Chapter 10
The Second Law of Thermodynamics

Name： Liu Fengyan

Office： 数理楼3303

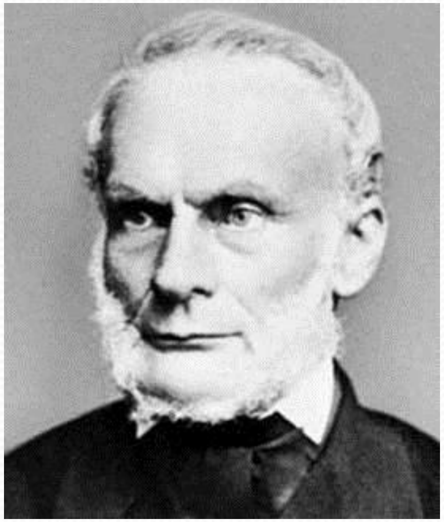
Tel： 67392201-202

Email: Liufengyan@bjut.edu.cn

- **Perpetual mobile of the second kind**

A perpetual motion machine of the second kind is a machine which spontaneously converts thermal energy into mechanical work. When the thermal energy is equivalent to the work done, this does not violate the law of conservation of energy. However, it does violate the more subtle second law. The signature of a perpetual motion machine of the second kind is that there is only one heat reservoir involved, which is being spontaneously cooled without involving a transfer of heat to a cooler reservoir. This conversion of heat into useful work, without any side effect, is impossible, according to the second law of thermodynamics.

Two great persons

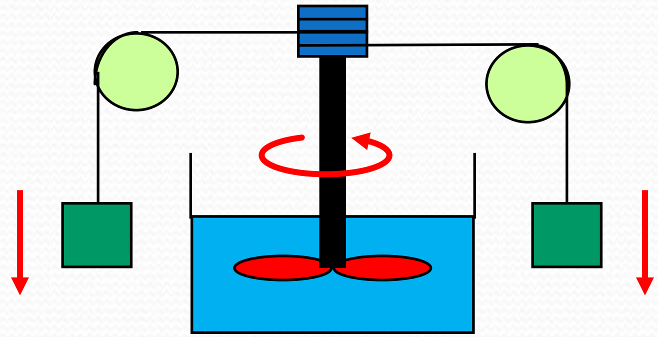


William Thomson, 1st Baron Kelvin (第一代开尔文勋爵 26 June 1824 – 17 December 1907), was an Irish and British mathematical physicist and engineer.

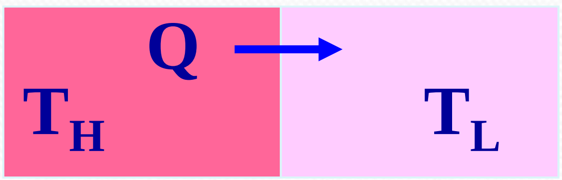
Rudolf Julius Emanuel Clausius (克劳修斯，January 1822 – 24 August 1888), was a German physicist and mathematician and is considered one of the central founders of the science of thermodynamics.

◆Directions of Thermodynamic Processes

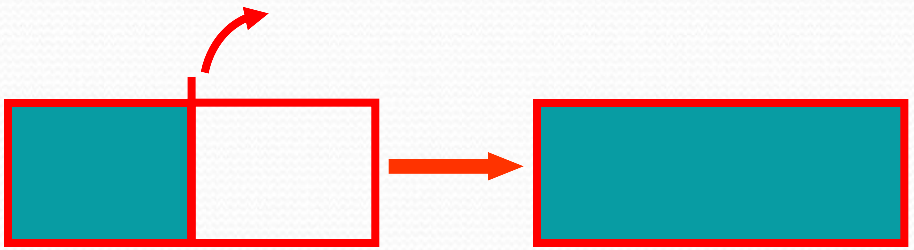
① Convert mechanical energy completely into heat.



② Heat by itself always flows from a hot body to a cooler body, never the reverse.



③Adiabatic free expansion



- The Second Law of Thermodynamics

- Reversible Processes and Irreversible Processes

- The Microscopic Interpretation of the second law of thermodynamics

- Entropy

◆The Second Law of Thermodynamics

1. the Kelvin–Planck statement

It is impossible for any system to undergo a cyclic process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.

Notes:

① It is a cyclic process.

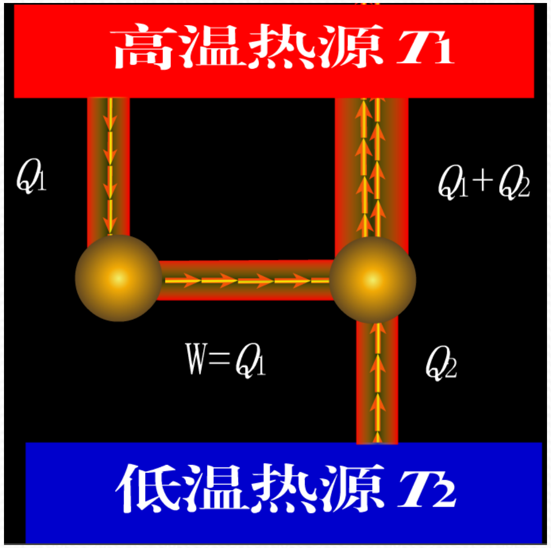
②It is impossible to build an engine with 100% thermal efficiency.

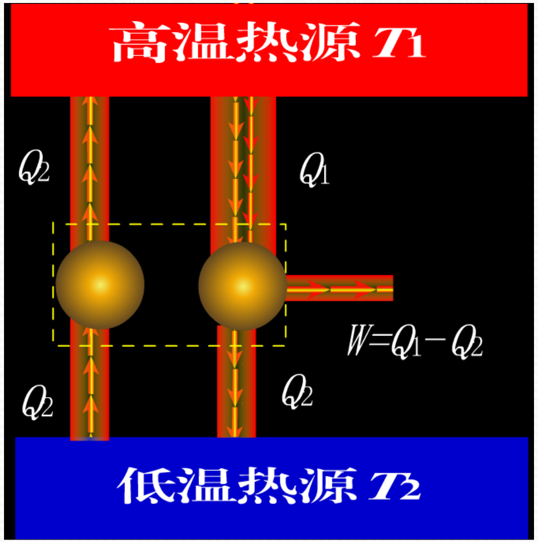
③ The second law, therefore, is not a deduction from the first but stands by itself as a separate law of nature. The first law denies the possibility of creating or destroying energy; the second law limits the *availability* of energy and the ways in which it can be used and converted.

2. Clausius statement

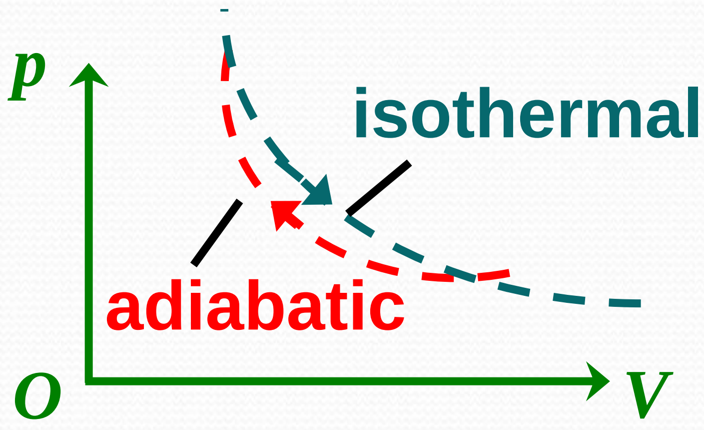
Heat can never pass from a colder to a warmer body without some other change.

3.Equivalence of the Clausius and the Kelvin statements





Can an adiabatic line cross a isothermal line twice?



No, it violates the second law of thermodynamic.

◆Reversible Processes and Irreversible Processes

Reversible process

In thermodynamics, a reversible process -- or reversible cycle if the process is cyclic -- is a process that can be "reversed" by means of infinitesimal changes in some property of the system without entropy（熵） production.

Irreversible process

In an irreversible process, finite changes are made; therefore the system is not at equilibrium throughout the process. At the same point in an irreversible cycle, the system will be in the same state, but the surroundings are permanently changed after each cycle.

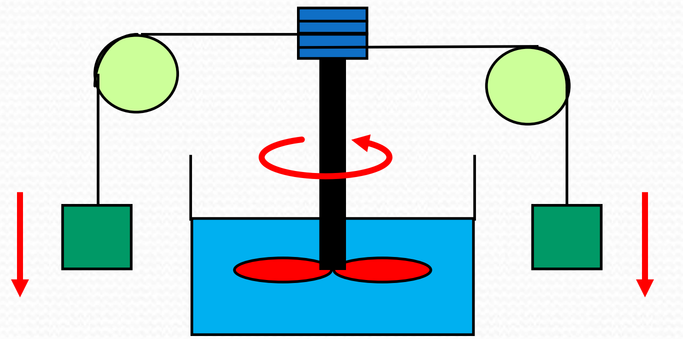
Reversible process $\longleftrightarrow$ **a quasistatic process without friction**

◆The Microscopic Interpretation of the second law of thermodynamics

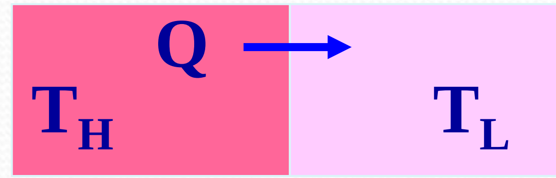
——Directions of thermodynamic processes in microcosmos

e.g.

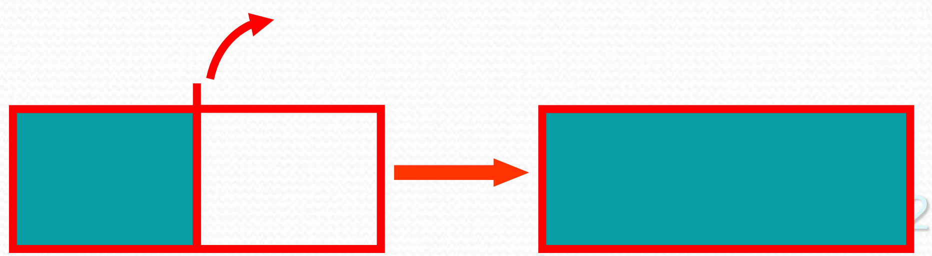
① convert mechanical energy completely into heat



② heat by itself always flows from a hot body to a cooler body, never the reverse.



③Adiabatic free expansion



Notes: **Orderly motion changes to disorderly motion. Disorder degree increases.**

Any process proceeds naturally in the direction of increasing disorder

一切自然过程总是沿着分子热运动无序程度增大的方向进行.

——The Microscopic Interpretation of the second law of thermodynamics

◆Entropy

- ◆The second law of thermodynamics, as we have stated it, is not an equation or a quantitative relationship but rather a statement of impossibility.
- ◆However, the second law can be stated as a quantitative relationship with the concept of Entropy.

◆**In the 1850s and 1860s, German physicist Rudolf Clausius described entropy as the transformation-content, i.e. dissipative energy use, of a thermodynamic system or working body of chemical species during a change of state.**

◆**Later, scientists such as Ludwig Boltzmann, Josiah Willard Gibbs, and James Clerk Maxwell gave entropy a statistical basis.**

Microscopic expression for entropy

$$S = k \ln \Omega$$

k——Boltzmann constant

Ω——represent the number of possible microscopic states for a given macroscopic state

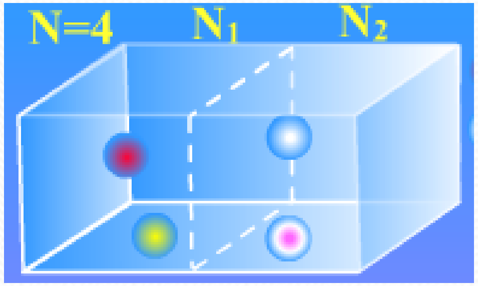
Notes:

Entropy is a measure of the disorder of the system as a whole.

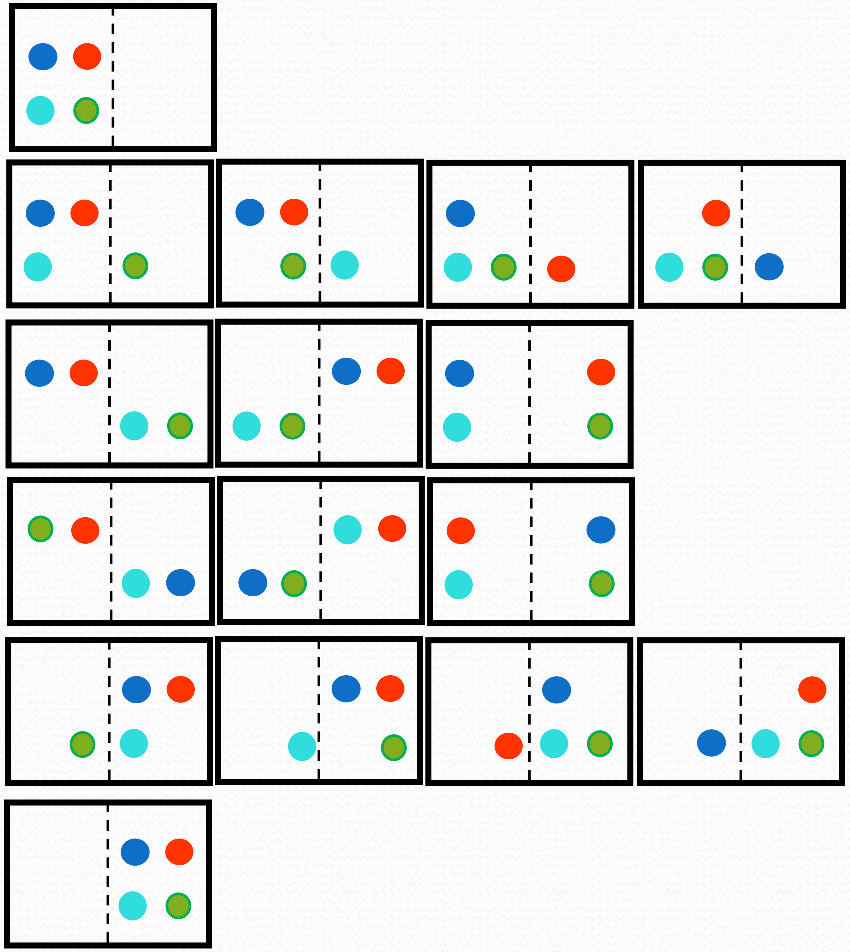
Thermodynamic probability

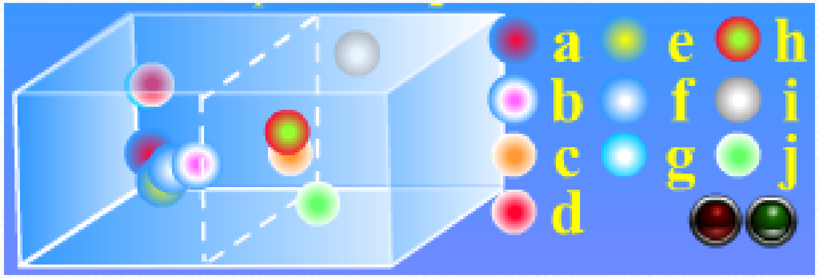
——the number of possible microscopic states for a given macroscopic state

e.g.



- **There are 4 molecules in the box.**
- **The box is divided into two identical parts——left part and right part.**
- **Detect the distribution of the 4 molecules.**

Microscopic states	Macroscopic state	Microscopic states
	Left 4, Right 0	1
	Left 3, Right 1	4
	Left 2, Right 2	6
	Left 1, Right 3	4
	Left 0, Right 4	1



宏观状态	包括的微观状态数 Ω
左 20 右 0	1
左 18 右 2	190
左 15 右 5	15504
左 11 右 9	167960
左 10 右 10	184765
左 9 右 11	167960
左 5 右 15	15504
左 2 右 18	190
左 0 右 20	1

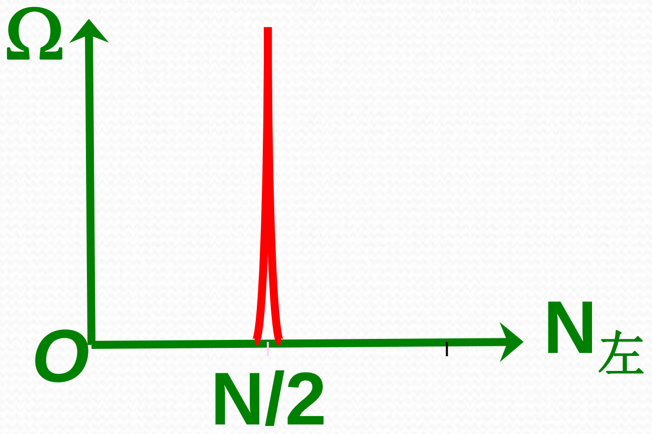
If there are 10 molecules in the box?

If there are 20 molecules in the box?

If there are N molecules in the box?

N_{left}	N_{right}	Ω
0	N	*1*
1	N-1	C_N^1
2	N-2	C_N^2
………		
N	0	C_N^N

If N is a large number:



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.

When all systems taking part in a process are included, the entropy either remains constant or increases.

In other words:

No process is possible in which the total entropy decreases, when all systems taking part in the process are included.

Heat death of the universe

The heat death of the universe is a historically suggested ultimate fate of the universe in which the universe has diminished to a state of no thermodynamic free energy and therefore can no longer sustain processes that consume energy (including computation and life). Heat death does not imply any particular absolute temperature; it only requires that temperature differences or other processes may no longer be exploited to perform work. In the language of physics, this is when the universe reaches thermodynamic equilibrium (maximum entropy).

The result would inevitably be a state of universal rest and death, if the universe were finite and left to obey existing laws. But it is impossible to conceive a limit to the extent of matter in the universe; and therefore science points rather to an endless progress, through an endless space, of action involving the transformation of potential energy into palpable motion and hence into heat, than to a single finite mechanism, running down like a clock, and stopping for ever.

See you next time!