



Chapter 20

The Second Law of Thermodynamics



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Laws of Thermodynamics

3 Zeroth law:

The law of thermal equilibrium \Rightarrow Temperature

3 First law:

The law of conservation $\Rightarrow \Delta E_{\text{int}} = Q + W$

3 Second law:

Version 1: No perfect heat engine and refrigerator for any cyclic process." (thermodynamics)

Version 2: The law of increase of entropy (statistical mechanics)

3 Third law:

The entropy approaches a constant value as the temperature approaches zero.

Puzzles

- 3 Why heat always flows from the warmer object to the cooler object?
 - 3 Why a ball lying on the ground never gathers internal energy from the ground and begins bouncing on its own?
 - 3 Why does the gas do free expansion to an evacuated space spontaneously?
 - ⇒ Energy is conserved, but why are all the processes are **irreversible**?
- ⌚ **The second law of thermodynamics** determines the preferred direction for such processes!

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Outline

1. Directions of thermodynamic processes.
2. Heat engine & Kelvin-Planck form of the 2nd law of thermodynamics.
3. Heat pump, Refrigerator & Clausius statement of the 2nd law of thermodynamics.
4. Carnot engine.
5. Gasoline and diesel engines.
6. Entropy and the 2nd law of thermodynamics

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1. Directions of thermodynamic processes.
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1. Directions of thermodynamic processes

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Reversible and Irreversible Processes

- 3 A **reversible** process is a process that the system can return to its initial state **along the same path**, with **no increase in entropy**. It must have the following features.
 1. Every point along the path is in a “**nearly equilibrium state**” so that its state can be identified in the process.
 2. **No dissipative effects** that convert **mechanical energy** to **internal energy**, e.g., no friction or turbulence (i.e., no nonconservative effects).
- 3 An **irreversible process** does not meet the above requirements.
 - All natural processes are known to be irreversible.

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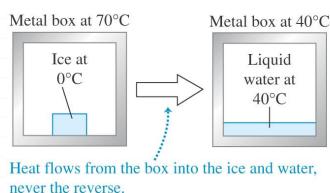
⌚ A real process that can be a good approximation of a reversible one must occur **very slowly** quasi-equilibrium and without energy dissipation.

- Spontaneous process, which is **not in an equilibrium state**, is **irreversible**, e.g., heat flows from hot to cold substances and adiabatic free expansion.
- No dissipation in the process does not mean it is reversible, for example, the adiabatic free expansion case. It also has to occur **slowly** in order to be reversible.

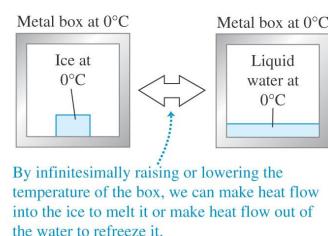
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⌚ Temperature change due to not thermal equilibrium is irreversible.

(a) A block of ice melts **irreversibly** when we place it in a hot (70°C) metal box.



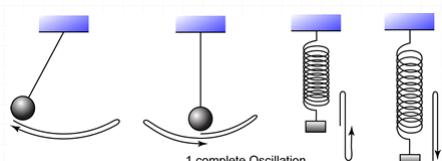
(b) A block of ice at 0°C can be melted **reversibly** if we put it in a 0°C metal box.



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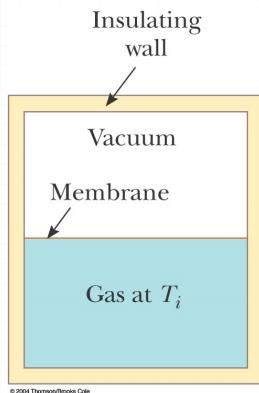
(Non-equilibrium)
Irreversible



(Quasi-equilibrium)
Quasi-reversible

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⚠ Adiabatic free expansion is an “irreversible” process.



During “free expansion”, the intermediate state is **not in equilibrium**; the path can’t be described in the PV diagram.

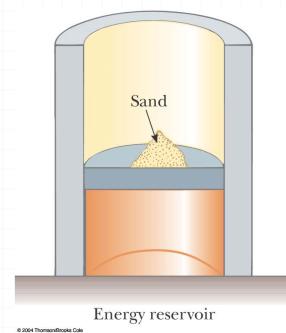
It requires exchange of W and Q in order to return to the initial state.

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Quasi-reversible process: Isothermal “infinitesimal” expansion/compression

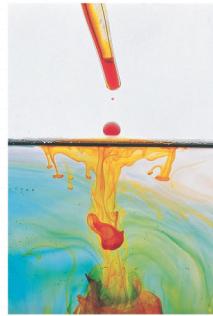
- A real process that is a good approximation of a reversible one will occur very *slowly*.
⇒ The system is always very nearly in an **equilibrium state**.
- A general characteristic of a reversible process is that there are *no dissipative effects* that convert mechanical energy to internal energy (e.g., no friction or turbulence).



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⚠ Mixing of different substances is irreversible.



The mixing of colored ink and water starts from a state of relative order (low entropy) in which each fluid is separate and distinct from the other. The final state after mixing is more disordered (greater entropy). Spontaneous unmixing of the ink and water, a process in which there would be a net decrease in entropy, is never observed.

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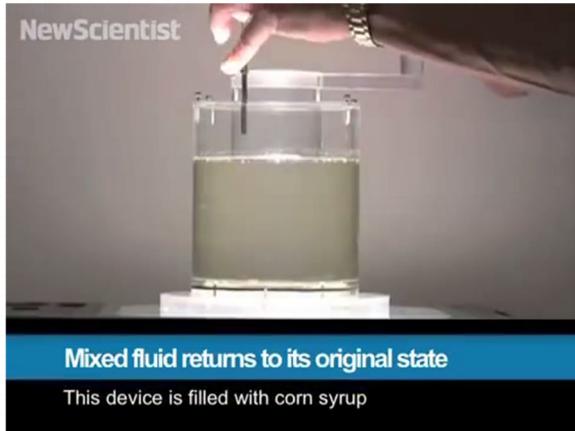
Dye in Water

PIRA # 4F10.15

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<https://www.youtube.com/watch?v=UpJ-kGII074>

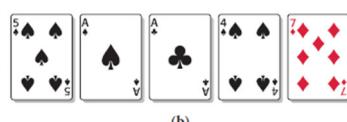
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⌚ The process of tossing and picking up the cards is irreversible!



(a)



(b)

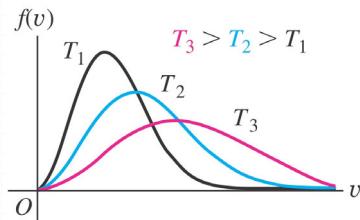
- In fact, the irreversibility of a process is related to the increasing **randomness or disorder** of the system.

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☺ In fact, all the irreversible processes drive systems toward an equilibrium state of **increasing randomness**.

☺ Conversion of mechanical energy into heat due to friction also involves an increase of randomness or disorder. Because the rising temperature due to friction broadens the particle speed distribution.



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2. Heat engine & Kelvin-Planck form of the 2nd law of thermodynamics

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Steam engine



Car engine

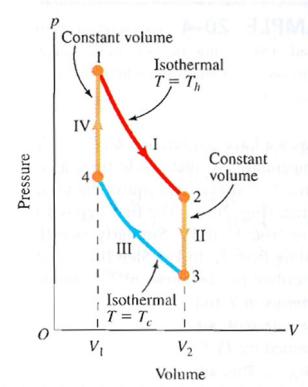
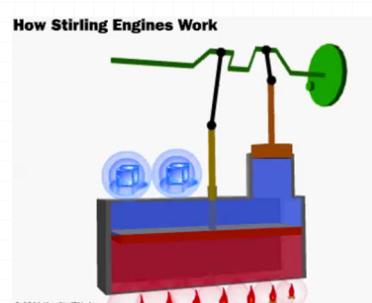
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Stirling engine



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<https://www.youtube.com/watch?v=zCGTNArwJ0s>

<http://auto.howstuffworks.com/stirling-engine2.htm>

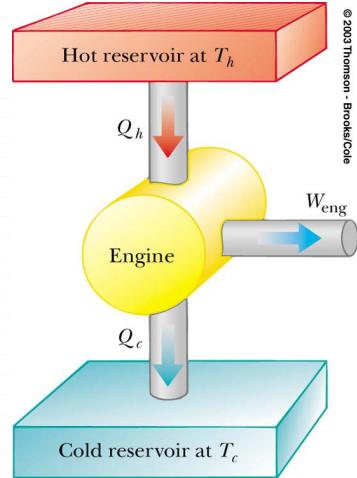
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Heat Engine

3 A **heat engine** is a device that takes in energy by **heat** and, operating in a **cyclic process**, expels a fraction of that energy by means of **work**.

- The **working substance** absorbs energy by heat from a high temperature energy reservoir (Q_h).
- Work is done by the engine (W_{eng}).
- Energy is expelled as heat to a lower temperature reservoir (Q_c).



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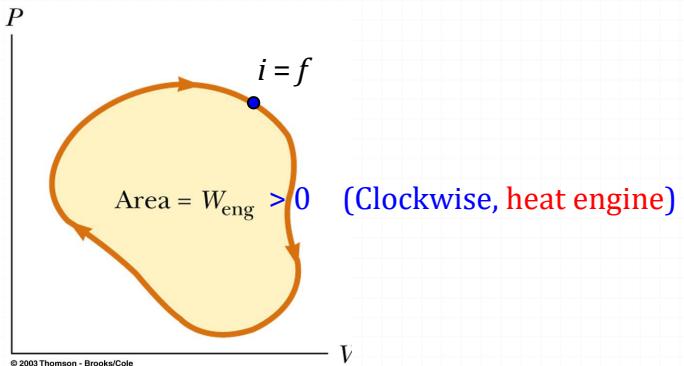
⌚ A heat engine can also operate in a cycle with **more than two reservoirs** so that all the heat transfers do not occur at the maximum and minimum temperatures.

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For the working substance in the engine,

$\Delta E_{\text{int}} = 0$ in a cyclic process.

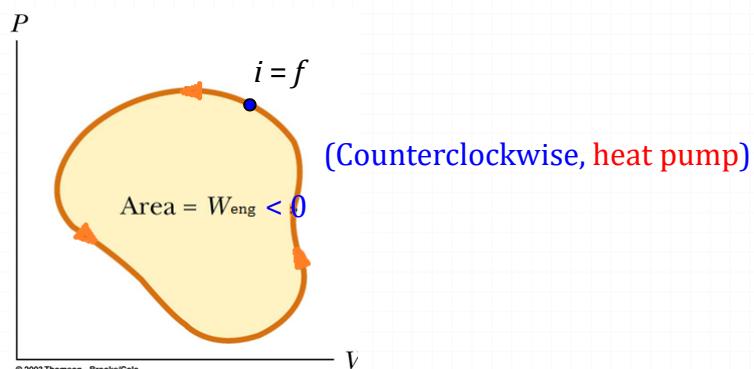


$$\underbrace{W_{\text{eng}}}_{\text{Work done by engine (gas)}} = (-) \underbrace{W_{\text{on gas}}}_{\text{work done on gas}} = \oint P dV$$

= area in the enclosed $P - V$ curve

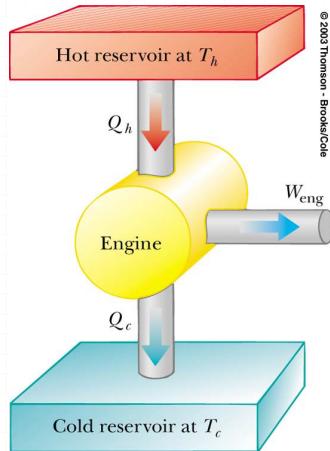
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For a cyclic process,

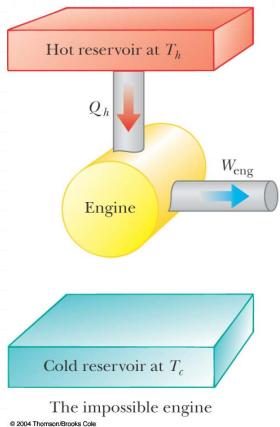
$$\begin{aligned}\Delta E_{\text{int}} &= 0 = Q + W \\ &= (|Q_h| - |Q_c|) - W_{\text{eng}} \\ \Rightarrow W_{\text{eng}} &= |Q_h| - |Q_c|\end{aligned}$$

Thermal efficiency:

$$e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

Kelvin-Planck form of the 2nd Law of Thermodynamics

- 3 A machine that operates **in a cycle**, taking in energy by **heat** and expelling an equal amount of energy by **work**, cannot be constructed.
- This limits the efficiency of heat engines.
 - **Although the 1st law of thermodynamics says**
- $\Delta E_{\text{int}} = Q + W$, a 100% conversion between heat and work is impossible for **a cyclic process**.



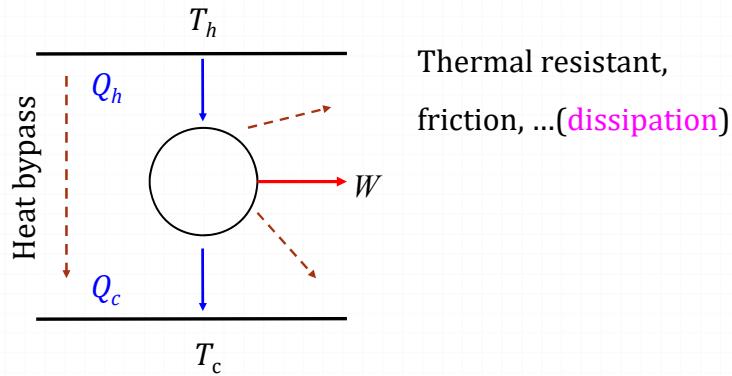
Kelvin-Planck's 2nd law of thermodynamics:
"No perfect heat engine" ($e = 1$) can be constructed for any cyclic process.

In practice,
 automobile gasoline engine $e \sim 20\%$
 diesel engine $e \sim 35\% - 40\%$.

⌚ The maximum efficiency for a heat engine is given by the ideal “reversible” Carnot engine.

A real engine always operates in an “irreversible” process so that it has lower efficiency than the ideal Carnot engine.

The real engine involves irreversible processes:



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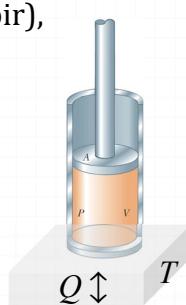
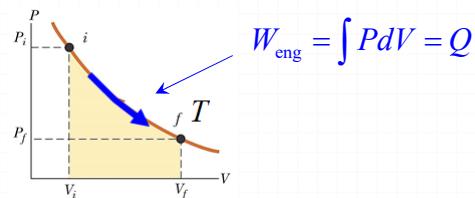
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A useful engine must have the two features:

1. Work in cycles
2. More than one heat reservoir.

Note: For a “one-time” isothermal process (i.e., one reservoir),

$$\Delta E_{\text{int}} = 0 = Q + W_{\text{on gas}} \Rightarrow Q = -W_{\text{on gas}} = W_{\text{eng}}$$

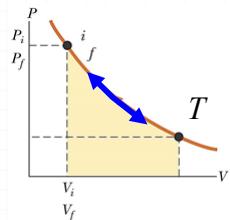


All input heat is converted to work, but this is not a useful engine.

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$$\therefore W_{\text{eng}} = -W_{\text{on gas}} = \oint PdV = 0$$

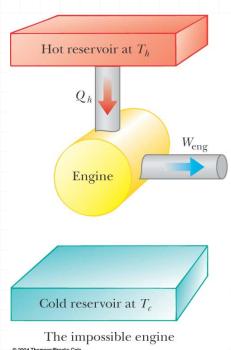


A useful engine must contact with more than one reservoirs.

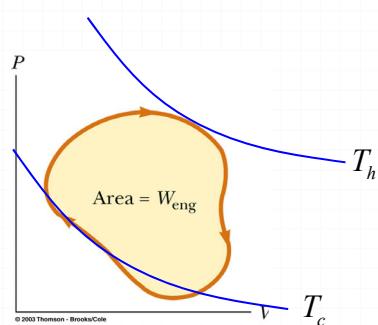
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Therefore, a useful heat engine requires a clockwise loop to make $\oint PdV > 0$. This means that a second different thermal bath T_c is required and $Q_c = 0$ is impossible!



Impossible!



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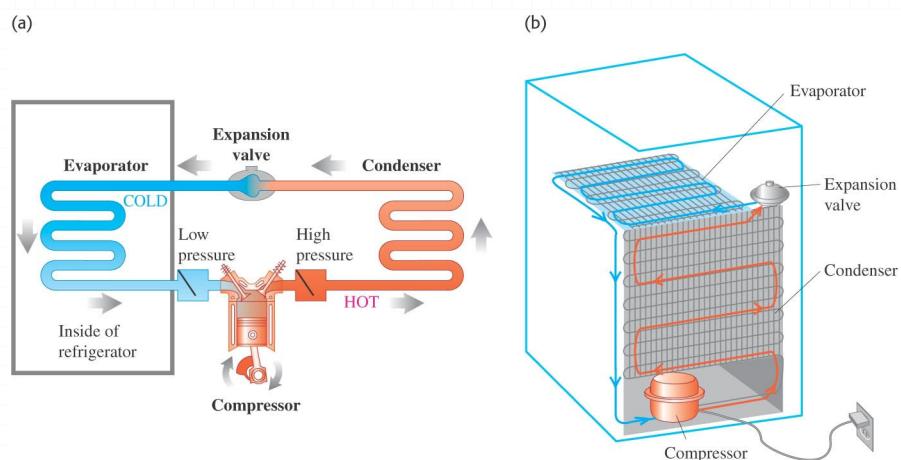
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3. Heat pump, Refrigerator & Clausius statement of the 2nd law of thermodynamics.

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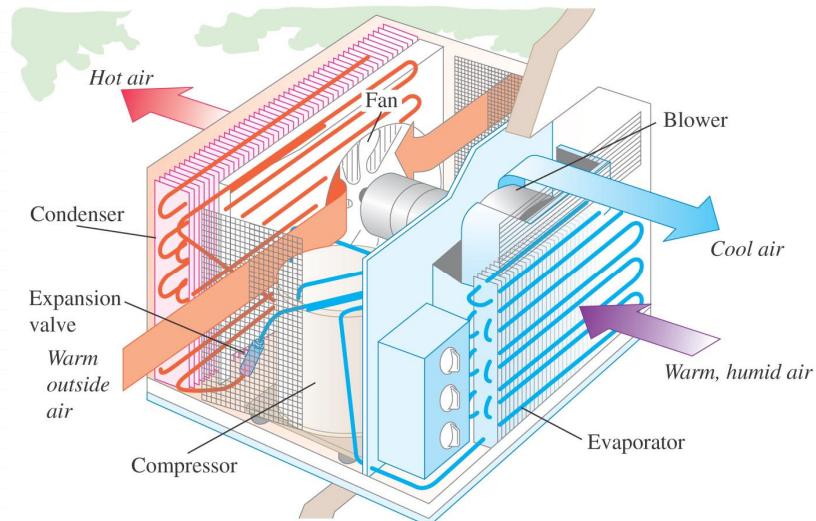
Some heat pumps, refrigerators:



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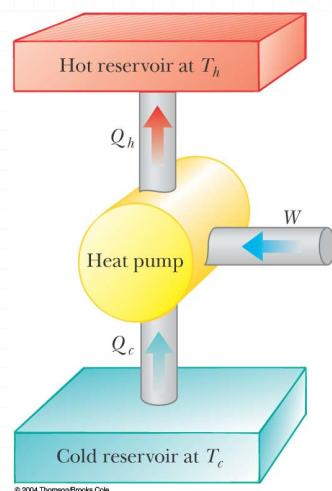
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Heat Pump and refrigerator

- 3 Heat engines can run in reverse; this is called **heat pump** or **refrigerator**, e.g., air conditioner, refrigerator.
- Energy is extracted from the cold reservoir, Q_c .
 - Energy is transferred to the hot reservoir, Q_h .
 - Work must be done *on* the engine, W .



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Coefficient of Performance

- 3 The effectiveness of a heat pump is described by a number called the **coefficient of performance (COP)**
- 3 In **heating mode**, COP generally > 1 .

$$\text{COP} (\text{heating}) \equiv \frac{|Q_h|}{W}$$

- 3 In **cooling mode**, a good refrigerator COP ~ 5 or 6.

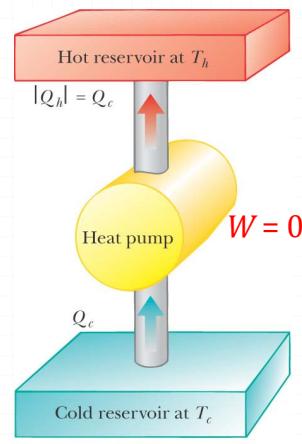
$$\text{COP} (\text{cooling}) \equiv \frac{|Q_c|}{W}$$

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Clausius's 2nd law of thermodynamics:
No "perfect heat pump" or refrigerator
($W = 0$) can be constructed for any cyclic
process.

i.e., Energy does not transfer
spontaneously by heat from a cold object
to a hot object.



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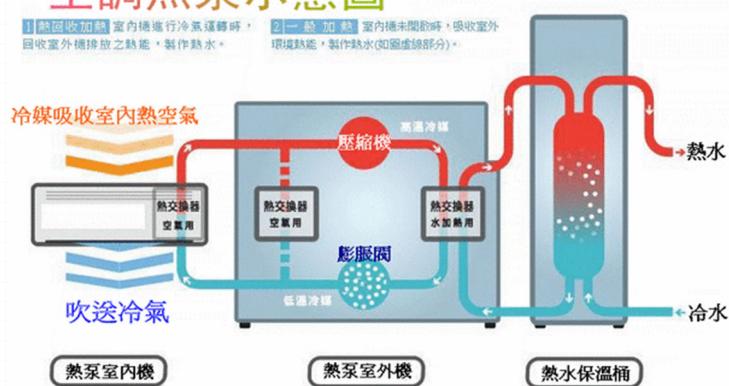
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熱泵熱水器

空調熱泵示意圖

1. 热回收加熱：室內機進行冷氣運轉時，回收室外機排放之熱能，製作熱水。

2. 一級加熱：室內機未開時，吸收室外環境熱能，製作熱水(如圓虛線部分)。



<http://blog.udn.com/escos/5000981>

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6:

環境熱能 用之不竭

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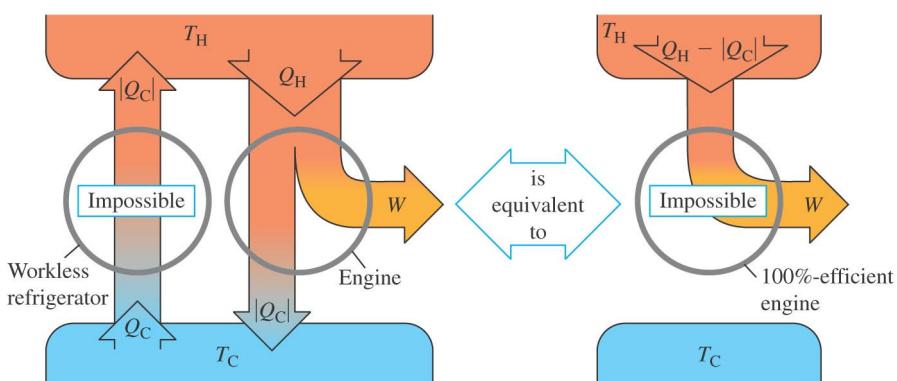
 The refrigerator statement of the 2nd law is equivalent to the heat engine statement.

For example, if we could build a workless refrigerator, violating the second or "refrigerator" statement of the second law, we could use it in conjunction with a heat engine, pumping the heat rejected by the engine back to the hot reservoir to be reused. This composite machine would violate the "engine" statement of the second law because its net effect would be to take a net quantity of heat $Q_H - |Q_C|$ from the hot reservoir and convert it completely to work W .

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(a) The "engine" statement of the second law of thermodynamics



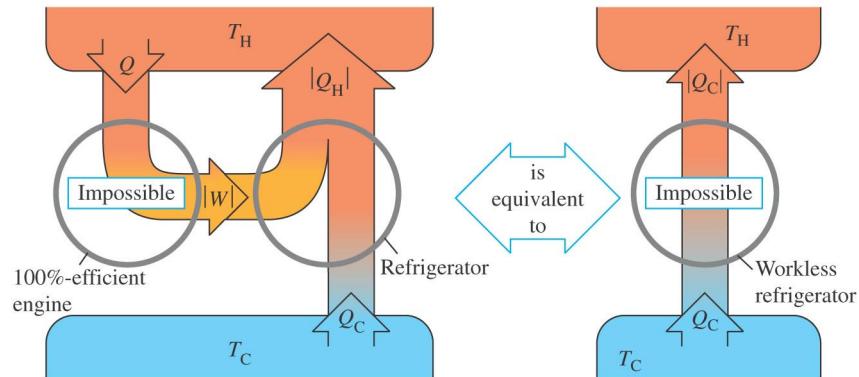
If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

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(b) The “refrigerator” statement of the second law of thermodynamics



If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

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4. Carnot engine

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Carnot Engine

- 3 A theoretical engine developed by Sadi Carnot.
- 3 A heat engine operating in an ideal, **reversible** cycle (now called a **Carnot cycle**) between two reservoirs is **the most efficient engine possible**.
 - All real engines are less efficient than the Carnot engine because they do not operate through a reversible cycle, which causes additional energy dissipation.
- 3 **Carnot's Theorem:**
 1. All the reversible engines operating between **two** given reservoirs have the same efficiency.
 2. No real heat engine has a greater efficiency than a reversible engine operating between **the same two temperatures (reservoirs)**.

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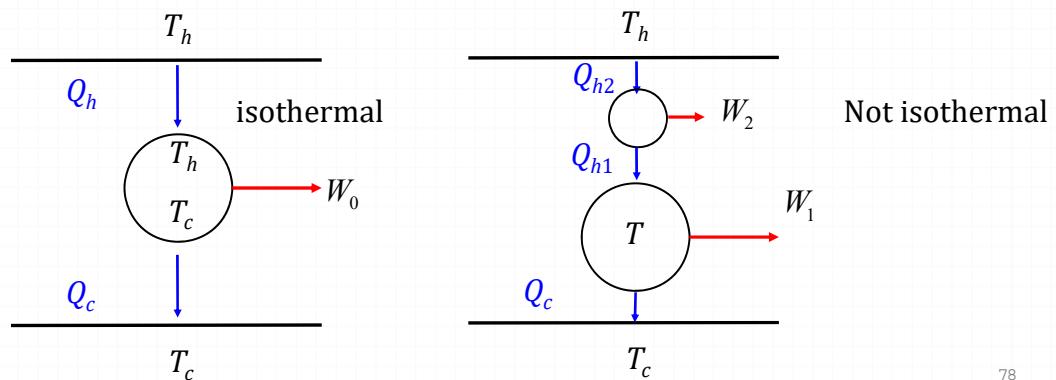
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⌚ For maximum heat-engine efficiency, all irreversible processes must be avoided as possible. For example, heat flow through a finite temperature difference is an irreversible process, and some of the heat may lose to other places instead of converting to work unless it is **adiabatic**. Therefore, the engine cycle involving **isothermal** and **adiabatic** can be quasi-reversible and will be favored for maximizing the engine efficiency, which are exactly the design of Carnot cycle.

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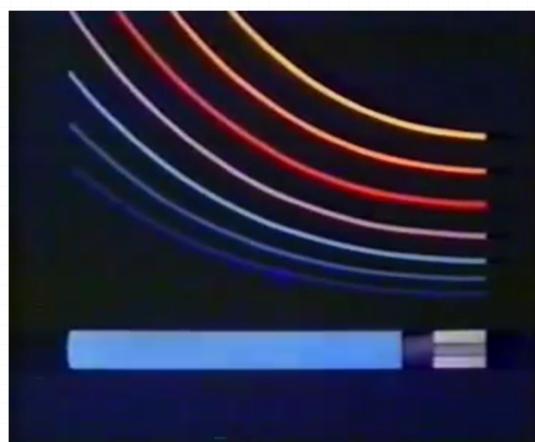
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If not in **isothermal processes**, there will be temperature difference between the hot reservoir and the engine. We can put another engine between the hot reservoir and the first engine to produce another work. Obviously, the first engine efficiency is reduced and can't be greater than the one in the isothermal processes. ($e_0 > e_1, e_2$)



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<https://youtu.be/2RvgpN0tkrU>

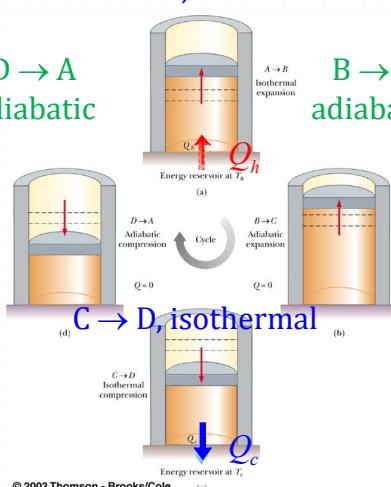
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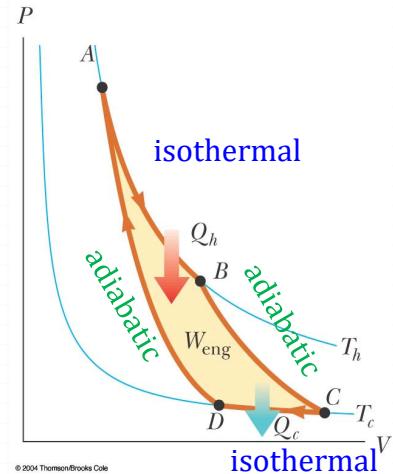
Carnot Cycle

$A \rightarrow B$, isothermal

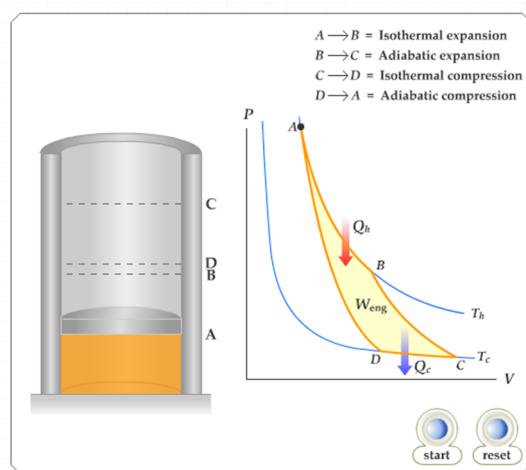
$D \rightarrow A$
adiabatic



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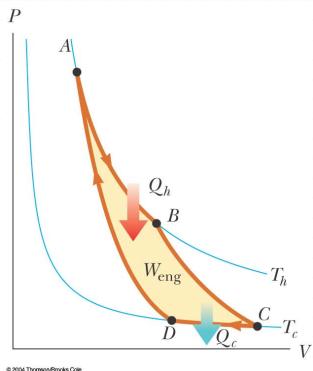
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Calculation of the Carnot engine efficiency:



$$e = \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

$A \rightarrow B$, isothermal, $\Delta E_{\text{int}} = 0$

$$\begin{aligned} |Q_h| &= |-W_{AB}| = \left| \int_{V_A}^{V_B} P dV \right| \\ &= \left| \int_{V_A}^{V_B} \frac{nRT_h}{V} dV \right| = nRT_h \ln \frac{V_B}{V_A} \end{aligned}$$

$C \rightarrow D$, isothermal,

$$|Q_c| = |-W_{CD}| = nRT_c \ln \frac{V_D}{V_C}$$

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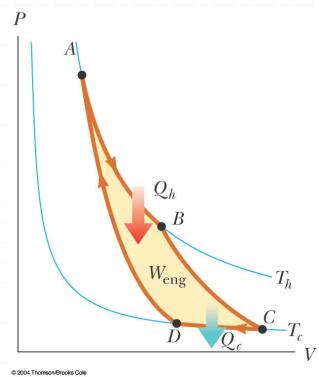
$$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h} \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)}$$

$B \rightarrow C$

$D \rightarrow A$, adiabatic

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\Rightarrow \begin{cases} T_h V_B^{\gamma-1} = T_c V_C^{\gamma-1} \\ T_h V_A^{\gamma-1} = T_c V_D^{\gamma-1} \end{cases} \Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$



$$\text{So } \frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h} \Rightarrow e = 1 - \frac{|Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h}$$

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Efficiency of a Carnot Engine

- 3 Carnot showed that the efficiency of the engine depends on the temperatures of the reservoirs:
- $$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h} \quad \text{and} \quad e_C = 1 - \frac{T_c}{T_h}$$
- Temperatures must be in Kelvins.
 - All Carnot engines operating between the same two temperatures will have the same efficiency, which could be used as the definition of Kelvin temperature.
- 3 In order for the processes in the Carnot cycle to be **reversible**, they must be carried out infinitesimally slowly, which will make the engine output power extremely small. In principle, **a Carnot engine is an ideal engine, but is impractical in reality.**

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Carnot Cycle in Reverse

- 3 Theoretically, a Carnot-cycle heat engine can run in reverse, because Carnot cycle is reversible and $\Delta S = 0$. This would constitute the most effective heat pump available.

➤ In heating mode:

$$COP_C = \frac{|Q_h|}{W} = \frac{T_h}{T_h - T_c}$$

➤ In cooling mode:

$$COP_C = \frac{|Q_c|}{W} = \frac{T_c}{T_h - T_c}$$

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💡 Although we derived the thermal efficiency for a Carnot engine using an ideal gas as its working substance, it is in fact valid for any Carnot engine, no matter what its working substance.

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Proof of Carnot engine's efficiency always greater than any real engines:

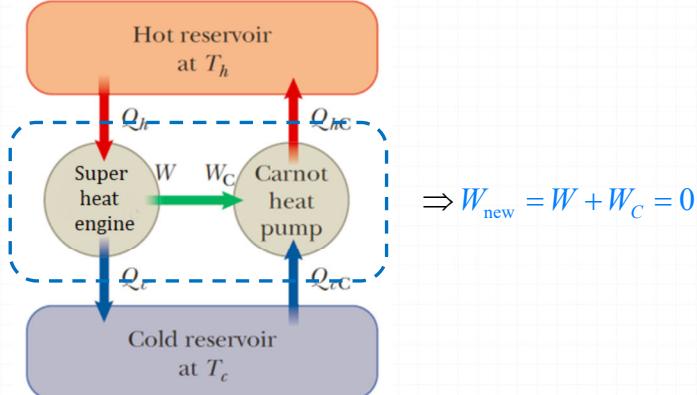
The proof is based on the reversible of Carnot engine, involving only isothermal and adiabatic processes.

Therefore, the Carnot engine contacts only with two environments, the hot and cold reservoirs. There is no other reservoir for the heat to flow!

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Let's design a new engine built by combining the superefficient heat engine and Carnot heat pump.



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Assume the super heat engine has an efficiency $e > e_C$ (Carnot),

$$e > e_C, \Rightarrow \frac{|W|}{|Q_h|} > \frac{|W_C|}{|Q_h|} \Rightarrow |Q_{hc}| > |Q_h|$$

$$|W| = |W_C|, \Rightarrow |Q_h| - |Q_c| = |Q_{hc}| - |Q_{cC}|$$

$$\Rightarrow \underbrace{|Q_{hc}| - |Q_h|}_{\sum Q_h} = \underbrace{|Q_{cC}| - |Q_c|}_{\sum Q_c} > 0$$

\Rightarrow Heat flows from T_c to T_h but with $\sum W = 0$, for the new engine.

\Rightarrow Violate Clausius's 2nd law of thermodynamics

$$\Rightarrow e < e_C$$

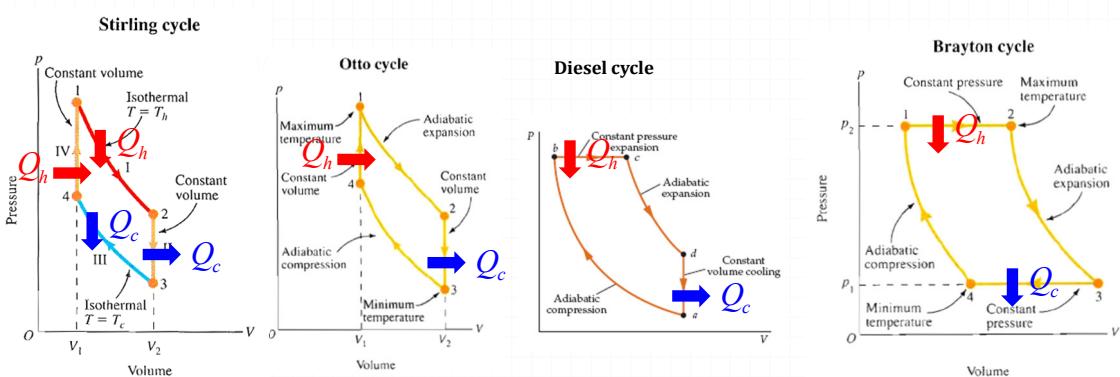
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1. Directions of thermodynamic processes.
2. Heat engine & Kelvin-Planck form of the 2nd law of thermodynamics.
3. Heat pump, Refrigerator & Clausius statement of the 2nd law of thermodynamics.
4. Carnot engine.
5. Gasoline and diesel engines.
6. Entropy and the 2nd law of thermodynamics

5. Gasoline and diesel engines

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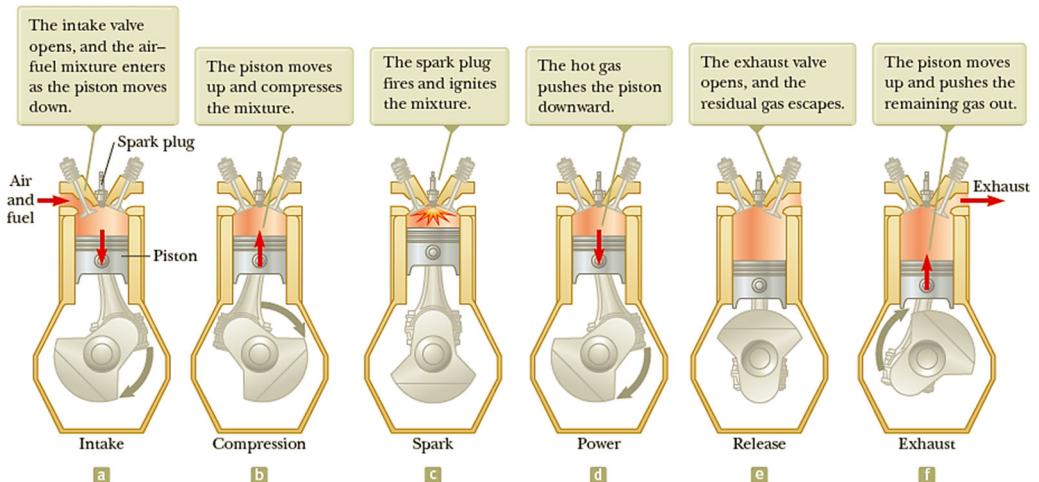


- Unlike Carnot cycle, these cycles do not have fixed reservoirs or temperatures T_h and T_c (isothermal), there are temperature difference along paths for Q_h so that they are **not reversible** and some of the heat will lose to other places because of not being adiabatic.

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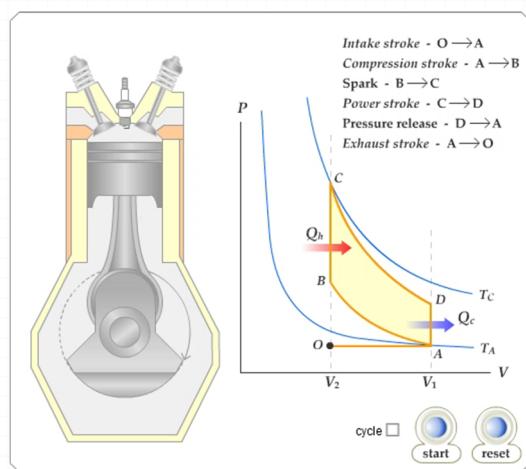
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The 4-stroke cycle of a Gasoline Engine



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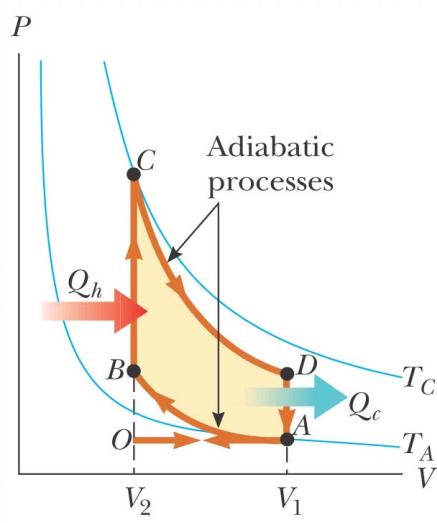
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- 3 In a gasoline engine, **six** processes occur during each cycle.
- 3 For a given cycle, the piston moves up and down twice; this represents a **four-stroke** cycle.
- 3 The processes in the cycle can be approximated by the **Otto cycle**.

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Otto Cycle



1. $O \rightarrow A$, intake stroke
2. $A \rightarrow B$, compression stroke
3. $B \rightarrow C$, spark (Q_h) (irreversible)
4. $C \rightarrow D$, power stroke
5. $D \rightarrow A$, exhaust (Q_c) (irreversible)
6. $A \rightarrow O$, exhaust stroke

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Otto Cycle Efficiency

- 3 If the air-fuel mixture is assumed to be an ideal gas, then the efficiency of the **Otto cycle** is

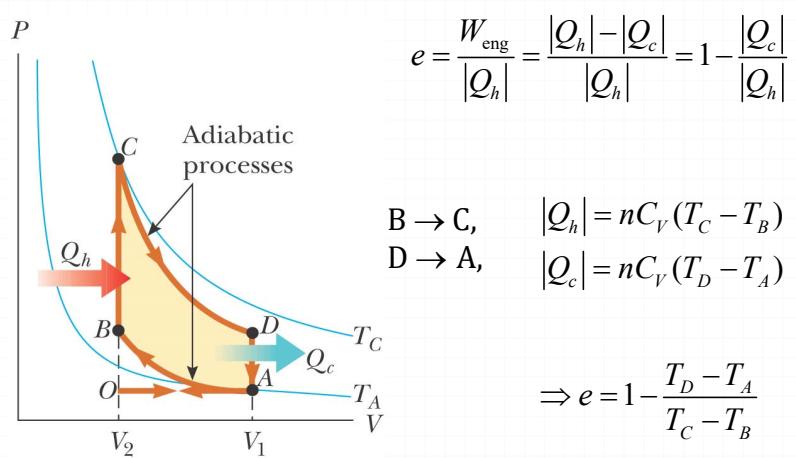
$$e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

- $\gamma = C_p/C_v$ is the ratio of the molar specific heats.
- V_1 / V_2 is called the **compression ratio**.
- Typical values: $V_1 / V_2 \sim 8; \gamma = 1.4; \Rightarrow e = 56\%$
- Efficiencies of real engines are 15% to 20%
Mainly due to friction, energy transfer by conduction, incomplete combustion of the air-fuel mixture.

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Otto Cycle Efficiency:



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$$\begin{array}{ll} A \rightarrow B, \text{adiabatic}, & T_A V_A^{\gamma-1} = T_B V_B^{\gamma-1} \\ C \rightarrow D, \text{adiabatic}, & T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1} \end{array}$$

$$V_A = V_D = V_1, \quad V_B = V_C = V_2$$

$$\Rightarrow T_A = T_B \left(\frac{V_2}{V_1} \right)^{\gamma-1}, \quad T_D = T_C \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$$\Rightarrow \frac{T_D - T_A}{T_C - T_B} = \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$$\Rightarrow e = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}}$$

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Is the Otto cycle efficiency smaller than the Carnot cycle efficiency?

$$\text{Otto cycle: } e = 1 - \frac{1}{(V_1/V_2)^{\gamma-1}} = 1 - \frac{T_A}{T_B} = 1 - \frac{T_D}{T_C}$$

$$\text{Carnot cycle: } e = 1 - \frac{T_A}{T_C}$$

$$\because T_A < T_D$$

\therefore efficiency: **Carnot cycle > Otto cycle.**

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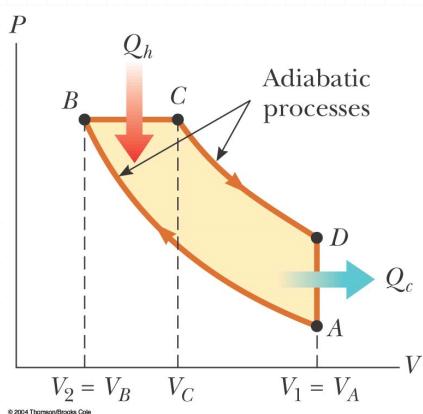
Diesel Engines

- 3 Operate on a cycle similar to the Otto cycle **without a spark plug**.
- 3 The compression ratio is much greater and so the cylinder temperature at the end of the compression stroke is much higher.
- 3 Fuel is injected and the temperature is high enough for the mixture to ignite without the spark plug.
- 3 Diesel engines are more efficient than gasoline engines, because of high compression ratio and combustion temperature.

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Diesel engine:



1. $A \rightarrow B$, adiabatic compression
2. $B \rightarrow C$, fuel-air mixture, $P = \text{const. } (Q_h)$
3. $C \rightarrow D$, adiabatic expansion
4. $D \rightarrow A$, exhaust, $V = \text{const. } (Q_c)$

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A single-atom heat engine

Science 352, 325 (2016)

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Ferdinand Schmidt-Kaler,¹ Kilian Singer^{1,4*}

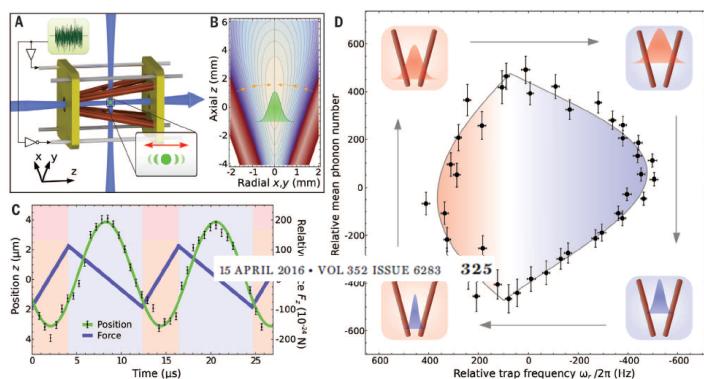


Fig. 1. Single-atom heat engine. (A) Experimental setup composed of a single trapped ion (green); lasers for cooling, damping, and observation of the ion (blue); radio-frequency electrodes in funnel geometry (red); end caps (gold); and outer electrodes (gray). The position of the ion is imaged on an ICCD camera. Opposing voltage noise waveforms are additionally supplied to the outer electrodes so as to generate electric-field noise without affecting the trap frequencies. (B) Cross section of the funnel-shaped pseudo-potential between the radio-frequency electrodes (red), with a minimum at the center. The gradient of the potential (orange arrows) has an axial component that increases with radial displacement x or y . A force in the axial direction arises as a function of the finite width of the radial thermal state of the ion (green Gaussian distribution). (C) Position of the ion (black symbols) determined from the average of more than 200,000 camera images at each time step. The error bars result from the uncertainty of Gaussian fits to the recorded fluorescence images. The measured positions are described by a sinusoidal fit (green line). Background colors indicate the periodic interaction with the hot (red) and cold (blue) reservoirs, which gives rise to a periodic driving force (blue line) according to Eq. 1, shown relative to its mean value of 5.03×10^{-21} N. (D) Thermodynamic cycle of the engine for one radial direction. Trap frequencies in the radial direction ω_r are deduced directly from the measured z -positions. The temperature T_0 of the radial state of motion, and thus the corresponding mean phonon number \bar{n}_0 , is determined from separate measurements (see text and Fig. 2). The values of ω_r and \bar{n}_0 are given with respect to the center of the cycle at $\omega_{0r}/2\pi = 447.9 \pm 0.2$ kHz and $\bar{n}_0 = 2.61 (\pm 0.04) \times 10^4$ phonons. The shaded area enclosed by the cycle is proportional to the work performed by the engine, where red and blue colors indicate heating and cooling periods, respectively. The black line is the calculated trajectory of the cycle (see text). The pictograms in the corners illustrate the different stages of an idealized cycle.

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6. Entropy and the 2nd law of thermodynamics

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Macroscopic Entropy and the 2nd Law of Thermodynamics

- 3 The original formulation of entropy dealt with the transfer of energy by heat in a **reversible process**.
- 3 Let dQ_r be the amount of energy transferred by heat when a system follows a **reversible** path.
- 3 The change in entropy, dS is (**macroscopic**)

$$dS = \frac{dQ_r}{T} \quad (\text{only for infinitesimal } \text{reversible} \text{ path})$$

- 3 **Entropy is a state variable**, i.e., the change in entropy depends only on the endpoints and is **independent of the path** followed.

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⌚ In the (reversible) phase transition with latent heat, T is fixed. The entropy might be thought as a quantity to characterize the changes in the system while T remains constant but with heat flow.

Compare entropy with heat capacity,

$$T \text{ varies:} \quad C = \frac{dQ}{dT} \Rightarrow dQ = CdT$$

$$T \text{ fixed:} \quad dS = \frac{dQ_r}{T} \Rightarrow dQ_r = TdS$$

(latent heat)

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Entropy also provides a quantitative measure of disorder or randomness.

Consider an infinitesimal isothermal expansion (reversible),

$$dQ = -dW = PdV = \frac{nRT}{V} dV$$

A measure of disorder $\Rightarrow \frac{dV}{V} = \frac{1}{nR} \left(\frac{dQ}{T} \right)$

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

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Q: True or false: The entropy change in an adiabatic process must be zero because $Q = 0$.

Ans: False. The determining factor for the entropy change is Q_r , not Q . If the adiabatic process is **not reversible**, the entropy change is not necessarily zero because a reversible path between the same initial and final states may involve energy transfer by heat.

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Q: Which of the following is true for the entropy change of a system that undergoes a reversible, adiabatic process?

- (a) $\Delta S < 0$ (b) $\Delta S = 0$ (c) $\Delta S > 0$

Ans: (b). Because the process is reversible and adiabatic, $Q_r = 0$; therefore, $S = 0$.

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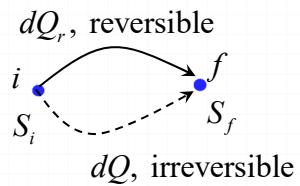
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ΔS in Irreversible Processes

- 3 To calculate the change in entropy in a real system, remember that **entropy depends only on the state of the system**.
- 3 Distinguish this from Q_r , the amount of energy that would have been transferred by heat **along a reversible path**.
- 3 Do not use Q , the actual energy transfer in the process; Q_r is the correct value to use for ΔS .

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$$\Delta S = S_f - S_i = \int_i^f \frac{dQ_r}{T} \neq \int_i^f \frac{dQ}{T}$$

Note that,

The entropy change does not always involve heat transfer,
e.g., adiabatic free expansion.

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沤 ΔS in a temperature change:

$$T_c \quad \Rightarrow \quad T_h$$

The process of heating an object is **irreversible**. Since the entropy depends only on the initial and final states, the change of entropy is the same whether the process is reversible or irreversible. We can take the reversible path by raising the temperature in steps of infinitesimal amount dT .

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_{T_c}^{T_h} \frac{ncdT}{T} = nc \ln \frac{T_h}{T_c} > 0,$$

if $T_h > T_c$ for this irreversible process.

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沤 ΔS in a calorimetric process:

(mol) (specific heat) (temperature)

$$\begin{array}{ccc} n_1 & c_1 & T_c \\ n_2 & c_2 & T_h \end{array} \Rightarrow T = T_f$$

The calorimetric process is **irreversible** because the system goes through a series of nonequilibrium states.

ΔS can be calculated in terms of the reversible path by exchanging Q slowly.

$$\begin{aligned} dQ = ncdT & \quad \Delta S = \int_1 \frac{dQ_{cold}}{T} + \int_2 \frac{dQ_{hot}}{T} \\ & = n_1 c_1 \int_{T_c}^{T_f} \frac{dT}{T} + n_2 c_2 \int_{T_h}^{T_f} \frac{dT}{T} \\ & = n_1 c_1 \ln \frac{T_f}{T_c} + n_2 c_2 \ln \frac{T_f}{T_h} \end{aligned}$$

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$$\boxed{T_h} \quad \boxed{T_c} \quad \Rightarrow \quad \boxed{T_f} \quad \boxed{T_f}$$

$$nc(T_h - T_f) + nc(T_c - T_f) = 0 \Rightarrow T_f = \frac{T_h + T_c}{2}$$

$$\begin{cases} \Delta S_{hot} = nc \ln \frac{T_f}{T_h} < 0 \\ \Delta S_{cold} = nc \ln \frac{T_f}{T_c} > 0 \end{cases} \Rightarrow \begin{cases} \Delta S_{total} = \Delta S_{hot} + \Delta S_{cold} \\ = nc \ln \frac{T_f^2}{T_h T_c} = nc \ln \frac{[(T_h + T_c)/2]^2}{T_h T_c} \\ \because [(T_h + T_c)/2]^2 - T_h T_c = \frac{(T_h - T_c)^2}{4} > 0 \end{cases}$$

$$\Rightarrow \Delta S_{total} = nc \ln \frac{[(T_h + T_c)/2]^2}{T_h T_c} > 0$$

In fact, ΔS_{total} is always > 0 for such an irreversible calorimetric process.

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沤 ΔS in a “phase transition”:

Phase transition is a **reversible** process.

The latent heat is L for a phase transition in H₂O, at temperature T_m .

$$\Delta S_{\text{H}_2\text{O}} = \int \frac{dQ_r}{T} = \frac{1}{T_m} \int dQ = \frac{mL}{T_m} > 0$$

$$\Delta S_{\text{Environment}} = \int \frac{dQ_r}{T} = -\frac{mL}{T_m}$$

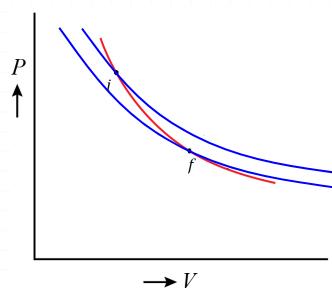
$$\Delta S_{\text{total}} = \Delta S_{\text{H}_2\text{O}} + \Delta S_{\text{Environment}} = 0 \text{ for phase transition.}$$

In fact, $\Delta S_{\text{total}} = 0$ for a reversible process.

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沤 ΔS for ideal gases in a quasi-static reversible process.



$$\Delta S = \int_{\substack{i \\ \text{reversible} \\ \text{path}}}^f \frac{dQ}{T} = \int_i^f \frac{dE_{\text{int}} + PdV}{T} = \int_i^f \frac{nc_V dT}{T} + \int_i^f \frac{nRdV}{V}$$

$$\Rightarrow \Delta S = n(c_V \ln T_f + R \ln V_f) - n(c_V \ln T_i + R \ln V_i)$$

(Indep. of path, so entropy is indeed a state variable!)

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☺ ΔS in an “adiabatic reversible” expansion.

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\Delta S = n(c_V \ln T_f + R \ln V_f) - n(c_V \ln T_i + R \ln V_i)$$

$$= nc_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$= nc_V \ln \frac{V_i^{\gamma-1}}{V_f^{\gamma-1}} - nR \ln \frac{V_i}{V_f}$$

$$= n[c_V(\gamma-1) - R] \ln \frac{V_i}{V_f} \quad \Leftarrow \begin{cases} c_p - c_v = R \\ \frac{c_p}{c_v} = \gamma \end{cases}$$

$$= 0$$

In consistent with $dS = \frac{dQ_r}{T} = 0$.

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☺ ΔS in an irreversible adiabatic free expansion.

An adiabatic free expansion: $Q = 0$ but cannot be used since that is not a reversible process.

$\Delta S(\text{free expansion}) = \Delta S(\text{isothermal expansion})$

(1)

adiabatic free expansion

(irreversible)

$$V_i \rightarrow V_f$$

$$\Delta E_{\text{int}} = 0$$

$$T_i = T_f$$

$$Q = 0$$

$$W = 0$$

(2)

isothermal expansion

(reversible)

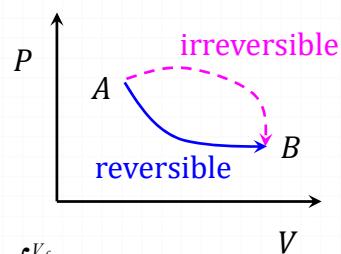
$$V_i \rightarrow V_f$$

$$\Delta E_{\text{int}} = 0$$

$$T_i = T_f$$

$$\begin{aligned} Q_r &= -W = \int_{V_i}^{V_f} P dV \\ &= \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \ln \frac{V_f}{V_i} \end{aligned}$$

$$\Rightarrow \Delta S = \frac{Q_r}{T} = nR \ln \frac{V_f}{V_i}$$



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Q: An ideal gas is taken from an initial temperature T_i to a higher final temperature T_f along two different reversible paths: Path A is at constant pressure; Path B is at constant volume. The relation between the entropy changes of the gas for these paths is (a) $\Delta S_A > \Delta S_B$ (b) $\Delta S_A = \Delta S_B$ (c) $\Delta S_A < \Delta S_B$.

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Ans:(a).

From the first law of thermodynamics, for these two reversible processes, $Q_r = E_{\text{int}} - W$. During the constant-volume process, $W = 0$, while the work W is nonzero and negative during the constant-pressure expansion. Thus, Q_r is larger for the constant-pressure process, leading to a larger value for the change in entropy. In terms of entropy as disorder, during the constant-pressure process, the gas must expand. The increase in volume results in more ways of locating the molecules of the gas in a container, resulting in a larger increase in entropy.

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Physics about Entropy

- 3 For any “reversible” cycle,

$$\Delta S = \oint \frac{dQ_r}{T} = 0 \quad (\text{for closed loop or cyclic process only!})$$

- 3 The **direction of thermal energy transfer** is not determined by energy conservation, but **by the change in entropy** of a system.
- 3 A **spontaneous** process or **irreversible** process in an isolated system increases the systems entropy, $\Delta S > 0$.
- 3 For an isolated system, **entropy** drives the system toward equilibrium, and the state of equilibrium is the state of **maximum entropy**.

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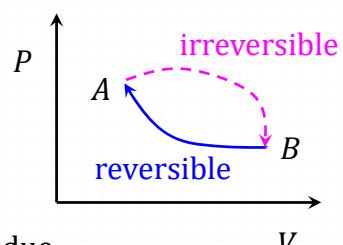
⌚ Why does the entropy of an isolated system increase in a **spontaneous** process or an **irreversible** process, $\Delta S > 0$?

Clausius' inequality: $\oint \frac{dQ}{T} \leq 0$, for **any paths**.

1. $\oint \frac{dQ}{T} < 0$, if containing any **irreversible paths**.

∴ More heat flow out than heat flow into the system, due to dissipation loss along the irreversible path.

2. $\oint \frac{dQ}{T} = 0$, for **reversible paths**.

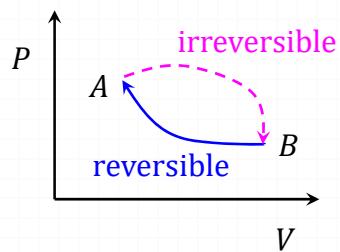


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If containing any irreversible paths,

$$\oint \frac{dQ}{T} < 0.$$



$$\Rightarrow \int_{\text{reversible}}^A \frac{dQ}{T} + \int_{\text{irreversible}}^B \frac{dQ}{T} = S(B) - S(A) + \int_{\text{irreversible}}^B \frac{dQ}{T} < 0$$

$$\Rightarrow S(B) - S(A) > \int_{\text{irreversible}}^B \frac{dQ}{T}$$

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For an isolated system,

$$dQ = 0 \Rightarrow \int_{\text{irreversible}}^B \frac{dQ}{T} = 0 \Rightarrow S(B) > S(A)$$

A spontaneous or irreversible process in an isolated system

ALWAYS increases the systems entropy. For example, the entropy increases in an adiabatic free expansion.

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☺ One way of conceptualizing a change in entropy is to relate it to **energy spreading**. A natural tendency is for energy to undergo spatial spreading in time, representing an increasing in entropy.
[Serway, P.574]

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☺ The **total entropy** (engine + environment) change in a **Carnot cycle** is zero, because of its reversibility.
However, other cycles such as **Otto, Stirling ...** involve some irreversible processes and the **total entropy change is greater than zero**, where the environment entropy increases but the engine entropy remains unchanged in a cycle.

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Microscopic Entropy and the 2nd Law of Thermodynamics

Entropy (microscopic):

$$S \equiv k_B \ln W \quad (\text{Boltzmann})$$

W : numbers of “microstates” for the macrostate of a system.

⇒ Entropy is a measure of the probability of microstates (or degrees of freedom) in a system, representing the level of uncertainty, choice, and possibility in a system..

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3 Entropy is a state variable. The entropy change is path-independent.

Another statement of the second law of thermodynamics:

3 Law of increase of entropy

The entropy of a closed system increases in all irreversible processes,

$\Delta S > 0$.

p.s., For reversible process, $\Delta S = 0$.

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Microstates vs. Macrostates

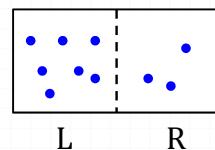
- ③ A **microstate** is a particular configuration of the individual constituents of the system.
- ③ A **macrostate** is a description of the conditions from a macroscopic point of view.
 - It makes use of macroscopic variables such as pressure, density, and temperature for gases.

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E.g., 10 molecules

$$\text{Total arrangements: } \underbrace{2 \times 2 \times \cdots \times 2}_{10} = 2^{10} = 1024$$

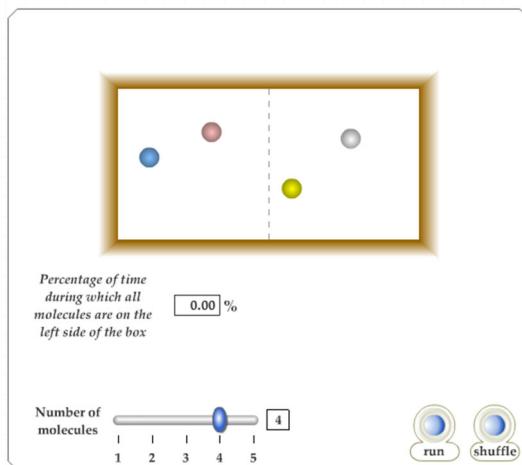


$$S = k_B \ln(2^{10})$$

Configuration (R, L) Macrostates	Number of ways $W = {}^nC_r = \frac{n!}{(n-r)!r!}$	Probability
(10, 0) or (0, 10)	1	$\frac{1}{1024}$
(9, 1) or (1, 9)	10	$\frac{10}{1024}$
(8, 2) or (2, 8)	$\frac{10 \times 9}{2 \times 1} = 45$	$\frac{45}{1024}$
(7, 3) or (3, 7)	$\frac{10 \times 9 \times 8}{3 \times 2 \times 1} = 120$	$\frac{120}{1024}$
(6, 4) or (4, 6)	$\frac{10 \times 9 \times 8 \times 7}{4 \times 3 \times 2 \times 1} = 210$	$\frac{210}{1024}$
(5, 5)	$\frac{10 \times 9 \times 8 \times 7 \times 6}{5 \times 4 \times 3 \times 2 \times 1} = 252$	$\frac{252}{1024}$

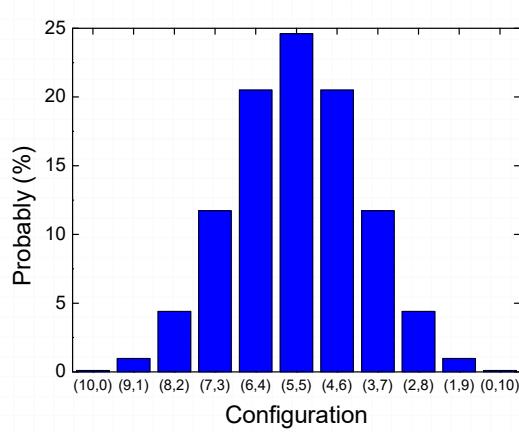
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The directionality of spontaneous processes is determined by what state has the highest probability.
E.g., adiabatic free expansion.

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<https://www.facebook.com/461822001292778/videos/749148278925775>

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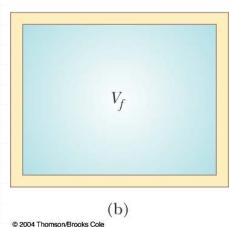
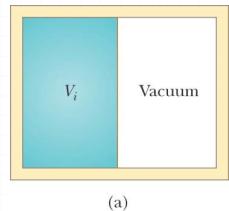
💡 For any system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest disorder and the greatest entropy.

💡 If we consider a system and its surroundings to include the Universe, **the Universe is always moving toward a macrostate corresponding to greater disorder.**

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沤 ΔS in an diabatic free expansion



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V_m : molecular volume

W : number of ways of locating
N molecules

$$W_i = \left(\frac{V_i}{V_m} \right)^N \quad W_f = \left(\frac{V_f}{V_m} \right)^N$$

$$\begin{aligned} \Delta S &= S_f - S_i \\ &= k_B \ln W_f - k_B \ln W_i \\ &= N k_B \ln \frac{V_f}{V_i} > 0 \end{aligned}$$

[Same as previous $\Delta S = \int \frac{dQ_r}{T}$ approach!]

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沤 ΔS in Thermal Conduction

The cold reservoir absorbs Q , $\Delta S_{\text{cold}} = Q/T_c$

The hot reservoir loses Q , $\Delta S_{\text{hot}} = -Q/T_h$

$$\Rightarrow \Delta S = Q/T_c - Q/T_h > 0.$$

If Q flows from T_c to T_h , then $\Delta S < 0$, which violates the law of increase of entropy.

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⌚ Why no perfect heat engine/heat pump is equivalent to the law of increase of entropy?

1.

$$\frac{\Delta S_h}{Q_h} \frac{T_h}{\Delta S_{gas}} \rightarrow W$$

$$\frac{\Delta S_c}{Q_c} \frac{T_c}{\Delta S_{gas}}$$

$$\Delta S = \underbrace{\Delta S_h}_{=\frac{-|Q_h|}{T_h}} + \underbrace{\Delta S_c}_{=\frac{+|Q_c|}{T_c}} + \underbrace{\Delta S_{gas}}_{=0, \text{cyclic process}} < 0$$

violates $\Delta S \geq 0 \Rightarrow$ no perfect heat engine.

2.

$$\frac{\Delta S_h}{Q_h} \frac{T_h}{\Delta S_{gas}} \rightarrow W$$

$$\frac{\Delta S_c}{Q_c} \frac{T_c}{\Delta S_{gas}}$$

$$\Delta S = \underbrace{\Delta S_h}_{=\frac{+|Q|}{T_h}} + \underbrace{\Delta S_c}_{=\frac{-|Q|}{T_c}} + \underbrace{\Delta S_{gas}}_{=0} = |Q| \left(\frac{1}{T_h} - \frac{1}{T_c} \right) < 0$$

violates $\Delta S \geq 0 \Rightarrow$ no perfect heat pump.

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⌚ Why Carnot cycle has the maximum thermal efficiency?

(By entropy argument)

Carnot cycle: reversible

$$\frac{\Delta S_h}{Q_h} \frac{T_h}{\Delta S_{gas}} \rightarrow W$$

$$\frac{\Delta S_c}{Q_c} \frac{T_c}{\Delta S_{gas}}$$

$$\Delta S = \underbrace{\Delta S_h}_{=\frac{-|Q_h|}{T_h}} + \underbrace{\Delta S_c}_{=\frac{+|Q_c|}{T_c}} + \underbrace{\Delta S_{gas}}_{=0} = 0$$

$$\Rightarrow \frac{|Q_h|}{T_h} = \frac{|Q_c|}{T_c}$$

$$e_{\text{Carnot}} = \frac{W}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{T_c}{T_h}$$

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Real engine: irreversible

$$\Delta S = \underbrace{\Delta S_h}_{=-\frac{|Q_h|}{T_h}} + \underbrace{\Delta S_c}_{=\frac{+|Q_c|}{T_c}} + \underbrace{\Delta S_{gas}}_{=0} > 0$$

$$\Rightarrow |Q_h| < \frac{|Q_c|}{T_c} T_h$$

$$W = |Q_h| - |Q_c| < \frac{T_h - T_c}{T_h} |Q_h|$$

$$\Rightarrow e = \frac{W}{|Q_h|} < \left(1 - \frac{T_c}{T_h} \right) = e_{\text{Carnot}}$$

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Heat Death of the Universe

- 3 Ultimately, the entropy of the Universe should reach a maximum value, if our universe is a closed isolated system. At this value, the Universe will be in a equilibrium state of uniform temperature and density. All physical, chemical, and biological processes will cease.
- The state of perfect disorder implies that no energy is available for doing work.
 - This state is called the **heat death of the Universe**.

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