Chapter 17 & 18 Thermodynamics

1. Internal Energy and Specific Heat

2. The First Law of Thermodynamics

3. Applying the First Law of Thermodynamics

4. Theorem of Equipartition of Energy

5. Adiabatic Expansion of an Ideal Gas

6. Heat Engines and the Efficiency

7. Entropy and the 2nd Law of Thermodynamics

比热容

The internal energy is the total amount of kinetic energy and potential energy of all the particles in the system.

热能

$$U = U_{micro\ kin} + U_{mirco\ pot}$$

广度性质

The internal energy is an extensive property: it depends on the size of the system, or on the amount of substance it contains.

Internal energy does not include the energy due to motion or location of a system as a whole.

内能不包括系统整体的动能与势能

The internal energy of *n* moles of an ideal monatomic (one atom per molecule) gas. 单原子分子气体

$$U = N\left(\frac{1}{2}m\overline{v^2}\right) = N\bar{K} = \frac{3}{2}NkT = \frac{3}{2}nRT$$

If the gas molecules contain more than one atom, then the rotational and vibrational energy 振动协能 **of the molecules must also be taken into account, but it will still be a function only of temperature for an ideal gas.**

$$U = U(T) \quad \text{(ideal gas)}$$

Specific heat (specific heat capacity)

Heat capacity (热容) **is a physical property of matter, defined as the amount of heat to be supplied to a given mass of a material to produce a unit change in its temperature. The SI unit of heat capacity J/K.**

$$C = \frac{dQ}{dT}$$

Heat capacity is an extensive property. The corresponding intensive property is the specific heat (capacity), which is the heat capacity divided by the mass of the substance.

$$c = \frac{C}{m} = \frac{1}{m}\frac{dQ}{dT}$$

比热容（质量）

The molar (specific) heat capacity is the heat capacity of a sample divided by the amount of substance of the sample.

$$C_m = \frac{C}{n} = \frac{1}{n}\frac{dQ}{dT}$$

摩尔比热容

The heat Q required to change the temperature from T_1 to T_2 is

$$Q = \int_{T_1}^{T_2} C(T)dT = m\int_{T_1}^{T_2} c(T)dT = n\int_{T_1}^{T_2} C_m(T)dT$$

The **specific heat** often varies with **temperature**, but for temperature changes that are not too great, c can often be considered **constant**.

$$Q = C(T_2 - T_1) = mc(T_2 - T_1) = nC_m(T_2 - T_1)$$

Example:

(a) How much heat is required to raise the temperature of an empty 20 kg vat made of iron from 10°C to 90°C?
(b) What if the vat is filled with 20 kg of water?
Specific heats: iron 450 J/kg·°C; water 4186 J/kg·°C

Solution:

(a) $Q = mc\Delta T = (20 \text{ kg})(450 \text{ J/kg·°C})(80 \text{ °C})$

$\qquad = 7.2 \times 10^5 \text{ J} = 720 \text{ kJ}$

(b) The water alone would require

$\quad Q = mc\Delta T = (20 \text{ kg})(4186 \text{ J/kg·°C})(80 \text{ °C})$

$\qquad = 6.7 \times 10^6 \text{ J} = 6700 \text{ kJ}$

The total, for the vat plus the water, is 720 kJ + 6700 kJ = 7420 kJ

热力学平衡　　没有能量物质的宏观移动

In **thermodynamic equilibrium** there are **no net macroscopic flows of matter or energy**.

The system can be described by several parameters, such as p, V, and T. That is in a p-V-T diagram, it is expressed by **a point** (in the absence of external forces).
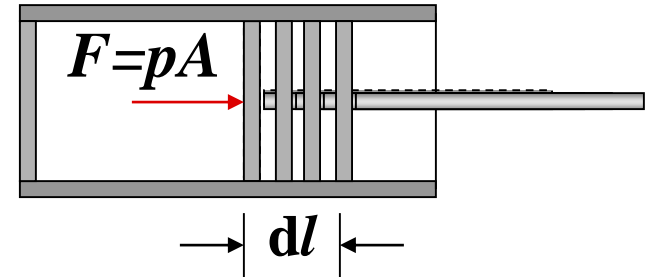
p_1, V_1 → p_2, V_2 →

p

Quasistatic process
(准静态过程)

1

2

V
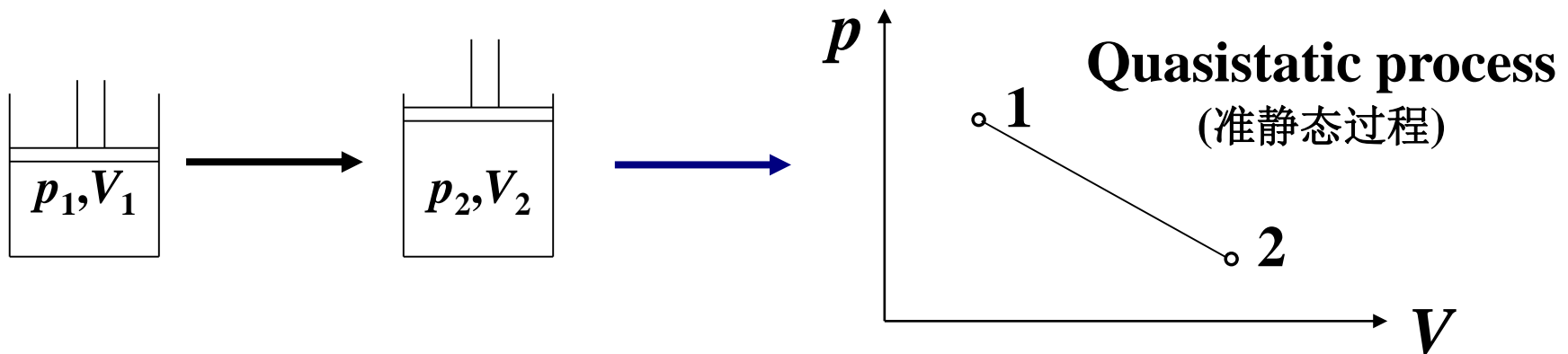
Now the system experiences a series changes from state 1 to state 2. Each state is a new equilibrium state.

Work:

**The work done by the gas
to move the piston is:**

$$dW = Fdl = pAdl = pdV$$

**where dV is the differential change in volume of
the gas owing to the movement of the piston.**
**When the piston is moved slowly and change the
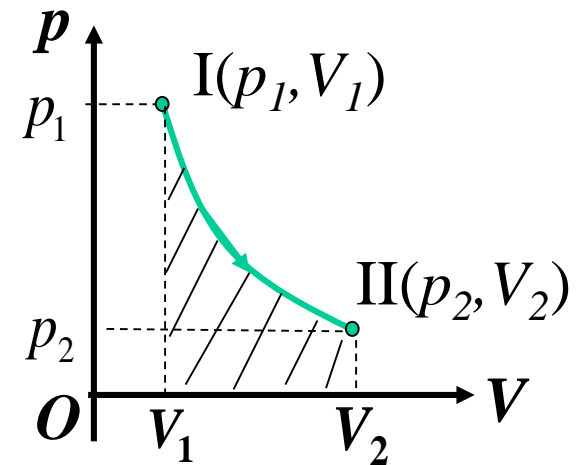volume of gas from V_i to V_f, the total work done
by the gas is:**

$$W = \int dW = \int_{V_i}^{V_f} pdV.$$

Descriptions:

(1) It is the shaded area under the *p-V* curve between initial and final states 功是过程曲线下的面积.

(2) The work done by the gas depends on the process 功与过程有关,功是过程量.

(3) The work done by the gas is positive when its volume expands; otherwise, negative.

The first law of thermodynamics (P407):

Experimentally, it is found that both work W and heat Q are dependent on the process. However, a surprising thing is that *the quantity Q - W is the same for all processes* between two states. It depends only on the initial and final states.

One can infer that the quantity *Q - W* must represent a change in some **intrinsic property** of the system. This intrinsic property is called the *internal energy U*, which is a function of state, or a **state-function**（内能是状态量）.

$$\Delta U = U_f - U_i = Q - W$$

—— **The First Law of Thermodynamics.**

For a differential process, it can be written as:

$$dU = dQ - dW$$

It is hold for any system and any process!
包括热现象在内的能量守恒定律！

The internal energy _U_ of a system tends to increase if energy is added as heat _Q_ and tends to decrease if energy is lost as work done by the system.

系统从外界吸收的热量, 一部分使系统的内能增加, 另一部分用于对外做功. (第一类永动机——不需要能量输入而能持续做功的机器——不存在)

About the sign of _W_, _Q_, and _U_:

Work done _by_ the system $W > 0$

System absorbs heat $Q > 0$

System's energy increases $\Delta U > 0$
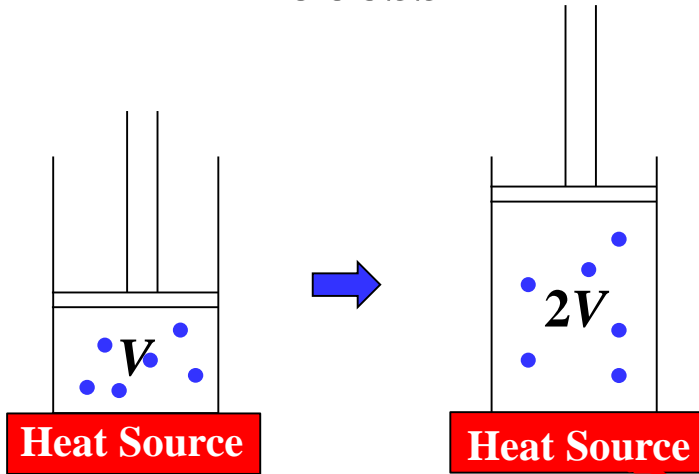
Two ways to change system's internal energy:

"**Energy may be transferred into or out of a system as either work *W* or heat *Q*.**"

Relationship between *W* and *Q*:

The transformation between work and heat is not direct, but on the system. The direct result is that the internal energy of the system changes.
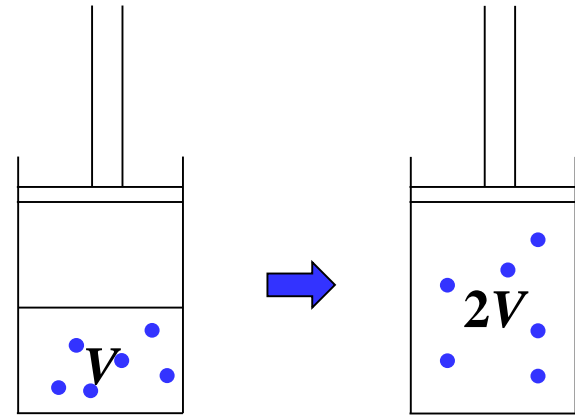
$\Delta U, W, Q$?

Process 1

$T = C$

$\Delta U = 0 \longleftrightarrow W > 0$

$Q > 0$

$\Delta U = Q - W$

Process 2

$Q = 0, W = 0$

$\Delta U = 0$

$T = C$

1. Adiabatic process

绝热

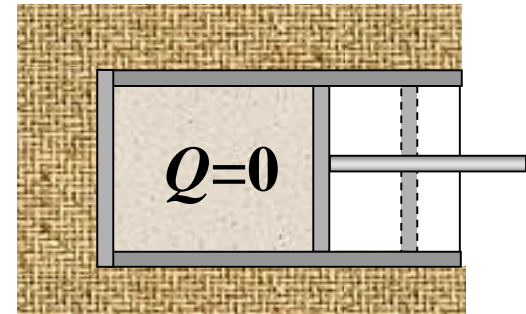It is one that occurs so rapidly or occurs in a system well isolated that no transfer of energy as heat between the system and its environment.

和无交换

$$Q = 0 \quad \rightarrow \quad \Delta U = -W$$

$Q=0$

—— **The change of the internal energy is by the amount of work.**

$\Delta U \begin{cases} < 0, & \text{if the work is done } by \text{ the system.} \\ > 0, & \text{if the work is done } on \text{ the system.} \end{cases}$

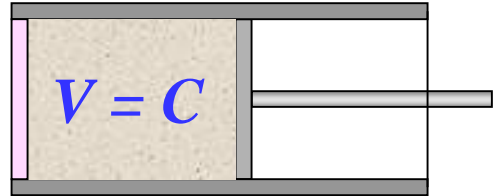## 2. Isochoric (constant-volume) process

The volume of the system is held constant, no work is done during the process.

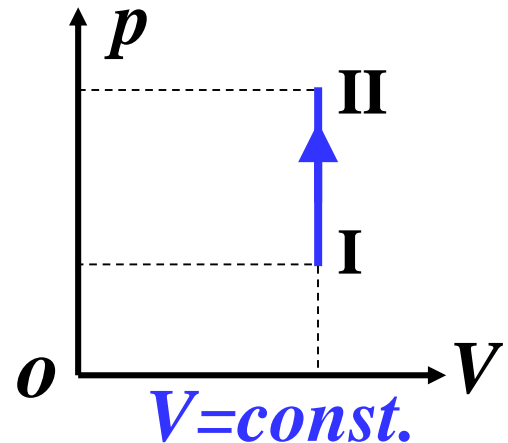$$dW = pdV = 0, \ or \ W = 0$$

$$Q = \Delta U = nC_V(T_2 - T_1)$$

$V = C$

$dV=0$

C_V —— **molar heat capacity at constant volume.**

$\Delta U \begin{cases} > 0, \text{system } \textbf{absorbs} \text{ heat from its environment;} \\ < 0, \text{then the system } \textbf{releases} \text{ heat.} \end{cases}$

State equation:

$$\frac{p}{T} = \textbf{constant} \ \ \textbf{or} \ \ \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

$V=const.$

3. **Isobaric** (constant-pressure) process

等压

The pressure of the system is held constant.

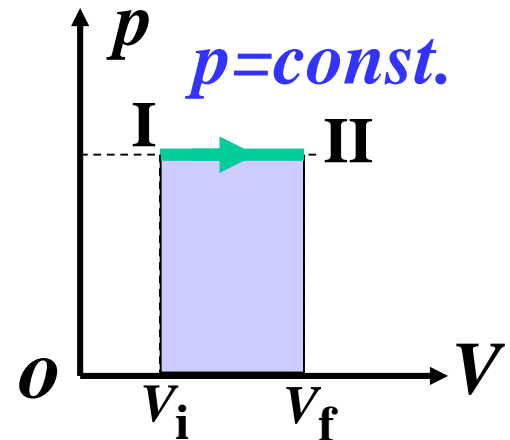$$W = \int_{V_i}^{V_f} p\,\mathrm{d}V \ = p(V_f - V_i) = nR\Delta T$$
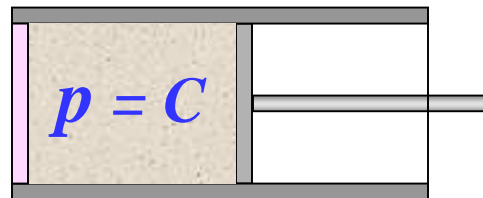
$$Q = \Delta U + W = nC_p(T_2 - T_1)$$

C_p — **molar heat capacity at constant pressure.**

The heat absorbed by gas is used for increasing its internal energy and doing work (气体吸收的热量一部分用于增加内能，另一部分用于对外作功).

State equation:

$$\frac{V}{T} = \text{constant}$$

$p = C$

p=const.

The relation between C_v and C_p

isobaric process
$$\begin{cases} W = p\Delta V = nR\Delta T \\ Q = \Delta U + W = nC_p(T_2 - T_1) \end{cases}$$

isochoric process
$$Q = \Delta U = nC_V(T_2 - T_1)$$

To relate molar heat capacities C_p and C_V, we consider an isobaric process $\quad Q = \Delta U + W$

$$nC_p\Delta T = nC_V\Delta T + nR\Delta T$$

$$C_p = C_V + R$$ (Mayer's formula)

4. Isothermal (constant-temperature) process

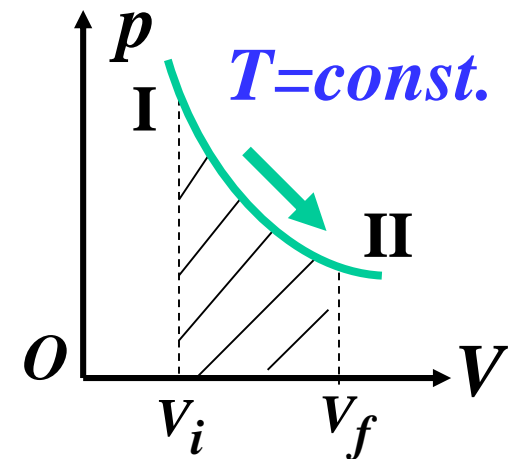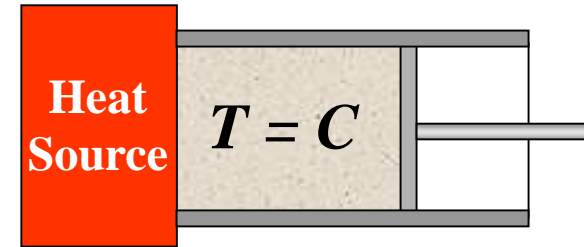**Gas expands (or compress) while keep the temperature constant.**

$$\Delta U = 0 \quad \rightarrow \quad Q = W$$

Heat Source $T = C$

State equation:

$pV = C$ —— **Isotherm** (等温线) **is hyperbola curve on a p-V diagram.**

$$W = \int_{V_i}^{V_f} p\,dV = \int_{V_i}^{V_f} \frac{p_i V_i}{V}\,dV$$

$$= p_i V_i \ln\frac{V_f}{V_i} = p_i V_i \ln\frac{p_i}{p_f}$$

$$\boxed{= nRT \ln\frac{V_f}{V_i} = nRT \ln\frac{p_i}{p_f}}$$
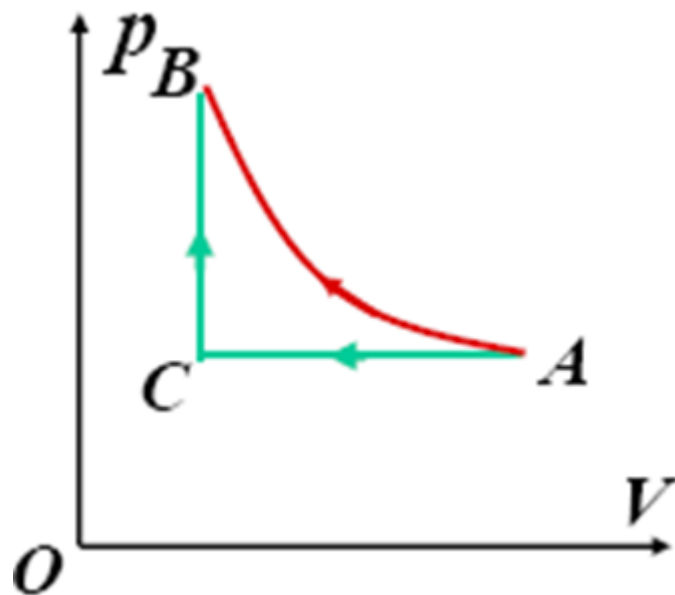
$T=const.$

$$V_f > V_i, \quad W > 0;$$
$$V_f < V_i, \quad W < 0.$$

Example:

N_2 of volume $100cm^3$ and pressure $1.013 \times 10^5 Pa$ is compressed to volume $20cm^3$, compute the change in internal energy ΔU, the heat Q and the work done W during processes: (1) Isothermal compress; (2) Two-step process of isobaric compress then isochoric increasing pressure to same state

Solution:

(1) For isothermal compress, $T = C, \Delta U = 0$

$$\text{so,} \quad Q = W = p_1 V_1 \ln\frac{V_2}{V_1} = -16.3\,\text{J}$$

(negative W, release heat)

(2) As the final state is the same, $\Delta U = 0$

$$\text{so,} \quad Q = W = p_1(V_2 - V_1) = -8.1\,\text{J}$$

(For different processes, both Q and W are different)

17-4 Theorem of Equipartition of Energy (P412)

Degrees of freedom (自由度)

The number of **independent motions** that are allowed to the body.

In other words, the number of **degrees of freedom** can be defined as **the minimum number of independent coordinates.**

（确定物体的空间位置所需要的独立坐标数目）

There are different kinds of molecules, monatomic molecules (contain only one single atom, helium); diatomic molecules (contain two atoms, oxygen); and polyatomic molecules (contain more than two atoms, methane 甲烷). Besides translational motion ($t = 3$), molecules may have rotational motion (r) or vibrational motion (s).

The degrees of freedom is:

$$f = t + r + s.$$
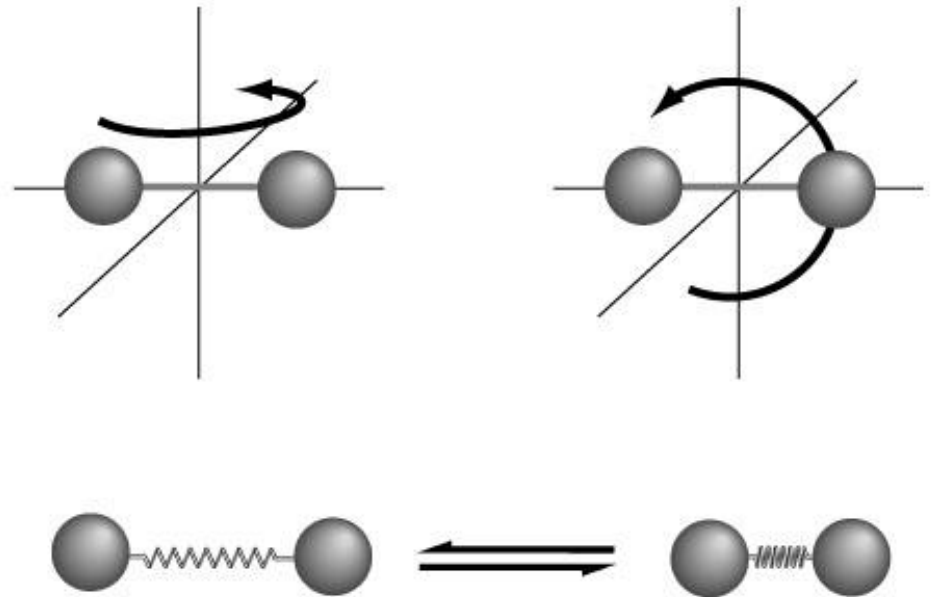
Average translational kinetic energy of molecules:

$$\overline{K} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v_x^2} + \frac{1}{2}m\overline{v_y^2} + \frac{1}{2}m\overline{v_z^2} = \frac{3}{2}kT$$

$$\frac{1}{2}m\overline{v_x^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}m\overline{v_y^2} = \frac{1}{2}kT$$

Maxwell introduced the *theorem of equipartition of energy* (能量均分定理) :

Every kind of molecule has a certain number *f* of *degrees of freedom*, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with (on average) an energy of $\frac{1}{2}kT$ per molecule (or $\frac{1}{2}RT$ per mole).

在温度为 *T* 的平衡态下, 气体分子每个自由度的平均能量都相等

The internal energy U

Based on the theorem of equipartition of energy,

the average **kinetic energy** of **1 molecule**:

$$\overline{\varepsilon_k} = \frac{f}{2}kT$$

the total **kinetic energy** of **n mole molecules**:

$$E_k = nN_A\overline{\varepsilon_k} = \frac{f}{2}nRT$$

For **internal energy** $\quad f = t + r + 2s$

The **internal energy** of an ideal gas is a function of the gas **temperature** only.

$$U = \frac{f}{2}nRT$$

Molar heat capacity at constant volume

For an isochoric process,

V = **constant, dV = 0, so dW = 0**

According to $dU = dQ - dW$:

$$dQ = dU = \frac{f}{2}nRdT$$

Based on definition of molar heat capacity at constant V,

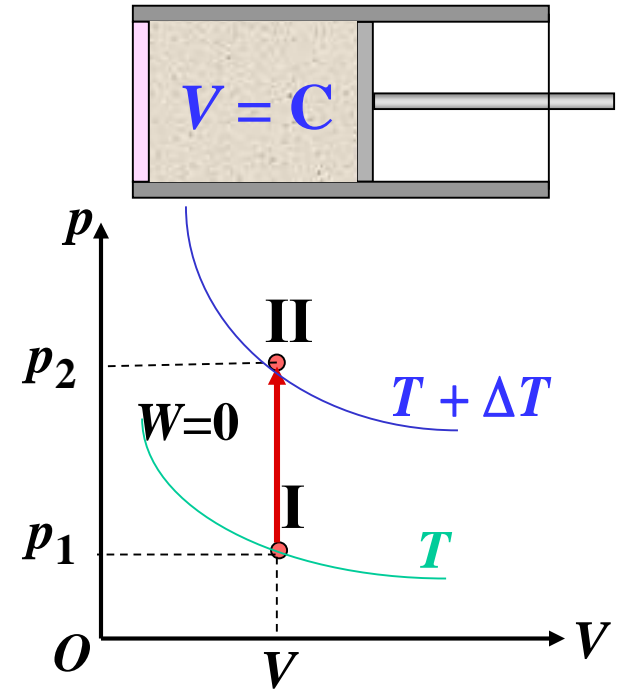$$C_V = \frac{1}{n}\frac{(dQ)_V}{dT} = \frac{1}{n}\frac{dU}{dT}$$

$\longrightarrow$

$$C_V = \frac{f}{2}R$$

So, we may express internal energy of ideal gas as:
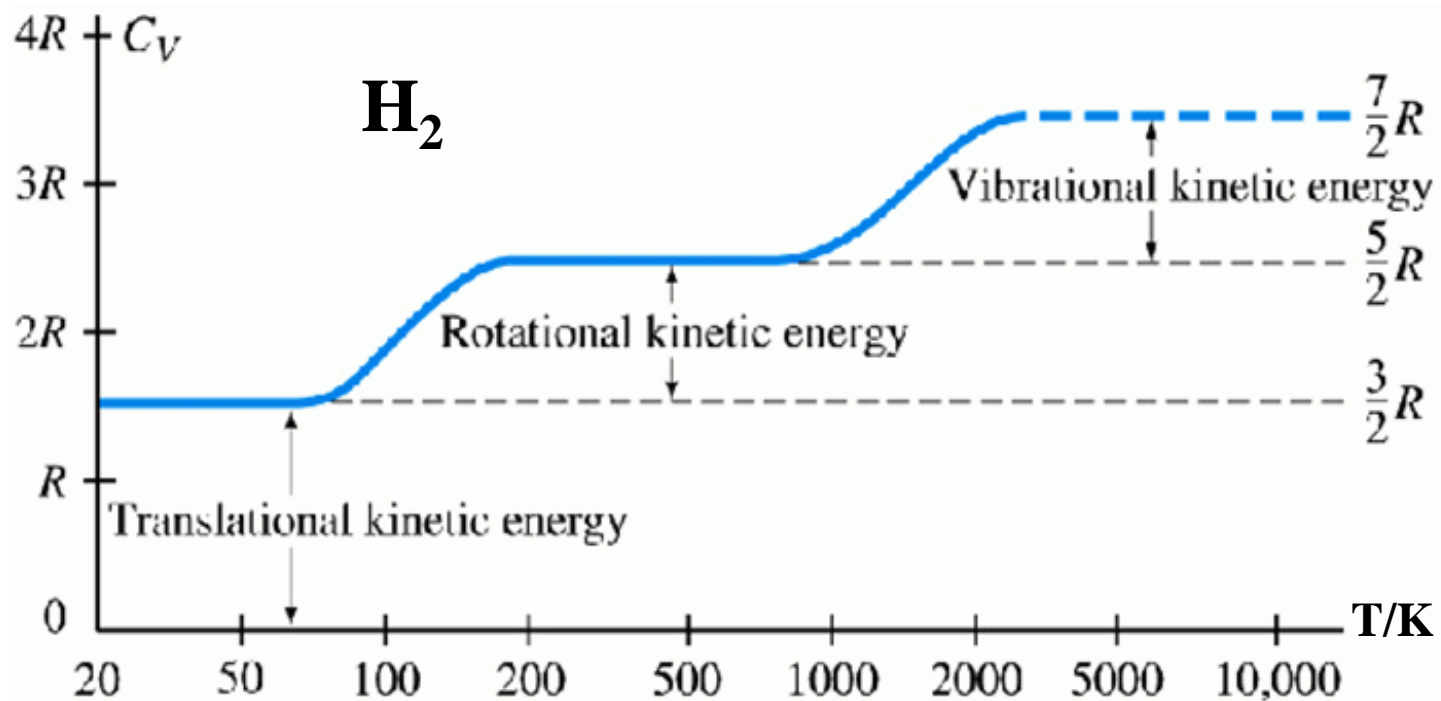
$$U = nC_V T \quad \text{or} \quad \Delta U = nC_V\Delta T$$

For any process

双原子

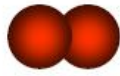**For diatomic gases at very low temperature, C_V has a value of only 3/2R, as if it had only 3 degrees of freedom. And at very high temperature, C_V was about 7/2R, as if there were 7 degrees of freedom. Just fewer degrees of freedom are "active" at lower temperatures.**
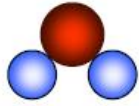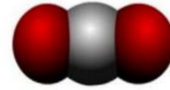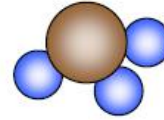
$$f = t + r + s$$

	He	O_2	H_2O	CO_2	NH_3	CH_3OH
$f =$	3	6	9	9	12	18
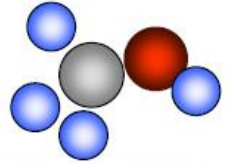
Rigid or neglect vibrational motion

$f =$	3	5	6	5	6	6

Non-linear: $f = 3N,\ \ t = 3,\ \ r = 3,\ \ s = 3N\text{-}6$

Linear: $f = 3N,\ \ t = 3,\ \ r = 2,\ \ s = 3N\text{-}5$

17-5 Adiabatic Expansion of an Ideal Gas (P416)

Adiabatic process: $Q=0$, $dQ=0$

Based on $dU = dQ - dW$,

$$dU = -dW = -pdV = nC_V dT \qquad (1)$$

In terms of the ideal gas law $pV=nRT$, we have

$$pdV + VdP = nRdT \qquad (2)$$

from (1) $n dT = -\dfrac{pdV}{C_V},$ **then substitute into (2)**

$$C_V(pdV + Vdp) + RpdV = 0$$

$$\because \quad R = C_p - C_V \quad \therefore \quad C_V Vdp + C_p pdV = 0$$

$$C_V V \mathrm{d}p + C_p p \mathrm{d}V = 0$$

let $\gamma = C_p / C_V$ then $\dfrac{\mathrm{d}p}{p} + \gamma \dfrac{\mathrm{d}V}{V} = 0$

$ln p + \gamma ln V = C$ then $ln p V^\gamma = C$

Combining $pV = nRT$,
$$\begin{cases} pV^\gamma = C \\ V^{\gamma-1} T = C \\ p^{\gamma-1} T^{-\gamma} = C \end{cases}$$

(Poisson's equation)

Example:

(1) Find the relation of the work done by the gases during adiabatic process 准静态绝热过程的功.

Solution: $\because \quad pV^{\gamma} = p_1V_1^{\gamma} = p_2V_2^{\gamma}$

$$\gamma = \frac{C_p}{C_V}$$

$$\therefore \quad W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{p_1V_1^{\gamma}}{V^{\gamma}} dV$$

$$= \frac{p_1V_1^{\gamma}}{\gamma - 1}\left[\frac{1}{V_1^{\gamma-1}} - \frac{1}{V_2^{\gamma-1}}\right] = \frac{p_1V_1}{\gamma - 1} - \frac{1}{\gamma - 1}\left(\frac{p_1V_1^{\gamma}}{V_2^{\gamma-1}}\right)$$

$$\because \quad \frac{p_1V_1^{\gamma}}{V_2^{\gamma-1}} = \frac{p_2V_2^{\gamma}}{V_2^{\gamma-1}} = p_2V_2 \qquad \therefore \quad W = \frac{p_1V_1 - p_2V_2}{\gamma - 1}$$
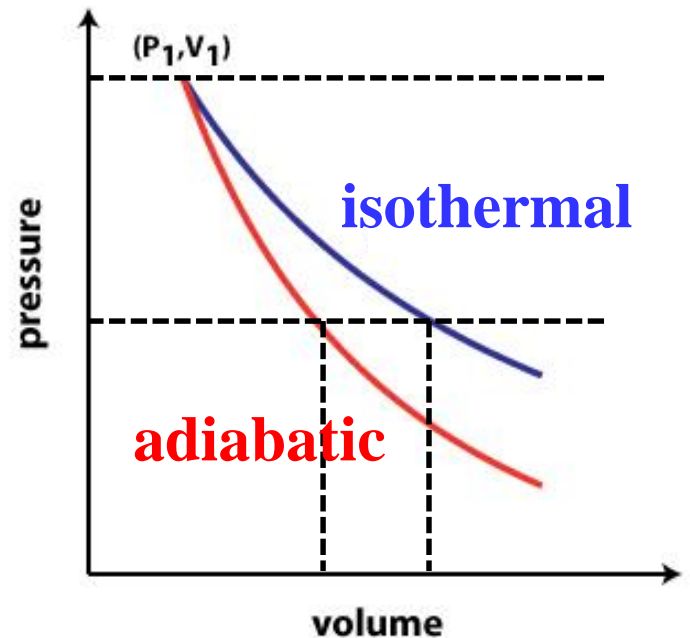
(2) **Adiabatic vs isothermal expansion.** **An ideal monatomic gas is allowed to expand slowly until its pressure is reduced to exactly half its original value. By what factor does the volume change if the process is (a) adiabatic; (b) isothermal?**

Solution: **(a)** $\because p_1 V_1^\gamma = p_2 V_2^\gamma$ and $\gamma = \dfrac{C_p}{C_V} = 5/3$

$$\therefore \quad \frac{V_2}{V_1} = \left(\frac{p_1}{p_2}\right)^{1/\gamma} = 2^{3/5} = 1.52$$

(b) $\because p_1 V_1 = p_2 V_2$

$$\therefore \quad \frac{V_2}{V_1} = \frac{p_1}{p_2} = 2$$

Summary

理想气体的各等值过程、绝热过程公式对照表

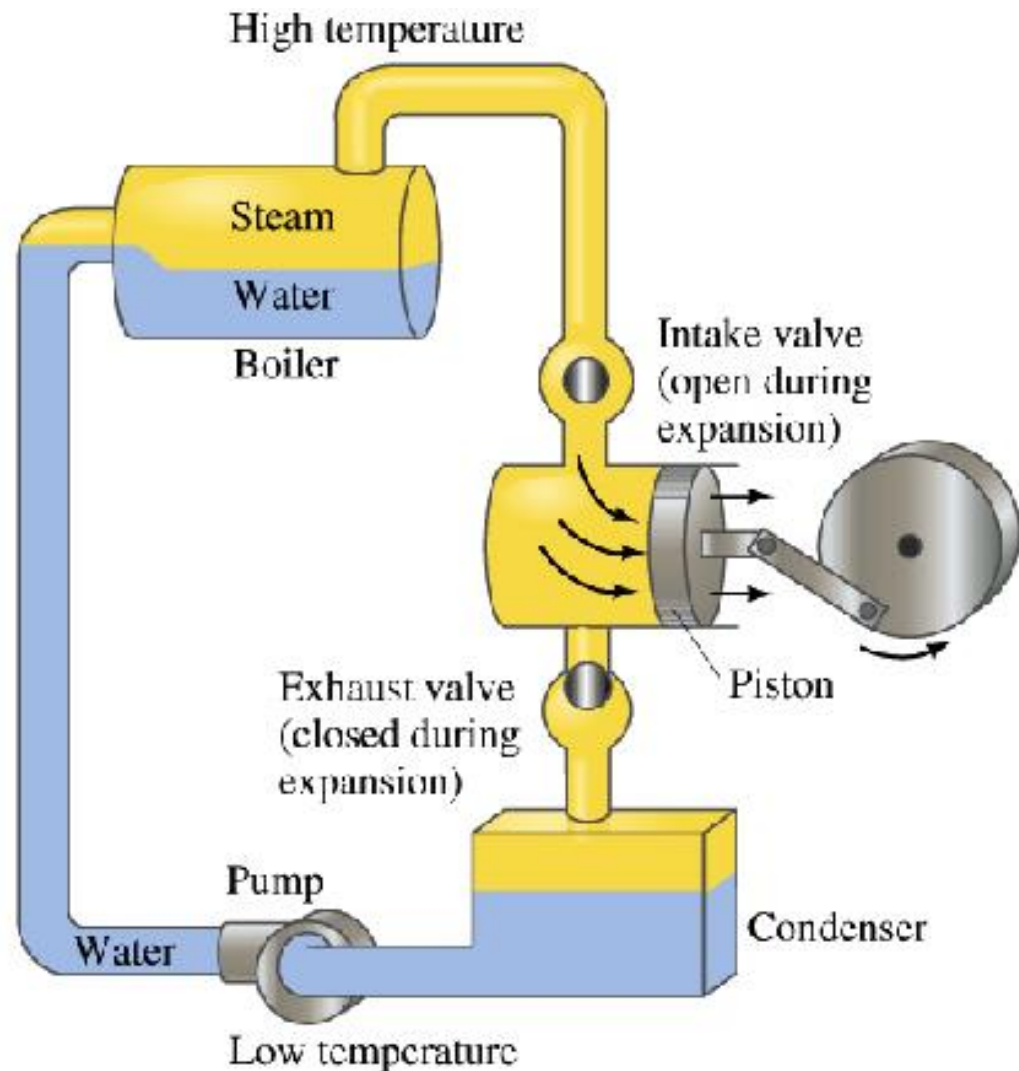| 过程	特征	过程方程	吸收热量	对外做功	内能增量
等体	V=常量	$\dfrac{P}{T} = $ 常量	$\dfrac{M}{\mu}C_V(T_2-T_1)$	0	$\dfrac{M}{\mu}C_V(T_2-T_1)$
等压	P=常量	$\dfrac{V}{T} = $ 常量	$\dfrac{M}{\mu}C_P(T_2-T_1)$	$P(V_2-V_1)$或 $\dfrac{M}{\mu}R(T_2-T_1)$	$\dfrac{M}{\mu}C_V(T_2-T_1)$
等温	T=常量	$PV = $ 常量	$\dfrac{M}{\mu}RT\ln\dfrac{V_2}{V_1}$或 $\dfrac{M}{\mu}RT\ln\dfrac{p_1}{p_2}$	$\dfrac{M}{\mu}RT\ln\dfrac{V_2}{V_1}$或 $\dfrac{M}{\mu}RT\ln\dfrac{p_1}{p_2}$	0
绝热	dQ=0	$PV^\gamma = $ 常量 $V^{\gamma-1}T = $ 常量 $P^{\gamma-1}T^{-\gamma} = $ 常量	0	$-\dfrac{M}{\mu}C_V(T_2-T_1)$ 或 $\dfrac{P_1V_1-P_2V_2}{\gamma-1}$	$\dfrac{M}{\mu}C_V(T_2-T_1)$

A **heat engine**, or simply, **an engine**, is a device that extracts energy from its environment in the form of heat and does useful work. At the heart of every engine is a **working substance**, such as gasoline-air mixture in automobile engines.

The working substances absorb heat from high temperature source (i.e. the boiler); one part of energy becomes work, and the other part release to the low temperature source (i.e. condenser). After a cycle, the working substances resume their original state.

Schematic working process of steam engine (P431).

High temperature

Steam
Water
Boiler

Intake valve
(open during
expansion)

Piston

Exhaust valve
(closed during
expansion)

Pump

Water

Condenser

Low temperature

In general, if a system starts from a certain initial state, through a closed series of thermodynamic processes, the system returns to its initial state, then these processes are called a **cycle**.
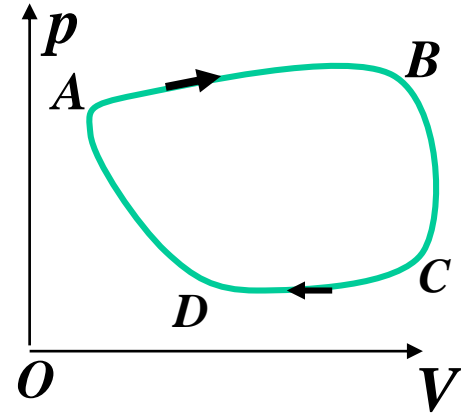
The **important feature of cyclic process** is:

$$\Delta U = 0$$

The cycle is called *reversible* (可逆的) if the cycle can be considered as a series of equilibrium states, and the whole process could be done in reverse with no change in magnitude of the work done or heat exchanged, otherwise, *irreversible* (**P433**).

A reversible process always can be plotted on a *pV* diagram.

(1) Efficiency of an engine

An Engine should operate **at least between two heat sources**, the high temperature source T_H, and the low temperature source T_L. The system absorbs heat Q_H (>0) from the high temperature source, and releases heat Q_L (<0) to the low temperature source, and does work W to the environment at the same time.
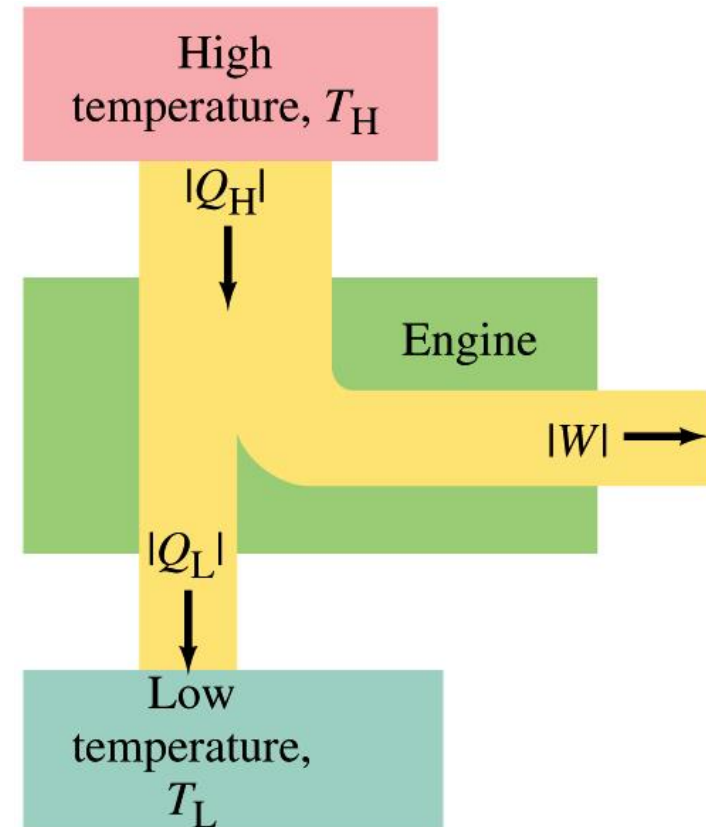
Using $\Delta U = Q - W$ to the **whole cyclic process,**

$$\Delta U = 0 \text{ and } Q = Q_H - |Q_L|$$

$$\downarrow$$

$$Q_H - |Q_L| = W$$

$$Q_H = W + |Q_L|$$

— indicates the **principle of engine:**

In each cycle, substance absorbs heat Q_H from T_H, partly does work outside; partly transfers Q_L to T_L .

The efficiency η of any engine is defined by

$$\eta = \frac{|\text{transformed work}|}{|\text{absorbed heat}|} = \frac{|W|}{|Q_H|}.$$

意义：在一次循环中工作物质对外所做的净功占它从高温热源吸收的热量的比例.

For a cyclic process, $\Delta U = 0$, and $W = |Q_H| - |Q_L|$

So the efficiency of an engine can be written as:

$$\eta = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

Eq. (18-1) of P432

(2) A Carnot engine and its efficiency (P433)

One of important **reversible cycles** is Carnot cycle. This ideal engine turns out to be the **best** (in principle) **at using energy as heat to do useful work.**

➤ **In an ideal engine, such as Carnot engine, all processes are reversible and no wasteful energy transfers occur due to friction and turbulence (湍流).**

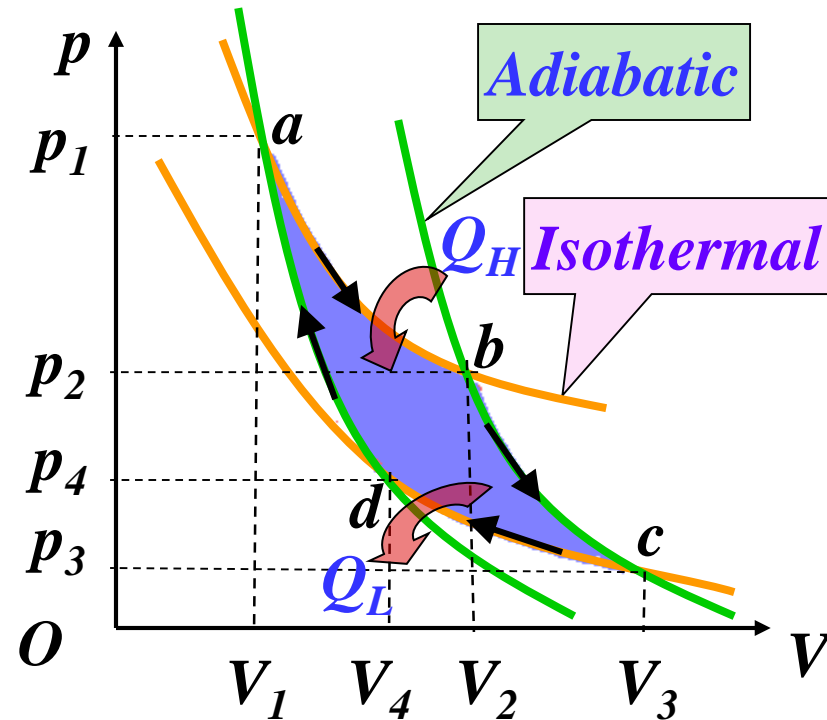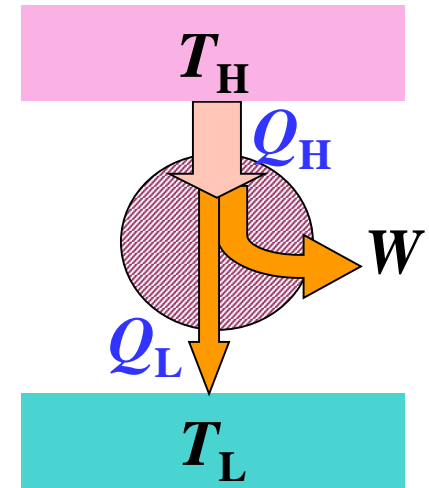**Carnot cycle consists of two isothermal processes and two adiabatic processes.**

State parameters:

(a) T_H, p_1, V_1

(b) T_H, p_2, V_2

(c) T_L, p_3, V_3

(d) T_L, p_4, V_4

1. $a \rightarrow b$, **isothermal process** T_H, **feature** is $\Delta U = 0$.

$$|Q_H| = W = \int_{V_1}^{V_2} p \, dV = nRT_H \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= nRT_H \ln \frac{V_2}{V_1} \quad (1)$$

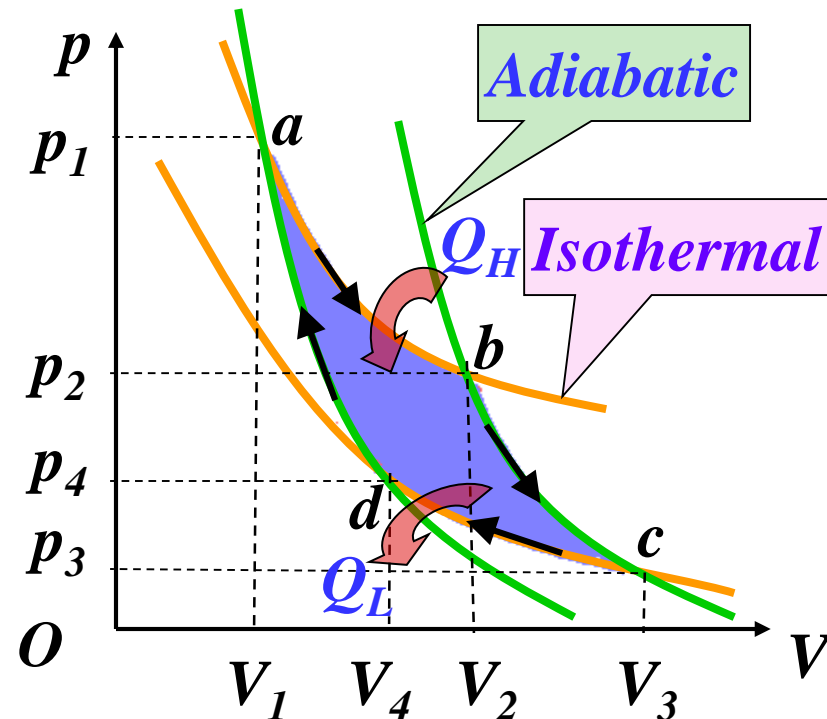**2. $c \rightarrow d$, isothermal process T_L , $|Q_L| = nRT_L \ln \dfrac{V_3}{V_4}$ (2)**

From the adiabatic process equations in $b \rightarrow c$ & $d \rightarrow a$:

$$T_H V_2^{\gamma-1} = T_L V_3^{\gamma-1} \quad \& \quad T_H V_1^{\gamma-1} = T_L V_4^{\gamma-1}$$

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

$$\therefore |Q_L| = nRT_L \ln \frac{V_2}{V_1} \quad (3)$$

$$\frac{(3)}{(1)}, \quad \frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H}$$

So, the **efficiency of the Carnot engine** is given by

$$\eta_{\mathrm{C}} = 1 - \frac{|Q_{\mathrm{L}}|}{|Q_{\mathrm{H}}|} = 1 - \frac{|nRT_{\mathrm{L}}\ln(V_1/V_2)|}{|nRT_{\mathrm{H}}\ln(V_2/V_1)|} = 1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$$

$$\eta_c = 1 - \frac{T_L}{T_H} \qquad \text{Eq. (18-3)}$$

Summary:

(1) The efficiency of the cycle of Carnot engine depends only on T_{L}, and T_{H}.

(2) The efficiency of Carnot engine is always less than 1.

Carnot's theorem

All **reversible engines** operating between the same two constant temperatures T_H and T_L have **the same efficiency**. Any **irreversible engine** operating between the same two fixed temperatures will have **an efficiency less than this**.

$$\eta \leq \eta_r = 1 - \frac{T_L}{T_H}$$

理想气体卡诺循环的效率是最高的

Example:

One mole of a **monatomic** ideal gas is taken through the reversible cycle as shown below. Process b-c is an **adiabatic expansion**, with p_b=10.0 atm and V_b=1.0×10⁻³ m³. Find **(a)** the energy added to the gas as heat, **(b)** the energy leaving the gas as heat, **(c)** net work done by the gas, and **(d)** the efficiency of the cycle.

Solution: $Q_{ab} > 0, Q_{ca} < 0, Q_{bc} = 0$

(a) $p_b V_b^\gamma = p_c V_c^\gamma = p_a V_c^\gamma$

$$\frac{p_b}{p_a} = \left(\frac{V_c}{V_b}\right)^\gamma = 32$$

$$Q_{in} = nC_V(T_b - T_a) = \frac{3}{2}(p_b - p_a)V_b = \frac{3}{2} \cdot \frac{31}{32} p_b V_b$$

$$= 1.47 \times 10^3 \text{ J}$$
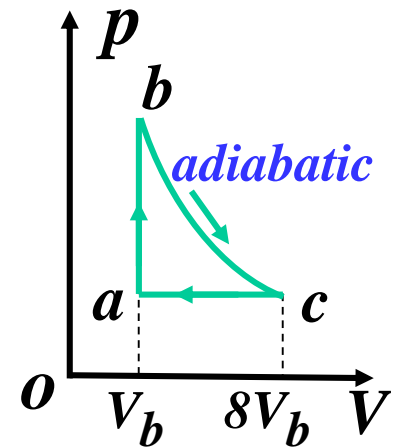
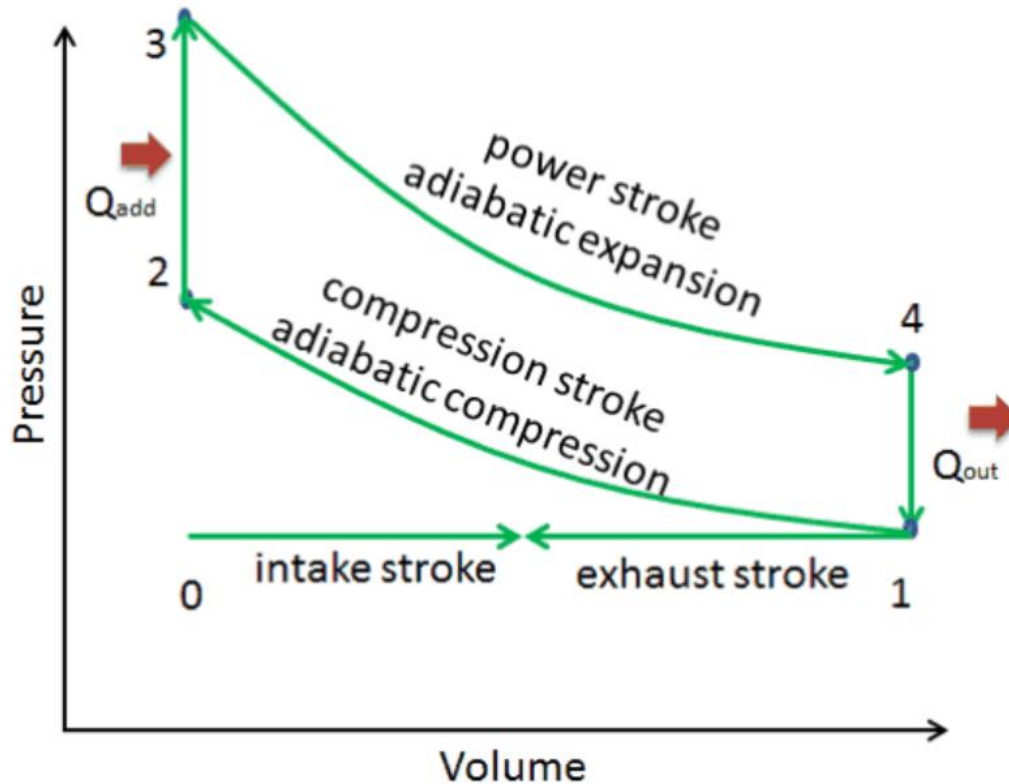**(b)** $Q_{out} = nC_p(T_a - T_c) = \dfrac{5}{2} p_a(V_a - V_c)$

$ = \dfrac{5}{2} \cdot \dfrac{1}{32} p_b(-7V_b)$

$ = -5.52 \times 10^2 \text{ J}$
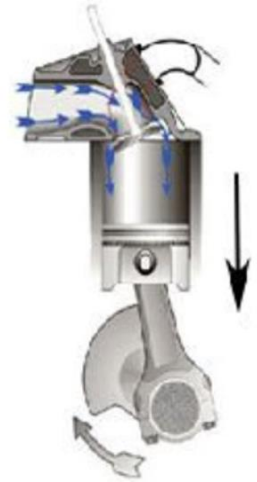
(c) $W = Q = |Q_{in}| - |Q_{out}| = 9.18 \times 10^2 J$

(d) $\eta = \dfrac{W}{Q_{in}} = 62.4\%$

(3) Otto Cycle and its efficiency (P436)

Otto Cycle is the theoretical thermodynamic cycle which describes the working of a spark ignition engine (火花点火式发动机). This type of spark ignition engines is the most common type of engines used in automobiles.
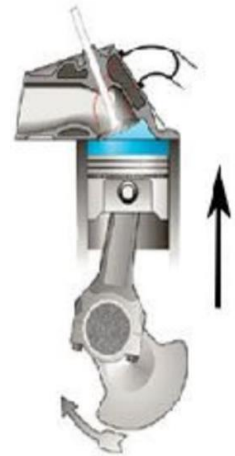
Process 0–1: Intake stroke (进气冲程), gasoline vapor and air drawn into engine at constant pressure.

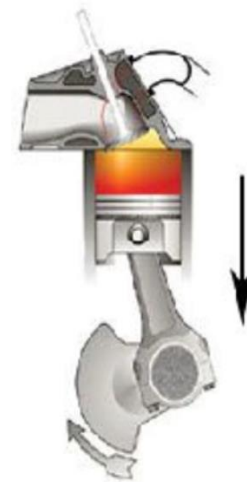**Process 1–2: Compression stroke (压缩冲程), an adiabatic compression, pressure and temperature increase.**

Process 2–3: Combustion (燃烧), short time, essentially constant volume, the piston is at the top dead center (TDC, 上止点).

Intake Stroke

Compression Stroke

Process 3–4: **Power stroke (动力冲程),** **an adiabatic expansion, pressure and temperature decrease.**

Power Stroke

Process 4–1: Complete the cycle by a constant-volume process, the piston is at the bottom dead center (BDC, 下止点).

Process 1–0: **Exhaust stroke (排气冲程),** **piston pushes remaining combustion products out of engine at constant pressure.**

Exhaust Stroke

Example:

For an ideal gas as working substance, show that the efficiency of an Otto cycle is
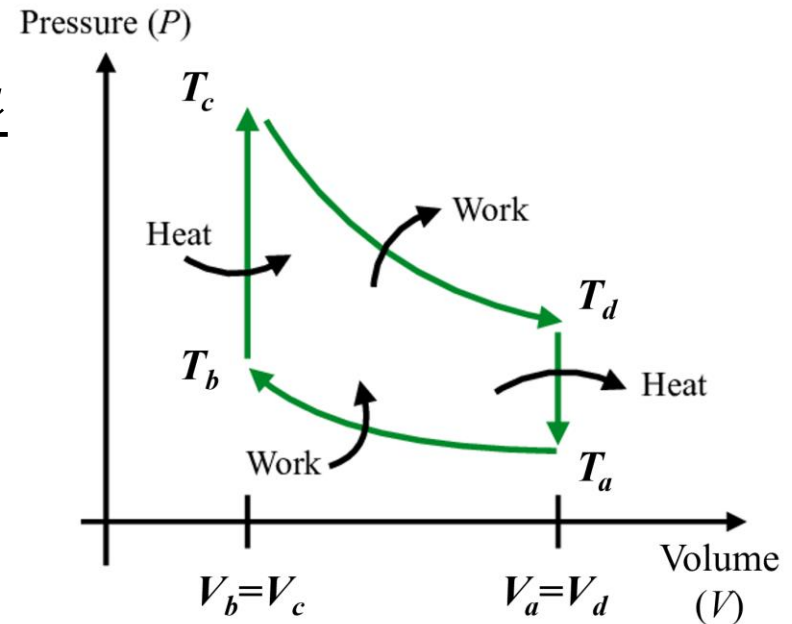
$$\eta = 1 - \left(\frac{V_a}{V_b}\right)^{1-\gamma}$$

Solution:

$\because \quad |Q_H| = nC_V(T_c - T_b) \quad$ and $\quad |Q_L| = nC_V(T_d - T_a)$

$\therefore \quad \eta = 1 - \dfrac{|Q_L|}{|Q_H|} = 1 - \dfrac{T_d - T_a}{T_c - T_b}$

$\because \quad T_b V_b^{\gamma-1} = T_a V_a^{\gamma-1} \quad$ and

$\qquad T_d V_d^{\gamma-1} = T_c V_c^{\gamma-1}$

$$\therefore \quad \frac{T_d - T_a}{T_c - T_b} = \frac{T_c \left(\frac{V_c}{V_d}\right)^{\gamma-1} - T_b \left(\frac{V_b}{V_a}\right)^{\gamma-1}}{T_c - T_b} = \left(\frac{V_b}{V_a}\right)^{\gamma-1}$$

$$\therefore \quad \boxed{\eta = 1 - \left(\frac{V_b}{V_a}\right)^{\gamma-1} = 1 - \left(\frac{V_a}{V_b}\right)^{1-\gamma}} \quad \text{(Otto cycle)}$$

where γ is the **ratio of specific heats** and V_a/V_b is the **compression ratio**.

(4) Refrigerators (制冷机) and its efficiency (P438)

A *refrigerator* is a device that uses work to transfer energy from a low temperature source to a high temperature source as it continuously repeated a set of series of thermodynamic processes.
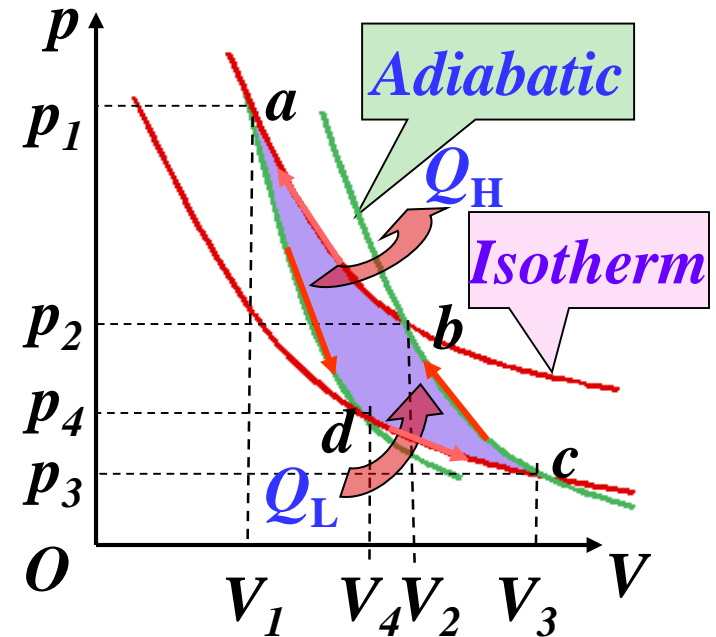
The **efficiency of any refrigerator** (*coefficient of performance* 制冷系数) can be defined as
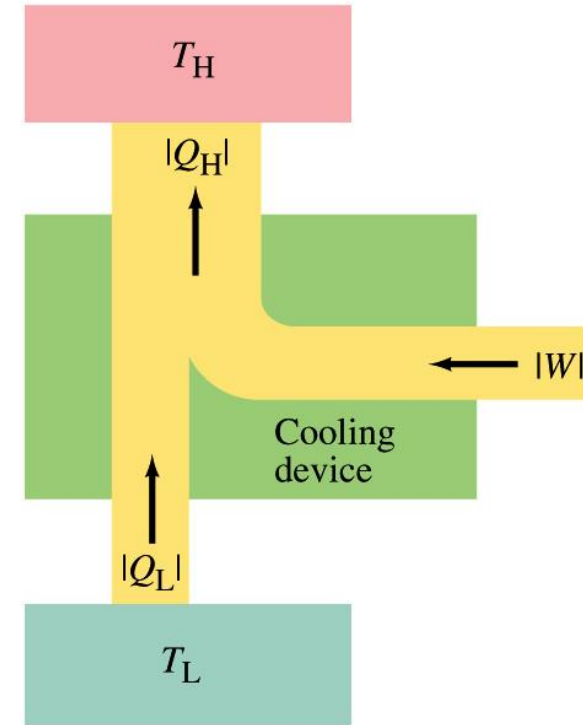
$$|W| = |Q_H| - |Q_L|$$

$$CP = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

Carnot Refrigerator —— **the basic elements of an ideal refrigerator that operates in the reverse of the Carnot engine.**

Since Carnot refrigerator is a Carnot engine operating in reverse, so (卡诺制冷机制冷系数)

$$CP = \frac{|Q_L|}{|Q_H| - |Q_L|}$$ **or** $$CP_{ideal} = \frac{T_L}{T_H - T_L}$$

Example:

If an **ideal refrigerator** keeps its contents at -15°C when the house temperature is 22°C, what is its coefficient of performance?

Solution:

$$CP = \frac{|Q_L|}{|W|} = \frac{T_L}{T_H - T_L} = \frac{258}{295 - 258} = 7.0$$

Summary

Efficiency of an engine

$$\eta = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

Efficiency of the Carnot engine

$$\eta_c = 1 - \frac{T_L}{T_H}$$

Efficiency of a refrigerator (coefficient of performance)

$$CP = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

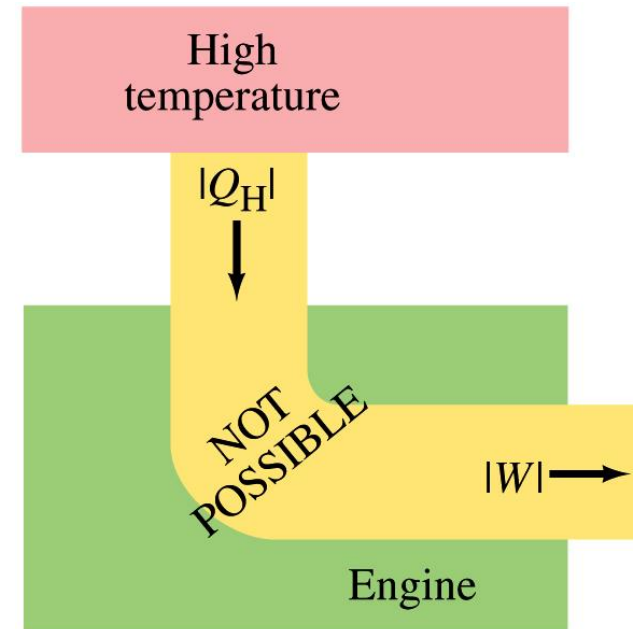**Efficiency of the Carnot refrigerator (ideal refrigerator)**

$$CP_{ideal} = \frac{T_L}{T_H - T_L}$$

Question: **Can we make an engine, $\eta = 100\,\%$?**

$$\eta = \frac{W}{Q_H} = 1 \quad \longrightarrow \quad W = Q_H \quad \text{Suit with the First Law!}$$

Precise statements of second law were proposed by Lord Kelvin, and by Rudolf Clausius in the early 1850s. Although worded differently, their statements are equivalent.

I. Kelvin-Planck statement (P432):

No device is possible whose sole effects is to transform a given amount of heat completely into work (不可能从单一热源吸取热量, 使之全部变为功, 而不产生其他影响). 理想气体等温膨胀？引起体积变化！

II. Clausius statement (P438):

No device is possible whose sole effects is to transfer heat from one system at one temperature into a second system at a higher temperature (热量不可能自动地从低温物体传向高温物体).
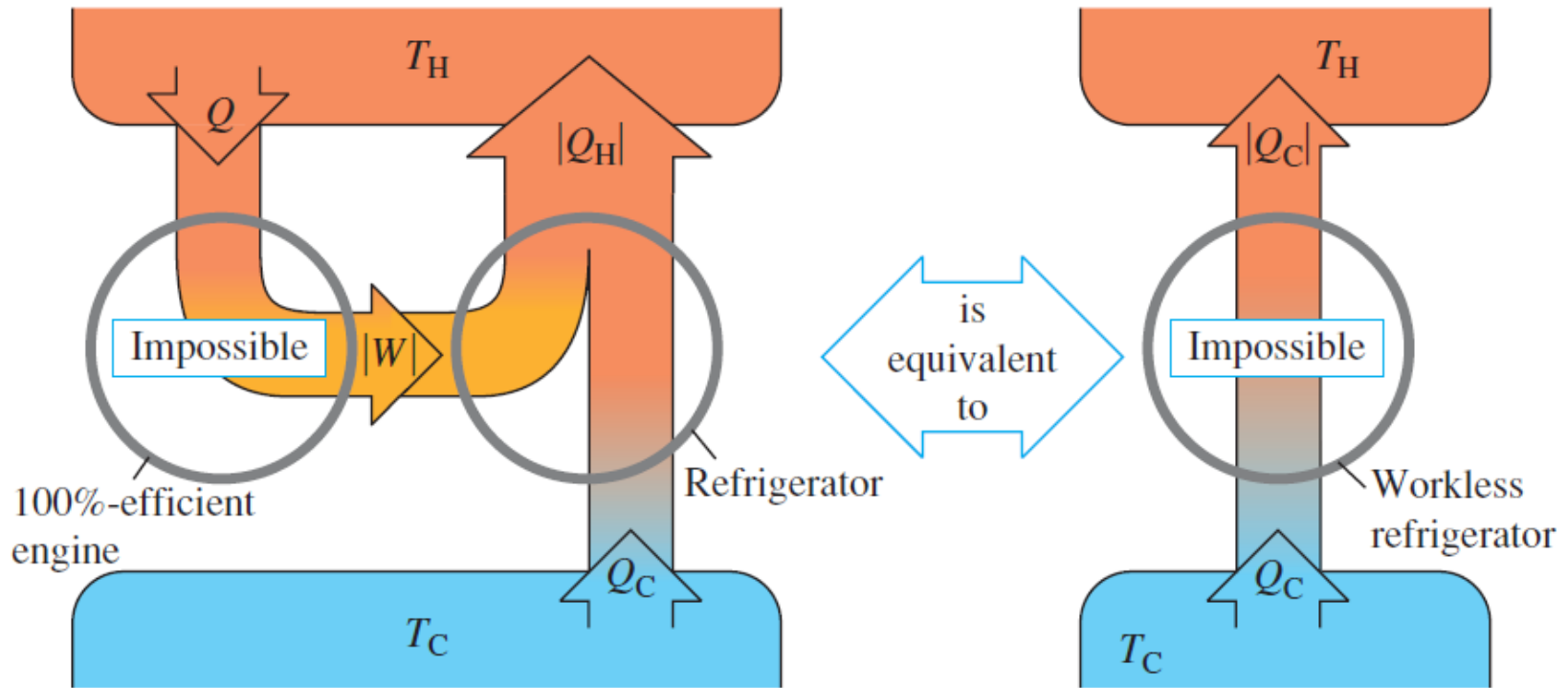
第二类永动机不可能制成，效率永远小于1

# If the Clausius statement is wrong, then the Kelvin statement is wrong!
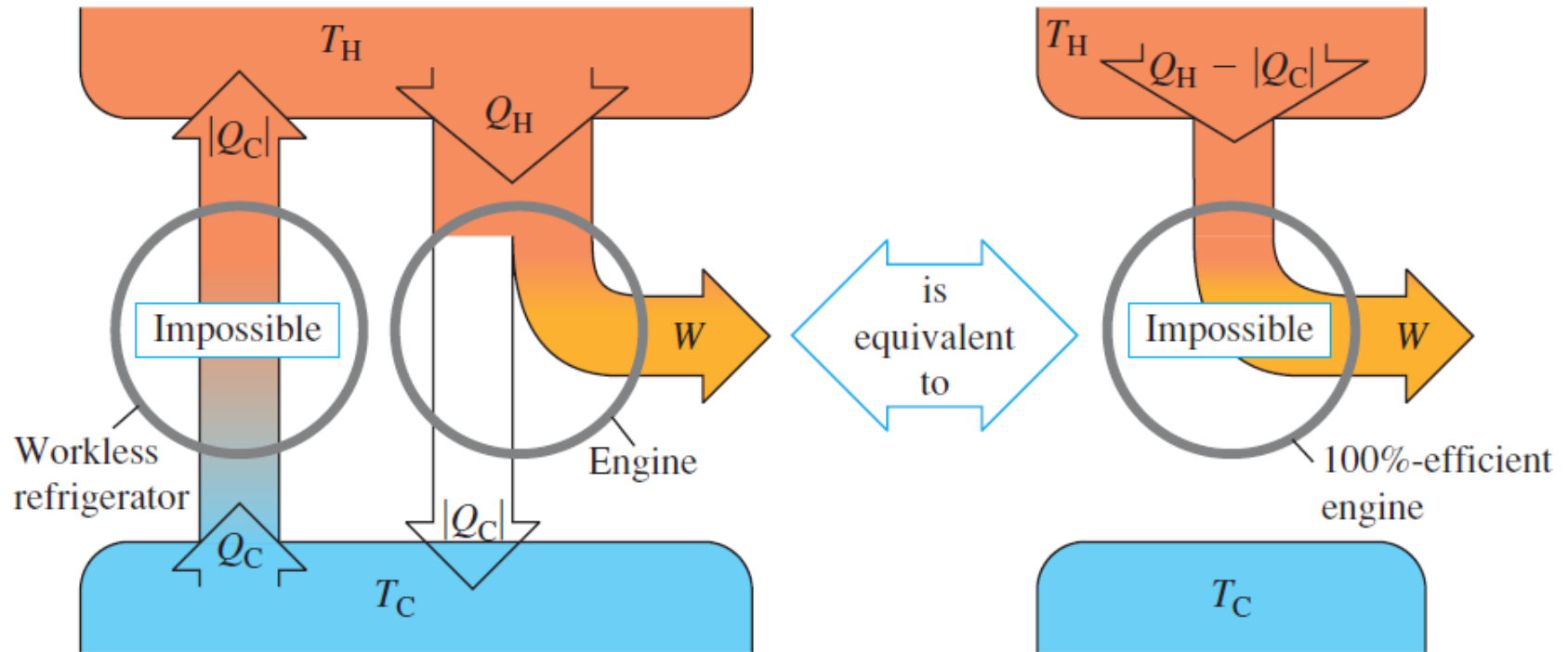
If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $|Q_H| - |Q_C|$ completely to work.

# If the Kelvin statement is wrong, then the Clausius statement is wrong!

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.
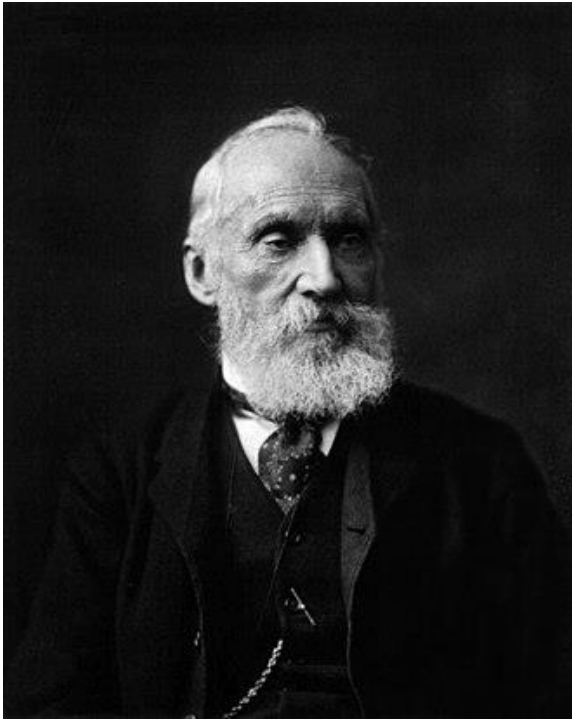
He was ennobled in 1892 in recognition of his achievements in **thermodynamics**, and of his **opposition to Irish Home Rule** (地方自治), becoming Baron (男爵) Kelvin, of Largs in the County of Ayr. He was the first British scientist to be elevated to the **House of Lords** (上议院). The title refers to the **River Kelvin**, which flows near his laboratory at the University of Glasgow.

Lord Kelvin
(开尔文勋爵)

William Thomson (1824-1907), was a British mathematical physicist and engineer who was born in Belfast. **Absolute temperatures** are stated in units of kelvin in his honor.
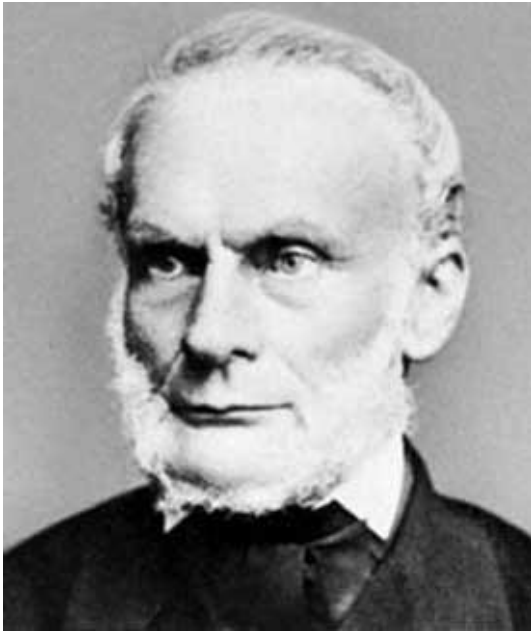
He gave the theory of heat a truer and sounder basis, by his restatement of **Sadi Carnot**'s principle known as the Carnot cycle. His most important paper, "**On the Moving Force of Heat**", published in 1850, first stated the basic ideas of the second law of thermodynamics. In 1865 he introduced the concept of **entropy (熵)**.

Rudolf Clausius
(鲁道夫·克劳修斯)

Rudolf Julius Emanuel Clausius (1822-1888) was a German physicist and mathematician and is considered one of the **central founders** of the science of **thermodynamics**.

Sadi Carnot
(萨迪·卡诺)

He published only one book, the **Reflections on the Motive Power of Fire** 《论火的动力》 (Paris, 1824), in which he expressed the first successful theory of the maximum efficiency of heat engines. In this work he laid the foundations of **an entirely new discipline, thermodynamics**. Carnot's work attracted little attention during his lifetime, but it was later used by Rudolf Clausius and Lord Kelvin to formalize the second law of thermodynamics and define the concept of entropy.

Nicolas Léonard Sadi Carnot (1796-1832) was a French mechanical engineer in the French Army, military scientist and physicist, often described as the "**father of thermodynamics.**"

17-7 Entropy & the 2nd Law of Thermodynamics

(1) Irreversible process (P433)

A process that is **not reversible** is called **irreversible**.

What is a reversible process?

An irreversible process is a process that cannot return **both the system and the environment** to their original conditions.

A system that undergoes an irreversible process may still **be capable of returning to its initial state**. However, the impossibility occurs in **restoring the environment to its own initial conditions**.

Examples of irreversible processes:

➤ **Friction**
➤ **Unrestrained expansion of a fluid**
➤ **Heat transfer through a finite temperature difference**
➤ **Spontaneous mixing of two different substances**

⋮

So, in nature, the 2nd law of thermodynamics reveals that all spontaneously thermodynamic processes in nature are irreversible processes along a single direction.

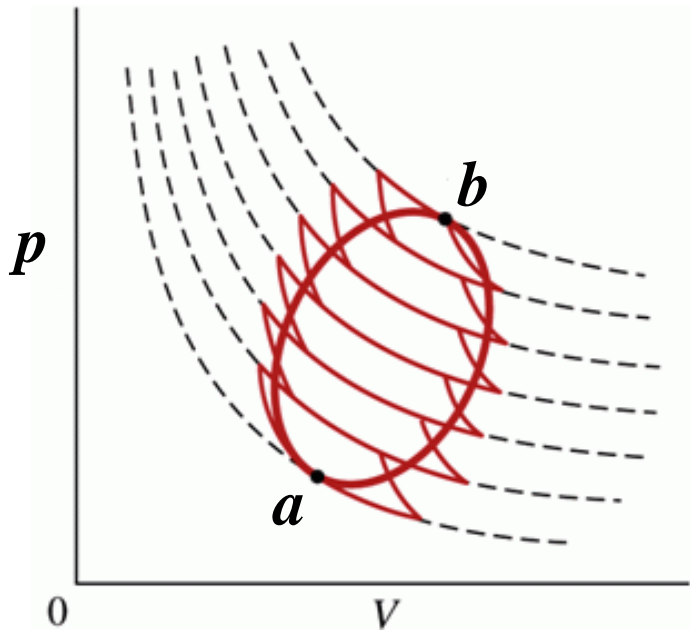(自然界的一切自发过程都是单向进行的不可逆过程)

(2) Entropy (P440)

In the study of the Carnot cycle, we found that

$$\frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \quad \Longrightarrow \quad \frac{|Q_L|}{T_L} = \frac{|Q_H|}{T_H}$$

Recalling our original convention as used in the first law, that Q is positive when it represents a heat flow into the system (as Q_H) and negative for a heat flow out of the system (as Q_L).

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \qquad \text{(Carnot cycle)}$$

Any reversible cycle can be approximated as **a series of Carnot cycles**. (The dashed lines represent isotherms.)

$$\sum \frac{Q}{T} = 0 \quad \text{(Carnot cycles)}$$

Note that the heat output Q_L of one cycle is approximately **equal to** the negative of the heat input, Q_H, **of the cycle below it**. Hence the heat flows on the **inner paths** of all these Carnot cycles **cancel out**.

Hence, in the limit of infinitely many Carnot cycles, we have

$$\oint \frac{\mathrm{d}Q}{T} = 0 \qquad \textbf{(reversible cycle)}$$

The symbol $\oint$ means take the integral around a closed path.

系统经历任意可逆循环一周后，其热温比之和为零.

Let's divide the cycle of Fig. into two parts, then

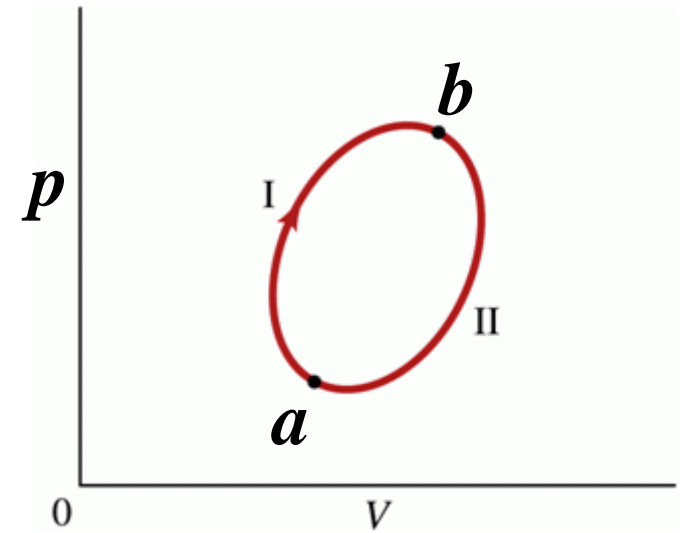$$\int_{a\,\mathrm{I}}^{b} \frac{\mathrm{d}Q}{T} + \int_{b\,\mathrm{II}}^{a} \frac{\mathrm{d}Q}{T} = 0$$

If one path is taken in reverse, p
dQ at each point becoms –dQ,
since the path is reversible, so

$$\int_{b\,\mathrm{II}}^{a} \frac{\mathrm{d}Q}{T} = -\int_{a\,\mathrm{II}}^{b} \frac{\mathrm{d}Q}{T}$$

$$\int_{a\,\mathrm{I}}^{b} \frac{\mathrm{d}Q}{T} = \int_{a\,\mathrm{II}}^{b} \frac{\mathrm{d}Q}{T}$$ **(reversible paths)**

—— **the integral of dQ/T between any two equilibrium states does not depend on the path of the process.**

We **define** a new quantity —— **entropy S**

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

From above Equ., for reversible cycle, we have

$$\oint dS = 0 \qquad \text{(reversible cycle)}$$

The change of entropy ΔS should be

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T} \qquad \text{(reversible processes)}$$

It is independent of the path between the two points *a* and *b*. This is an important result.

—— **entropy is a state variable!**

Explanations:

(i) Entropy is a state function $S=S(T,V),\ S=S(T,P)$

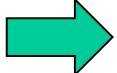**It can only be deduced by experiment, in general.**

To find the entropy change for an irreversible process occurring in a closed system, replace that process with any reversible process that connects the same initial and final states (P441).

(ii) SI unit for entropy and entropy change is the joule per kelvin (J/K).

Calculating the entropy change of an ideal gas:

$$\Delta S(T,V) = S_2 - S_1 = \int_1^2 \frac{dQ}{T} = \int_1^2 \frac{dU + pdV}{T}$$

$$= \int_{T_1}^{T_2} \frac{nC_V}{T} dT + \int_{V_1}^{V_2} \frac{nR}{V} dV$$

$$\Delta S = nC_V ln\frac{T_2}{T_1} + nRln\frac{V_2}{V_1}$$

$$T \uparrow \text{ or } V \uparrow, \ \Rightarrow \ S \uparrow$$

$$\Delta S = nC_V ln\frac{T_2}{T_1} + nRln\frac{V_2}{V_1}$$

For an isothermal process, $T_1=T_2$

$$\Delta S = nRln\frac{V_2}{V_1} = nRln\frac{p_1}{p_2}$$

For an isochoric process, $V_1=V_2$

$$\Delta S = nC_V ln\frac{T_2}{T_1}$$

For an isobaric process, $p_1=p_2$

$$\Delta S = \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{nC_p}{T} dT = nC_p ln\frac{T_2}{T_1}$$

Entropy change in a reversible adiabatic process (可逆绝热过程)

In an adiabatic process, no heat enters or leaves the system. Hence $dQ = 0$ and there is no change in entropy in this reversible process: $\Delta S = 0$. Every reversible adiabatic process is a constant-entropy process. That's why such process is also called isentropic process (等熵过程).
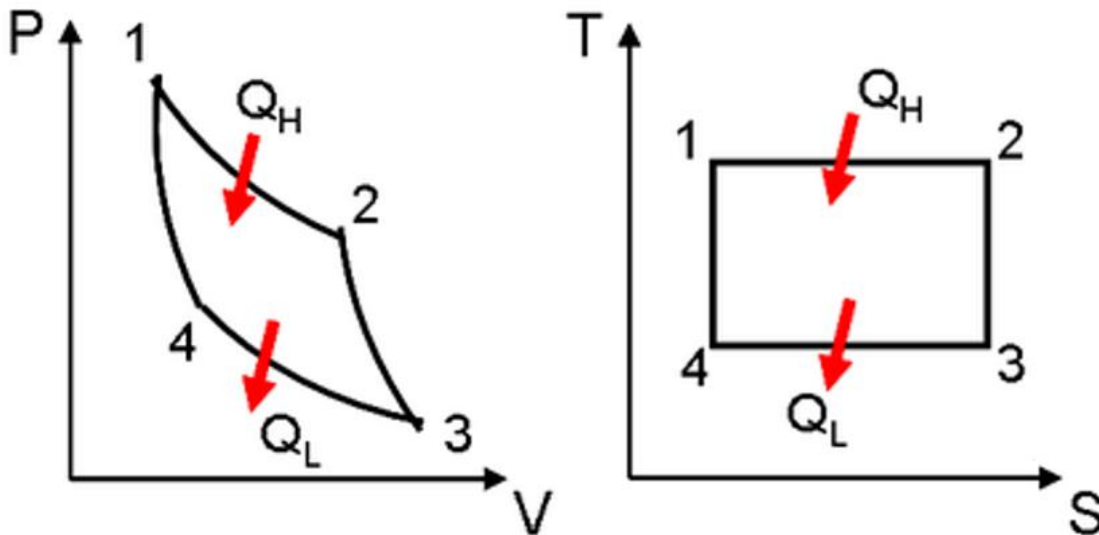
p-V and T-S diagrams of Carnot cycle

(3) Entropy and the 2nd law of thermodynamics

We have defined a new quantity, S, the entropy, which can be used to describe the state of the system, along with p, T, V, U, and n.

What does entropy have to do with the second law?

In an idealized, reversible process involving only equilibrium states, the total entropy change of the system and its environment is zero.

$$dQ_{syst} = -dQ_{env}, \quad dS_{syst} = \frac{dQ_{syst}}{T}, \quad dS_{env} = \frac{dQ_{env}}{T}$$

$$\Longrightarrow \quad dS_{syst} + dS_{env} = 0 \quad \text{or} \quad \Delta S_{syst} + \Delta S_{env} = 0$$

EXAMPLE 18–6 **Entropy change in melting.** A 1.00-kg piece of ice at 0°C melts very slowly to water at 0°C. Assume the ice is in contact with a heat reservoir whose temperature is only infinitesimally greater than 0°C. Determine the entropy change of (a) the ice cube and (b) the heat reservoir.

SOLUTION (a) The process is carried out at a constant temperature $T = 273$ K and is done reversibly, so we can use Eq. 18–12:

$$\Delta S = S_b - S_a = \int_a^b dS = \int_a^b \frac{dQ}{T}, \quad (18\text{–}12)$$

$$\Delta S_{ice} = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{Q}{T}.$$

Since the heat needed to melt the ice is $Q = mL$, where the heat of fusion $L = 79.7$ kcal/kg $= 3.33 \times 10^5$ J/kg, we have

$$\Delta S_{ice} = \frac{mL}{T} = \frac{(1.00 \text{ kg})(79.7 \text{ kcal/kg})}{273 \text{ K}} = 0.292 \text{ kcal/K},$$

or 1220 J/K.
(b) Heat $Q = mL$ is *removed* from the heat reservoir, so (since $T = 273$ K and is constant)

$$\Delta S_{res} = -\frac{Q}{T} = -0.292 \text{ kcal/K}.$$

Note that the *total* entropy change, $\Delta S_{ice} + \Delta S_{res}$, is zero.

Latent heat (相变潜热) **is energy released or absorbed, by a thermodynamic system, during a constant-temperature process.**

$$Q = mL \qquad L \text{ is the specific latent heat}$$

EXAMPLE 18–9 **Heat conduction.** A red-hot 2.0-kg piece of iron at temperature $T_1 = 880$ K is thrown into a huge lake whose temperature is $T_2 = 280$ K. Assume the lake is so large that its temperature rise is insignificant. Determine the change in entropy (a) of the iron and (b) of the surrounding environment (the lake).

SOLUTION (a) The process is irreversible, but the same entropy change will occur for a reversible process, and we use the concept of specific heat, Eq. 17–2. We assume the specific heat of the iron is constant at $c = 0.11$ kcal/kg·K. Then $dQ = mc\, dT$ and in a quasistatic reversible process

$$\Delta S_{iron} = \int \frac{dQ}{T} = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1} = -mc \ln \frac{T_1}{T_2}.$$

$$\boxed{Q = mc\, \Delta T, \quad (17\text{–}2)}$$

Putting in numbers, we find

$$\Delta S_{iron} = -(2.0 \text{ kg})(0.11 \text{ kcal/kg·K}) \ln \frac{880 \text{ K}}{280 \text{ K}} = -0.25 \text{ kcal/K}$$

or $\Delta S = -1100$ J/K.

(b) The initial and final temperatures of the lake are the same, $T = 280$ K. The lake receives from the iron an amount of heat

$$Q = mc(T_2 - T_1) = (2.0 \text{ kg})(0.11 \text{ kcal/kg·K})(880 \text{ K} - 280 \text{ K}) = 130 \text{ kcal}.$$

Strictly speaking, this is an irreversible process (the lake heats up locally before equilibrium is reached), but is equivalent to a reversible isothermal transfer of heat $Q = 130$ kcal at $T = 280$ K. Hence

$$\Delta S_{env} = \frac{130 \text{ kcal}}{280 \text{ K}} = 0.46 \text{ kcal/K}$$

or 1900 J/K. Thus, although the entropy of the iron actually decreases, the *total* change in entropy of iron plus environment is positive: 0.46 kcal/K − 0.25 kcal/K = +0.21 kcal/K, or 800 J/K.

$$\Delta S_{iron} + \Delta S_{env} = 800 \text{ J/K} > 0$$

Consider the **adiabatic free expansion** of 1 mole of ideal gas from volume V_1 to V_2, where $V_2 = 2V_1$. Calculate the change in entropy (a) of the gas and (b) of the surrounding environment.

Solution:

(a) **The process is irreversible, so we cannot apply**

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dQ}{T}$$

to this process. Instead we must think of a reversible process.

Isothermal expansion!

For an isothermal process

$$\Delta S_{\text{gas}} = nR \ln \frac{V_2}{V_1} = nR \ln 2 = 5.76 \text{ J/K}$$

(b) Since no heat is transferred to the environment, there is no change of the state of the environment due to this process.

Hence $\Delta S_{\text{env}} = 0$

Note that the total change in entropy is greater than zero.

$$\Delta S_{\text{gas}} + \Delta S_{\text{env}} > 0$$

In each of these examples, the entropy of our **system plus** that of the **environment** either **stayed constant or increased**.

We can thus make the general statement of the **second law of thermodynamics** as follows:

If a process occurs in an **isolated** system, the entropy of the system **increases** for **irreversible** processes and remains **constant** for **reversible** processes. It **never decreases**.

$$\Delta S \geq 0 \quad \text{(isolated system)}$$

在孤立系统中发生的任何不可逆过程, 都导致了整个系统熵的增加, 系统的总熵只有在可逆过程中才是不变的

Since all real processes are irreversible,

The total entropy of any system plus that of its environment increases as a result of any natural process.

$$\Delta S = \Delta S_{syst} + \Delta S_{env} > 0 \quad \text{(natural process)}$$

In general, we can say that irreversible processes generate entropy.

Although the entropy of one part of the universe may decrease in any process, the entropy of some other part of the universe always increases by a greater amount, so the total entropy always increases.

Heat Death (热寂)

Lord Kelvin originated the idea of heat death in 1852. The **heat death** of the universe is a **conjecture on the ultimate fate of the universe**, which suggests the universe would evolve to a state of no thermodynamic free energy and would therefore be unable to sustain processes that increase entropy. In the language of physics, this is when **the universe reaches thermodynamic equilibrium (maximum entropy)**.
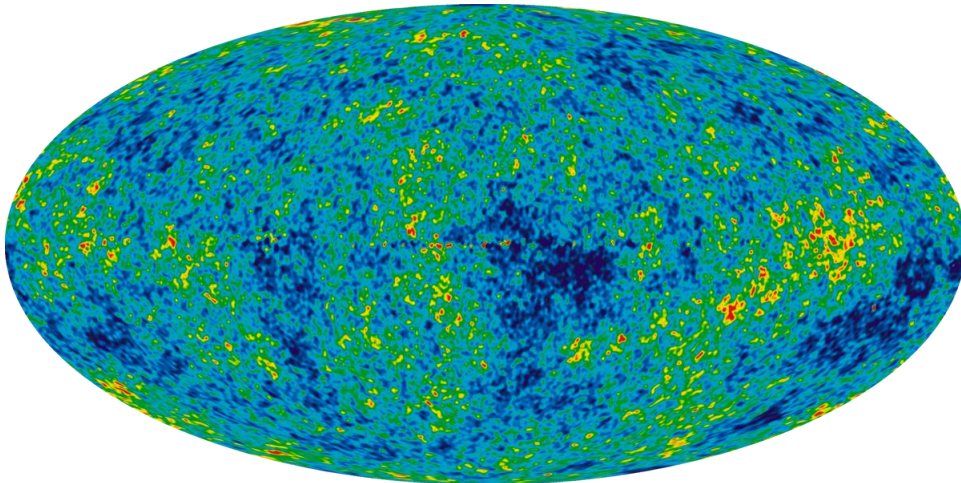
Cosmic Microwave Background

(4) A Statistical View of Entropy (P446)

Unlike **energy**, entropy is not something that belongs to each **individual particle** or **pair of particles** in the system. **Entropy is a measure of the disorder** of the system as a whole.

Two concepts for calculating entropy microscopically:

The **microscopic state** of a system would be specified when the **position** and **velocity** of **every particle** (or molecule) is given.

The **macroscopic state** of a system is specified by giving the macroscopic properties of the **system** — p, T, V, n and so on.

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One heads, three tails	
Four tails	

Specifying the number of heads and the number of tails is the macroscopic state of the system. Specifying each coin as being a head or a tail is the microscopic state of the system.

For instance, with $N = 4$ coins there are 6 possible states in which half are heads and half are tails. The number of microscopic states grows rapidly with increasing N. For $N = 100$ there are 2^{100} microscopic states in total, of which 90% is between 45 and 55 heads.

Now instead of N coins, consider a mole of an ideal gas. The **macroscopic state** of this gas is given by p, V, and T; a description of the **microscopic state** involves stating the **position** and **velocity** for each molecule in the gas.

If the gas undergoes a **free expansion** into a greater volume, the range of **possible positions increases**, as does the **number of possible microscopic states**. The system becomes **more disordered**, and the **entropy increases**.

Boltzmann showed that the entropy of a macroscopic state is

$$S = k ln \Omega$$

where Ω is the number of microscopic states.

We can draw the following general conclusion:

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**.

Explanations:

(1) For an isolated system, an equilibrium state is the one with the greatest number of microscopic states Ω.

微观状态数最多的宏观状态就是系统在一定宏观条件下的平衡态，平衡态是对应熵最大的状态。

That's why an isolated system always shifts from nonequilibrium to equilibrium state.

(2) A natural process, irreversible process, tends to move toward a state of greater disorder (or entropy).

If the system is initially not in the equilibrium. The system changes in the direction of Ω increasing, and finally it reaches its largest value, then the system reaches the macroscopic equilibrium state. This is the microscopic explanation of a real natural process.

(3) It is a statistical rule, so it only suits for system involving a great amount of molecules .

Example:

Consider the **adiabatic free expansion** of 1 mole of ideal gas from volume V_1 to V_2, where $V_2 = 2V_1$. Calculate the change in entropy of the gas by using the equation of $S = kln\Omega$.

Solution:

Since the number of molecules is N_A, the total number of microscopic states increases by a factor of 2^{N_A} when the volume doubles. That is

$$\frac{\Omega_2}{\Omega_1} = 2^{N_A}$$

$$\Delta S = S_2 - S_1 = kln\Omega_2 - kln\Omega_1 = kln\frac{\Omega_2}{\Omega_1} = kN_A ln2$$

$$= Rln2 = 5.76 \text{ J/K}$$

The problems of chapter 17:

17, 20, 21, 22, 25, 27, 28, 29, 33, 35, 39, 40, 42, 43, 44, 47, 48

The problems of chapter 18:

1, 6, 8, 11, 17, 21, 22, 25, 27, 42, 43, 48

48. a = 2.08 mJ/mol·K^2