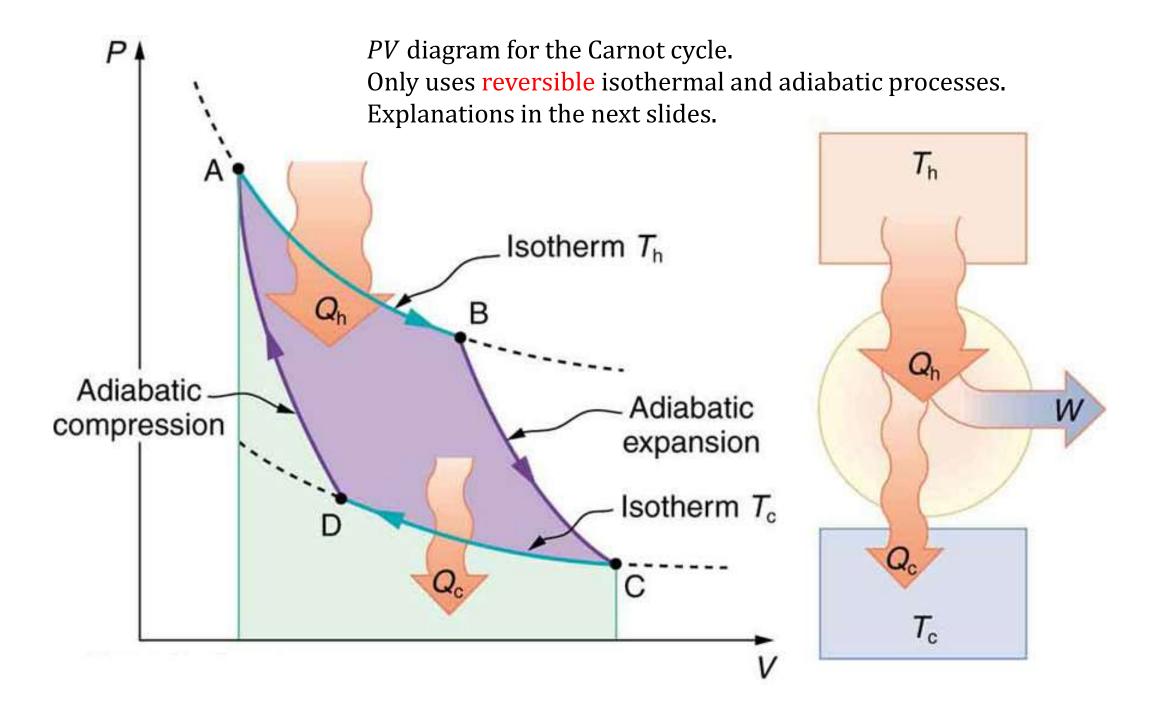


The Second Law of Thermodynamics (first version)

Heat flows spontaneously from a hot system to a cold system, but not in the other direction. The Second Law of Thermodynamics (second version)

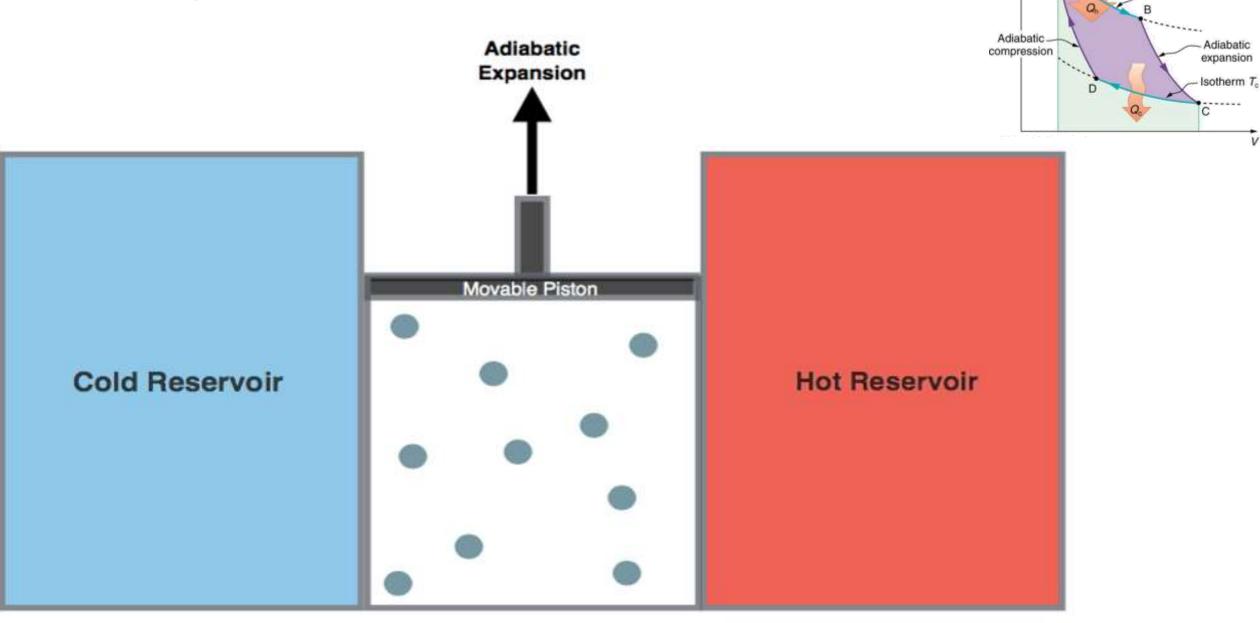
Heat engines are not perfect. That is, heat cannot be completely converted to work in a cyclical process. The Second Law of Thermodynamics (third version)

The maximum possible efficiency of any reversible heat engine is that of the Carnot engine.



P **AB:** Heat transferred from hot reservoir to the gas. Gas temperature stays constant, but it expands and does work. Isotherm T_h В Adiabatic Adiabatic compression expansion Isotherm T_c C Isothermal Expansion **Movable Piston Cold Reservoir Hot Reservoir QH**

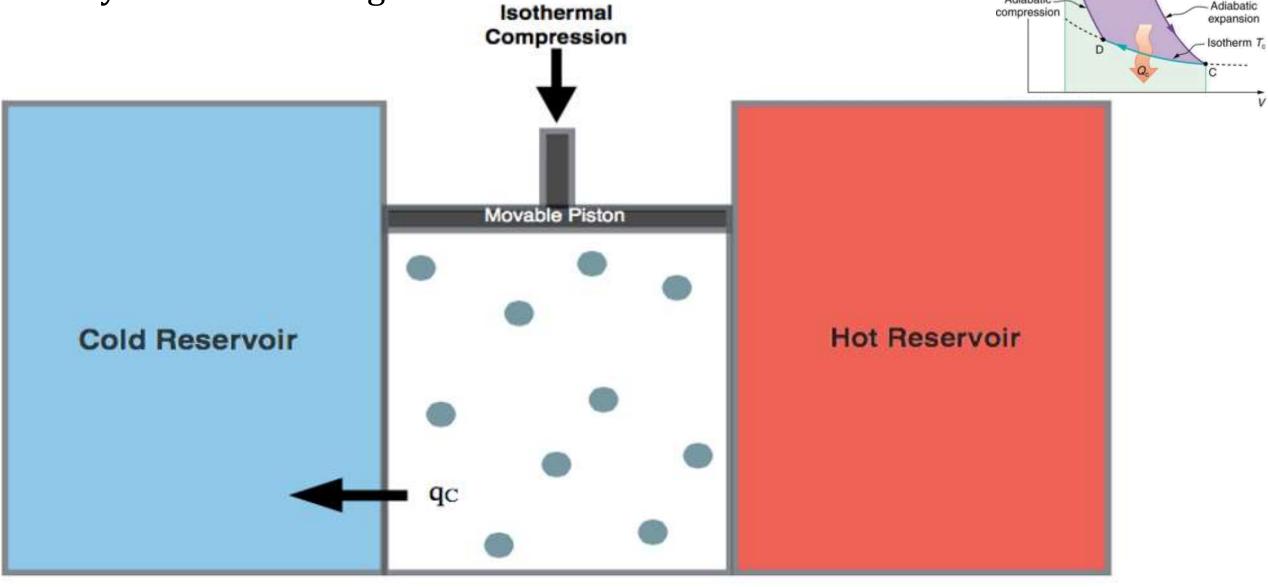
BC: No heat transfer, gas continues to expand and do work while cooling down.



PI

Isotherm Th

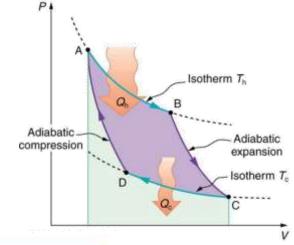
CD: Heat transferred from gas to the cold reservoir. Gas temperature stays constant, but it compresses and work is done on it by the surroundings.

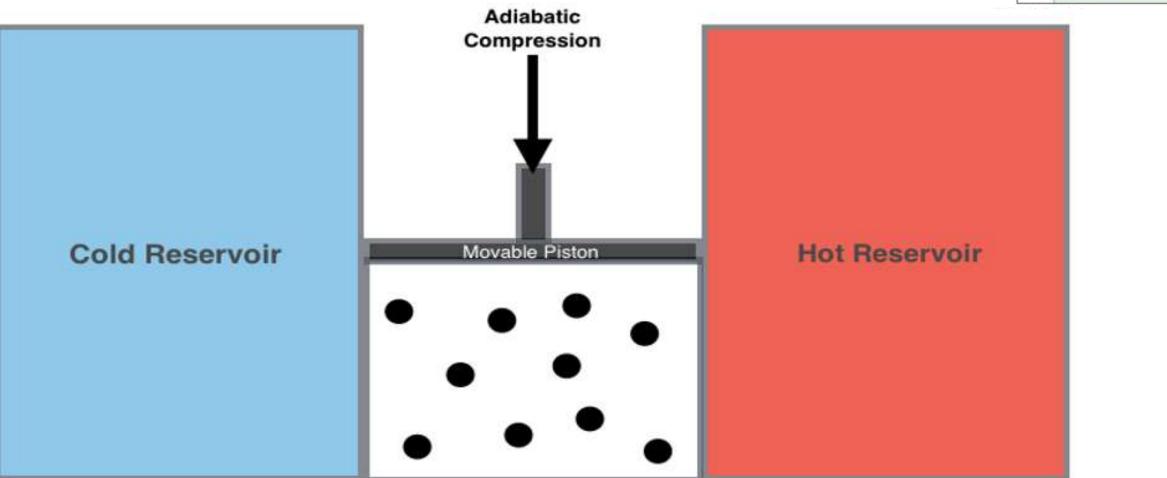


Isotherm T_h

В

DA: No heat transfer, gas continues to compress and work is done on it while heating up.



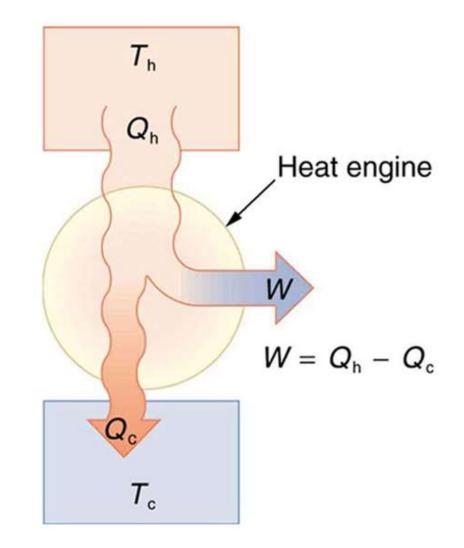


• In a Carnot engine:

$$\frac{Q_{\rm c}}{Q_{\rm h}} = \frac{T_{\rm c}}{T_{\rm h}} \quad \Rightarrow \quad \eta = 1 - \frac{Q_{\rm c}}{Q_{\rm h}} = 1 - \frac{T_{\rm c}}{T_{\rm h}}$$

(*T* is absolute temperature!)

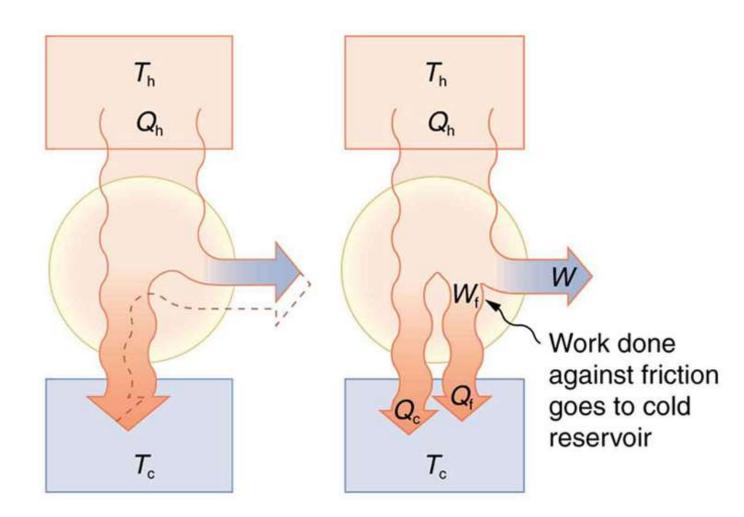
- $\eta = 1 = 100\%$ if $T_{\rm c} = 0$ (or $T_{\rm h} = \infty$)
- Neither option is realistically possible, therefore $\eta < 1$ in practice.
- To maximize:
 - $T_{\rm c}$ should be as small as possible, and/or
 - *T*_h should be as large as possible.



Real heat engines are less efficient than Carnot engines.

Solid = actual (irreversible, practical)

Dashed = Carnot (reversible, theoretical)

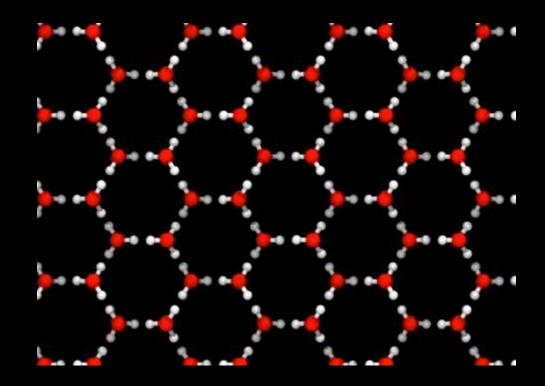


(Skipping section 15.5)

15.6 Entropy and the Second Law of Thermodynamics

- Colloquial definition: entropy is a measure of (microscopic) disorder.
- Ice: low entropy, molecules organized in lattice.
- Water: high entropy, molecules disorganized and free to move.
- Melting a block of ice increases entropy.





The Second Law of Thermodynamics (final version)

The total entropy of a system never decreases. It is constant for reversible processes, and increases for irreversible processes.

Precise definition of entropy

• For Carnot cycle (or any **reversible** process):

$$\frac{Q_{\rm c}}{Q_{\rm h}} = \frac{T_{\rm c}}{T_{\rm h}}$$

Therefore

$$\frac{Q_{\rm c}}{T_{\rm c}} = \frac{Q_{\rm h}}{T_{\rm h}}$$

We define the ratio on both sides as the **change in entropy**:

$$\Delta S \equiv \frac{Q}{T}$$

Remember that $Q \equiv |Q_{in}| - |Q_{out}|$.

Units of entropy

$$\Delta S \equiv \frac{Q}{T}$$

Pop Quiz: What are the units of entropy?

Answer:

$$\begin{bmatrix} Q \end{bmatrix} = \mathbf{J}$$
$$\begin{bmatrix} T \end{bmatrix} = \mathbf{K}$$

Therefore:

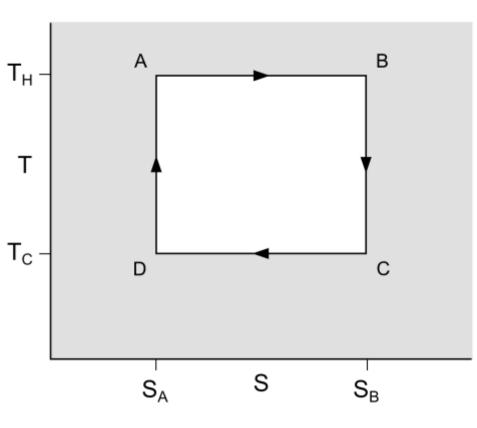
$$[S] = \frac{J}{K} \text{ or } J \cdot K^{-1}$$

Some calculus (not required for the course)

The precise relation between heat *Q*, temperature *T*, and entropy *S* is

$$Q = \int_{A}^{B} T \, \mathrm{d}S$$

This is the area under the curve in a *TS* diagram. If we just use average *T* and finite ΔS then we get $Q = T\Delta S$, so $\Delta S = \frac{Q}{T}$



ΔS for a **reversible** process

Hot reservoir **loses** entropy: (negative, heat is flowing **out** of it)

$$\Delta S_{\rm h} = -\frac{Q_{\rm h}}{T_{\rm h}}$$

Cold reservoir gains entropy: (positive, heat is flowing into it)

$$\Delta S_{\rm c} = + \frac{Q_{\rm c}}{T_{\rm c}}$$

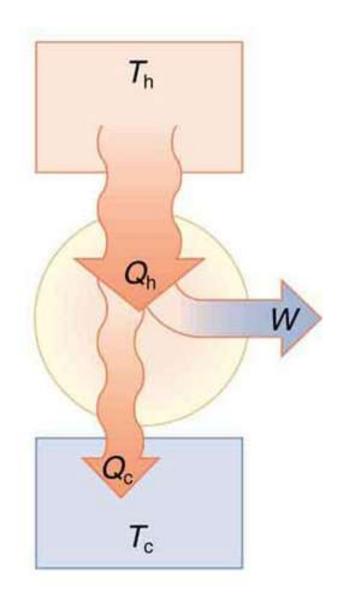
In total:

$$\Delta S_{\text{total}} = \Delta S_{\text{h}} + \Delta S_{\text{c}} = -\frac{Q_{\text{h}}}{T_{\text{h}}} + \frac{Q_{\text{c}}}{T_{\text{c}}} = 0$$

Because

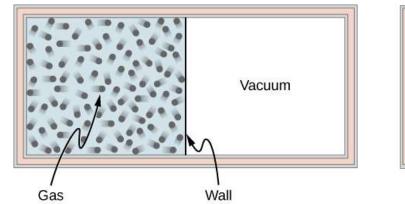
$$\frac{Q_{\rm c}}{T_{\rm c}} = \frac{Q_{\rm h}}{T_{\rm h}}$$

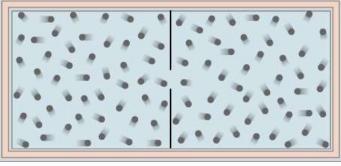
So total entropy doesn't change **in a reversible process**.



Examples of **irreversible** processes

- Heat transfer from hot to cold.
- Friction.
- Gas expanding to fill a container (see below).
- Mixing two fluids.
- Glass breaking.
- Any process that takes place spontaneously without doing work.





Gas fills the container

Can glass be spontaneously unbroken?

- We intuitively know when the video is played in reverse.
- Newton's laws, relativity, and quantum mechanics are **not** broken in the reverse process!
- Only the 2nd law of thermodynamics is broken, since entropy decreases.



The arrow of time

Open problem in physics:

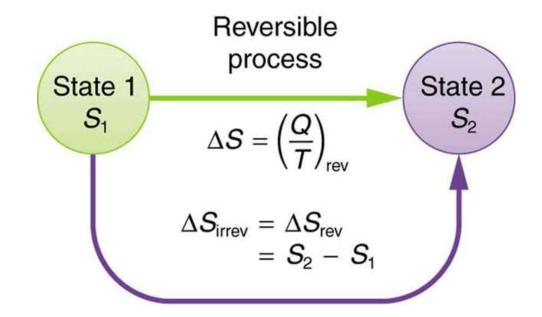
- M<u>i</u>croscopic processes are timereversible, m<u>a</u>croscopic processes are not.
- But any m<u>a</u>croscopic process is made of small m<u>i</u>croscopic ones.
- How to reconcile this?

Another problem:

- Time advances in the direction of increasing entropy.
- Other arrows of time exist, e.g. cosmological.
- Are they related?

ΔS for an **irreversible** process

- Entropy depends only on the state of the system, no matter how it got to that state.
- So ΔS between two states 1 and 2 is the same no matter how the system got from 1 to 2.
- To find ΔS for an **irreversible** process, find a hypothetical **reversible** process between the **same** states, and calculate $\Delta S = Q/T$.

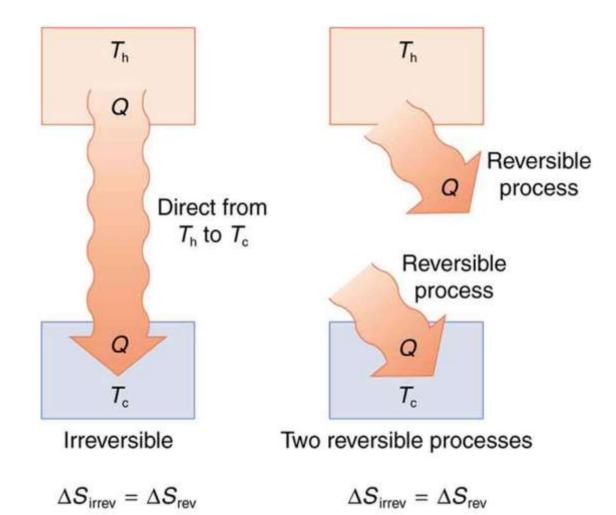


Irreversible process has the same ΔS

Example

- Irreversible process: spontaneous heat transfer from hot to cold.
- Instead consider two **reversible** processes with equivalent result:

$$\Delta S_{\rm h} = -\frac{Q_{\rm h}}{T_{\rm h}}, \qquad \Delta S_{\rm c} = \frac{Q_{\rm c}}{T_{\rm c}}$$
$$\Delta S_{\rm tot} = \Delta S_{\rm h} + \Delta S_{\rm c} = -\frac{Q_{\rm h}}{T_{\rm h}} + \frac{Q_{\rm c}}{T_{\rm c}}$$



Class Problem: Calculate the total change in entropy in heat transfer with: $Q_{\rm h} = Q_{\rm c} \approx 4000 \,\text{J}$ $T_{\rm h} \approx 600 \,\text{K}, \quad T_{\rm c} \approx 250 \,\text{K}$

Did entropy increase, decrease, or stay the same? Why?

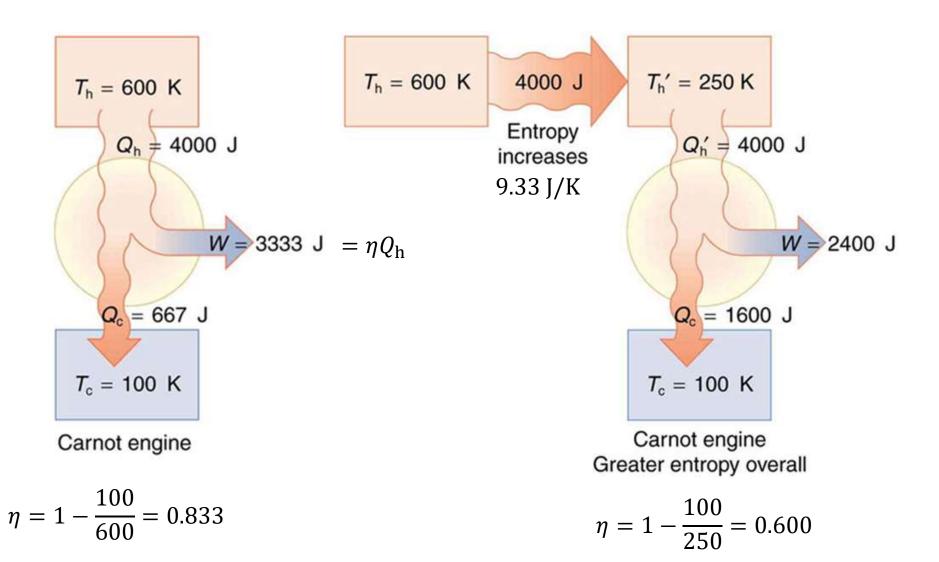
Solution:

$$\Delta S_{\text{tot}} = -\frac{Q_{\text{h}}}{T_{\text{h}}} + \frac{Q_{\text{c}}}{T_{\text{c}}}$$
$$\approx -\frac{4000 \text{ J}}{600 \text{ K}} + \frac{4000 \text{ J}}{250 \text{ K}}$$
$$= 9.33 \text{ J/K}$$

The 2nd law of thermodynamics: entropy always increases for irreversible processes!

Entropy and unavailability of energy for work

- There is 933 J less work from the same heat transfer in the process with the higher entropy.
- General result: $W_{\text{unavail}} = T_{\text{c}}\Delta S$



Heat death of the universe: the "Big Freeze"

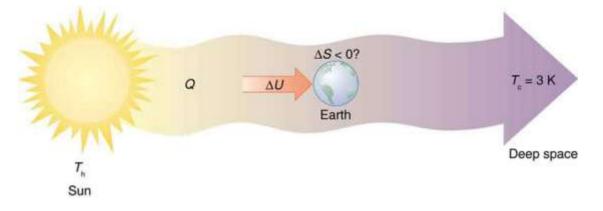
- Early universe was homogenous.
 - Lowest entropy, largest amount of energy available to do work.
- With time, temperature differences arose.
 - E.g.: stars > planets > asteroids > vacuum.
 - Temperature differences = heat engine = work.
 - Stars and planets have their own energy, but in finite amounts.
 - As time passes, by the 2nd law, entropy increases.
 - Less and less energy available to do work.

- When fuels on Earth (fossil, nuclear, wind, geothermal, tidal...) are used, some of the energy becomes permanently unavailable.
- The Sun will die in 5 billion years.
- In the very very far future (~10¹⁰⁰ years)...
 - All stars will die.
 - All temperatures will equalize.
 - Maximum entropy will be reached.
 - No heat engines possible, no more work can be done.
 - All activity will cease.

(This is just one possible scenario!)

2nd law of thermodynamics and evolution

- A common (but incorrect) argument against evolution: when complex life forms evolves from simple ones, entropy decreases.
- The 2nd law only says that the **total** entropy cannot decrease. The entropy of a **particular system** can decrease if the entropy of another increases.
- Entropy can be decreased by putting energy into the system.
 - Example: a glass cannot spontaneously unbreak itself, but I can use energy (work) to pick up the pieces and glue them together, decreasing entropy.
- The entropy on Earth can decrease because it absorbs energy from the Sun. The overall entropy of the solar system will increase.



Mathematical interlude: logarithms

Exponentiation

• Positive integer exponent (*b* = base):

$$b^n \equiv \underbrace{b \times \cdots \times b}_{n \text{ times}}$$

Example:

$$2^4 = 2 \times 2 \times 2 \times 2 = 16$$

• Zero exponent:

 $b^0 \equiv 1$

• Negative integer exponent:

$$b^{-n} \equiv \frac{1}{b^n}$$

Example:

$$5^{-2} = \frac{1}{5^2} = \frac{1}{5 \times 5} = \frac{1}{25}$$

• Unit fraction exponent:

 $b^{1/n} \equiv \sqrt[n]{b}$

Example:

$$27^{1/3} = \sqrt[3]{27} = 3$$

• Rational exponent:

 $b^{m/n} \equiv \sqrt[n]{b^m}$

Example:

$$8^{2/3} = \sqrt[3]{8^2} = \sqrt[3]{64} = 4$$

Identities

• Sum becomes product:

$$b^{m+n} = b^m \cdot b^n$$

• Difference becomes quotient:

$$b^{m-n} = \frac{b^m}{b^n}$$

• Product becomes power:

 $b^{mn} = (b^m)^n$

• Exponentiation "increases the level of the operation":

 $+ \Rightarrow \times \Rightarrow \blacksquare$

Logarithms

• Some examples of inverse functions:

$$x^2 \iff \sqrt{x} \longrightarrow \sqrt{x^2} = (\sqrt{x})^2 = x$$

 $\sin x \iff \arcsin x \longrightarrow \arcsin(\sin x) = \sin(\arcsin x) = x$

$$\frac{1}{x} \iff \frac{1}{x} \longrightarrow \frac{1}{1/x} = x$$

Definition

- The logarithm is the inverse function of exponentiation: $b^y = x \iff \log_h x = y$
- Logarithm cancels exponential:

$$\log_b b^x = b^{\log_b x} = x$$

- log_b x means "to what power should I raise b to get x?"
 - Example: log₁₀ 100 means "to what power should I raise 10 to get 100?", and the answer is 2.

Choice of base *b*

- *b* = 2 (binary logarithm) in computer science, information theory, etc.
 - Example: $\log_2 16 = 4$ because $16 = 2^4$.
- $b = e \approx 2.718...$ (natural logarithm) in math, statistics, physics, chemistry, engineering, etc.
 - Special notation: $\ln x \equiv \log_e x$.
 - Example: $\ln 7 \approx 1.946$ because $e^{1.946} \approx 7$.

Choice of base *b*

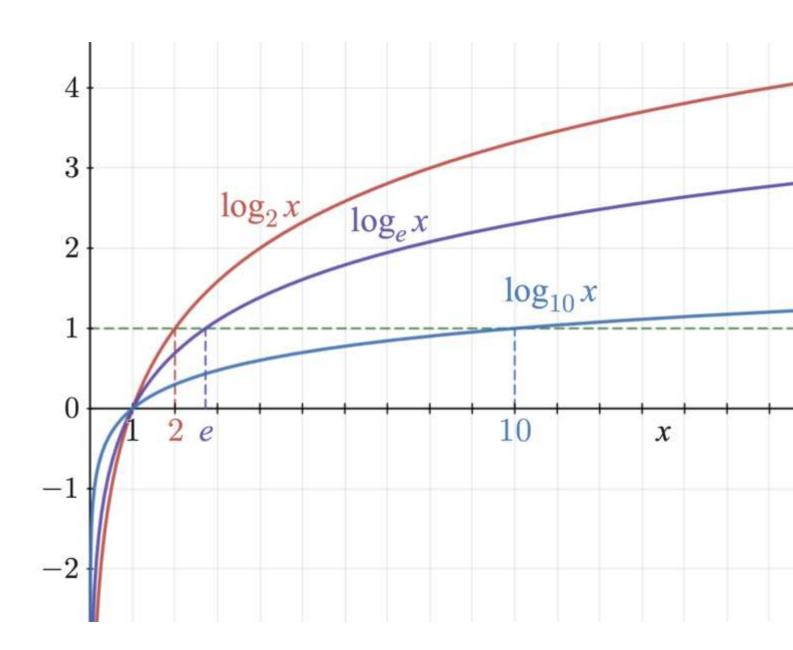
- b = 10 (decimal logarithm) in specific cases (e.g. decibels), historically was more useful due to logarithm tables.
 - Example: $\log_{10} 1000 = 3$ because $10^3 = 1000$.
- log *x* with no base: usually inferred from context.
 - Example: log *x* in physics is probably log_e *x*, in computer science it's probably log₂ *x*.

Plots and useful values

For any *b*: $\log_b 1 = 0$ Because $b^0 = 1$.

 $\log_b b = 1$ Because $b^1 = b$.

$$\frac{\log_b 0 \to -\infty}{\text{Because } b^{-\infty} \to 0 \text{ (for } b > 1)}$$



Useful identities

• Exponentiation turns sum to product:

 $b^{m+n} = b^m b^n$

So logarithm (the inverse) turns product to sum: $\log_b(xy) = \log_b x + \log_b y$

• Exponentiation turns difference to quotient:

$$b^{m-n} = \frac{b^m}{b^n}$$

So logarithm turns quotient to difference:

$$\log_b\left(\frac{x}{y}\right) = \log_b x - \log_b y$$

Useful identities

• Exponentiation turns product to power:

 $b^{mn} = (b^m)^n$

So logarithm turns power to product:

 $\log_b(x^y) = y \log_b x$

(powers "move behind the log")

• Exponentiation "increases the level of the operation":

 $+ \Rightarrow \times \Rightarrow \blacksquare$

So logarithm "decreases the level of the operation":

 $\blacksquare^{\blacksquare} \Rightarrow \times \Rightarrow +$

(Exercise: prove all the logarithm identities from the exponentiation identities!)

Class exercises

 $\log_4 16 = ?$

Answer: $16 = 4^2$, so $\log_4 16 = 2$.

 $\log_5 125 = ?$ Answer: $125 = 5^3$, so $\log_5 125 = 3$.

$$\log_4 \frac{1}{16} = ?$$
Answer: $\frac{1}{16} = 4^{-2}$, so $\log_4 \frac{1}{16} = -2$.

$$\log_{\frac{1}{5}} 125 = ?$$
Answer: $125 = 5^3 = \left(\frac{1}{5}\right)^{-3} \operatorname{so} \log_{\frac{1}{5}} 125 = -3.$

 $\log_{10} 0.0001 = ?$ Answer: $0.0001 = 10^{-4}$ so $\log_{10} 0.0001 = -4$.

 $\log_3(27\cdot 9) = ?$

Answer: $\log_3(27 \cdot 9) = \log_3 27 + \log_3 9 = 3 + 2 = 5$.

$$\log_2 \frac{32}{128} = ?$$
Answer:
$$\log_2 \frac{32}{128} = \log_2 32 - \log_2 128 = 5 - 7 = -2.$$

$$\log_3 9^5 = ?$$

Answer: $\log_3 9^5 = 5 \log_3 9 = 5 \cdot 2 = 10.$

15.7 Statistical Interpretation of Entropy and the Second Law

Probability of coin tosses (5 coins)

M <u>a</u> crostates	<u>Mi</u> crostates	# of m <u>i</u> crostates
5 heads, 0 tails	ННННН	1
4 heads, 1 tails	ННННТ, НННТН, ННТНН, НТННН, ТНННН	5
3 heads, 2 tails	НТНТН, ТНТНН, НТННТ, ТННТН, ТНННТ НТНТН, ТНТНН, НТННТ, ТННТН, ТНННТ	10
2 heads, 3 tails	ТТТНН, ТТННТ, ТННТТ, ННТТТ, ТТНТН, ТНТНТ, НТНТТ, ТНТТН, НТТНТ, НТТТН	10
1 heads, 4 tails	ΤΤΤΤΗ, ΤΤΤΗΤ, ΤΤΗΤΤ, ΤΗΤΤΤ, ΗΤΤΤΤ	5
0 heads, 5 tails	TTTTT	1
	Total:	32

Highest entropy states have the highest probability.

Probability of coin tosses (100 coins)

(Some) m <u>a</u> crostates	# of m <u>i</u> crostates
100 H	1
99 H, 1 T	100
95 H, 5 T	7.5×10^{7}
90 H, 10 T	1.7×10^{13}
75 H, 25 T	2.4×10^{23}
60 H, 40 T	$1.4 imes 10^{28}$
55 H, 45 T	6.1×10^{28}
51 H, 49 T	9.9×10^{28}
50 H, 50 T	1.0×10^{29}
Total:	1.3×10^{30}

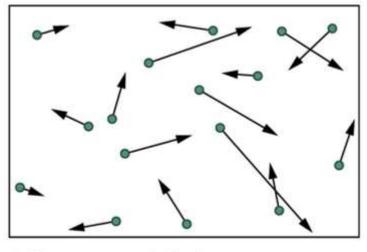
It becomes essentially, but not completely, impossible to get a low-entropy state.

The 2nd law of thermodynamics is actually **probabilistic**: entropy **can** decrease, but it's extremely unlikely.

If you toss a coin once per second, you will expect to get 100 heads once in 10^{22} years.

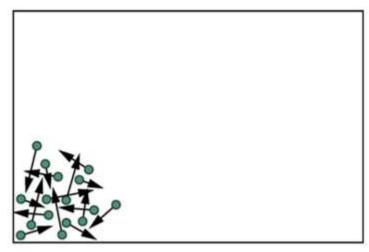
Now imagine tossing 1 mol $\approx 6 \times 10^{23}$ coins...

- Ordinary state of gas in a container: disorderly, random distribution of particles with a Maxwell-Boltzmann distribution of speeds.
- It is so unlikely that all these particles would ever end up in one corner of the container that it might as well be impossible.
- With energy transfer, the gas can be forced into one corner, its entropy greatly reduced.
- But left alone, it will spontaneously increase its entropy and return to the normal conditions, because they are immensely more likely.



Likely

(a)



(b) Highly unlikely

Precise microscopic definition of entropy

 $S \equiv k_B \log W$

- S =entropy.
- $k_B \equiv 1.380649 \times 10^{-23}$ J/K = Boltzmann's constant.
- *W* = number of microstates corresponding to the given microstate.
- $\log = natural \log arithm (\log_e or \ln)$
- This can be used to prove the macroscopic definition $\Delta S = Q/T!$

Numerical examples: 100 coin tosses

- 100 heads: $S = k_B \log 1 = 0$
- 99 heads: $S \approx 6.4 \times 10^{-23} \text{ J/K}$
- 75 heads: S \approx 7.4 \times 10⁻²² J/K
- 60 heads: $S \approx 8.9 \times 10^{-22} \text{ J/K}$
- 50 heads: S \approx 9.2 \times 10⁻²² J/K

(maximum entropy)

(Some) m <u>a</u> crostates	# of m <u>i</u> crostates
100 H	1
99 H, 1 T	100
95 H, 5 T	7.5×10^{7}
90 H, 10 T	1.7×10^{13}
75 H, 25 T	2.4×10^{23}
60 H, 40 T	1.4×10^{28}
55 H, 45 T	6.1×10^{28}
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