



The second law of thermodynamics

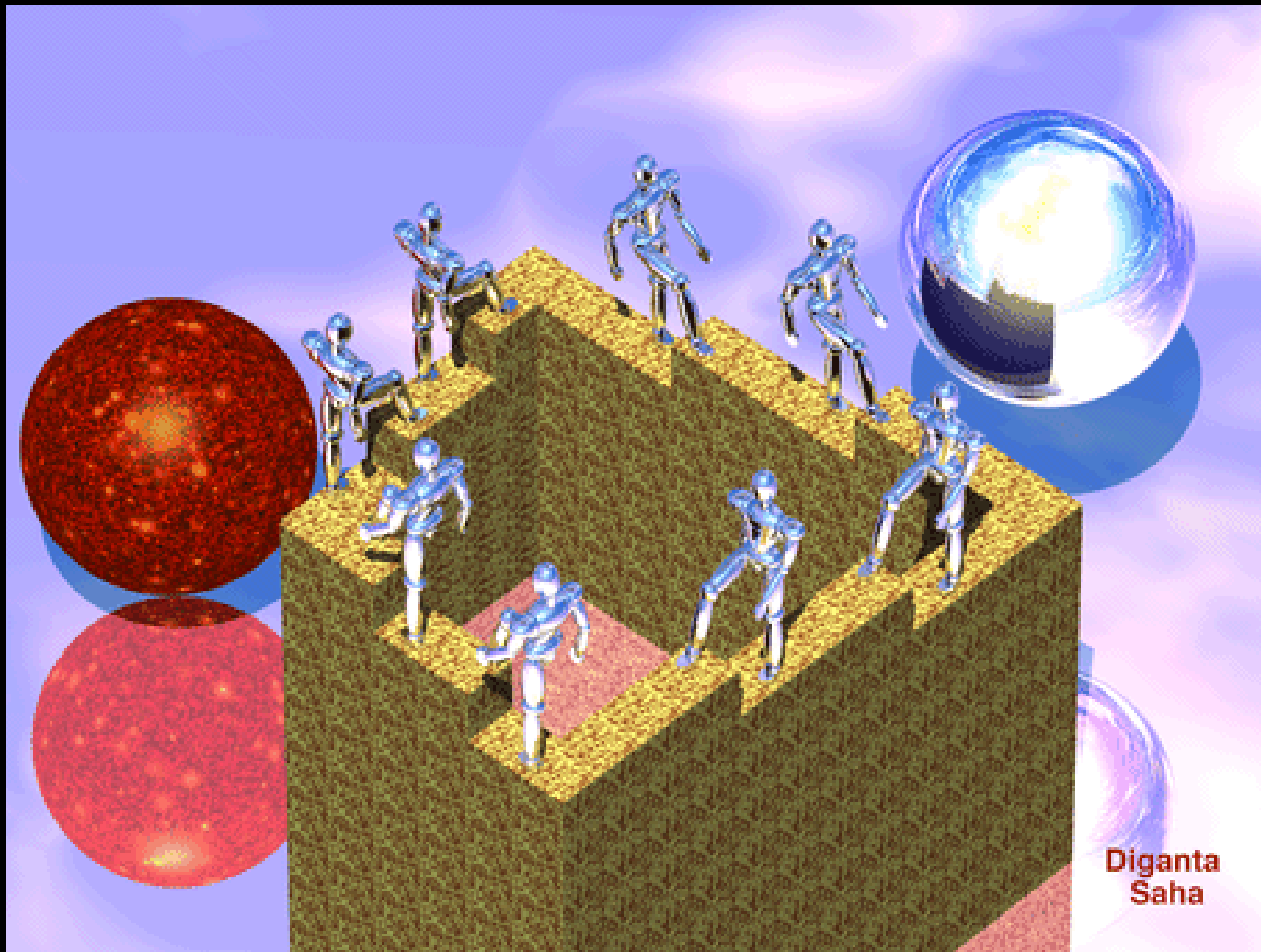
Agenda Today

- The efficiency of heat machine
- The second law of thermodynamics
- The concept of entropy

Reversible process and irreversible process (可逆过程和不可逆过程)

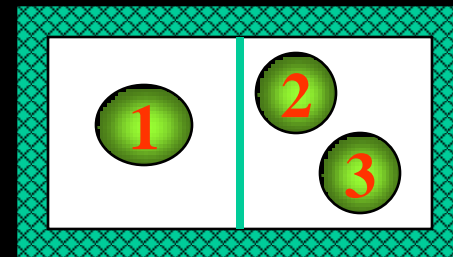
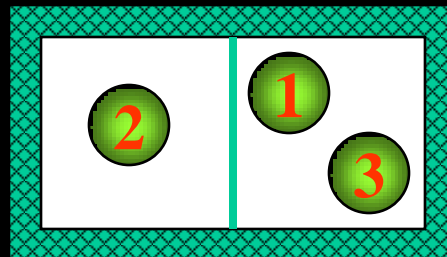
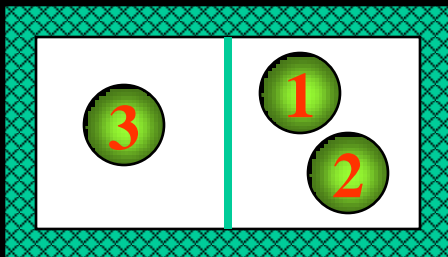
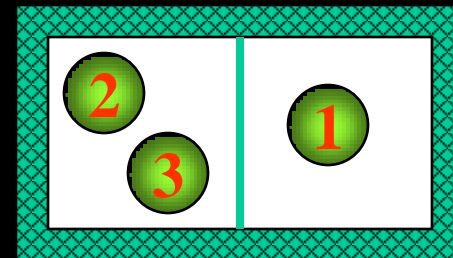
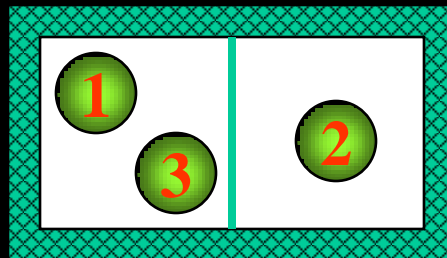
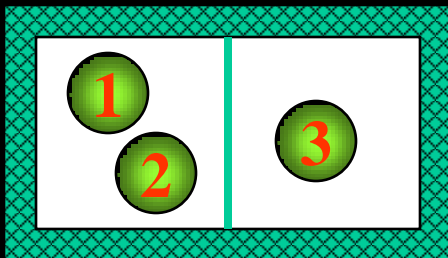
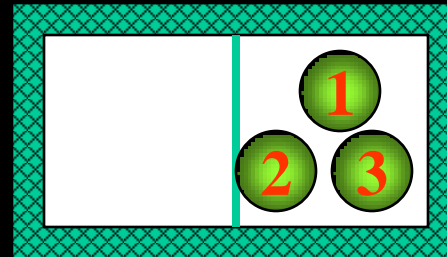
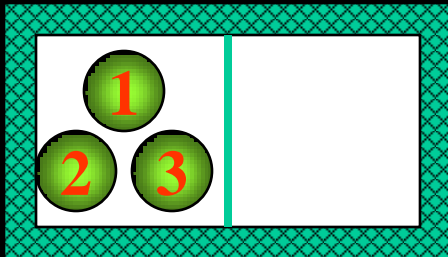
If a process is reversible:

1. No mechanical energy can be lost due to friction, or other dissipate forces that produce heat.
2. there is no heat conduction due to the temperature difference
3. the process is a quasi-static one.



Is perpetual motion machine possible?

Statistical interpretation of entropy



Boltzmann's definition for entropy

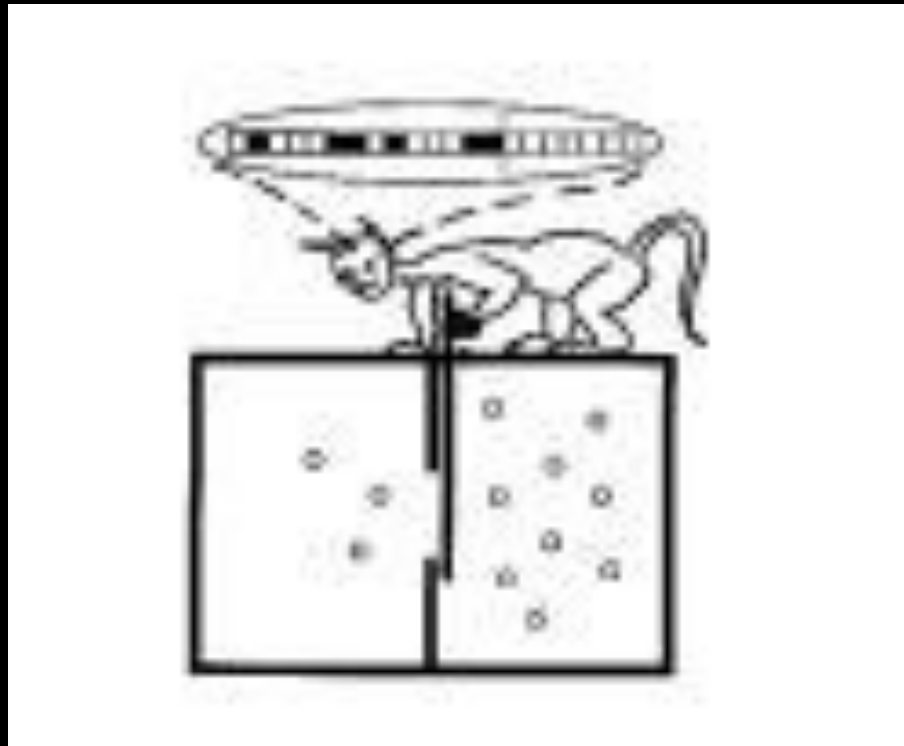
$$S = k \ln \Omega$$

Where k is Boltzmann's constant and Ω is the number of microstates corresponding to the macrostate.

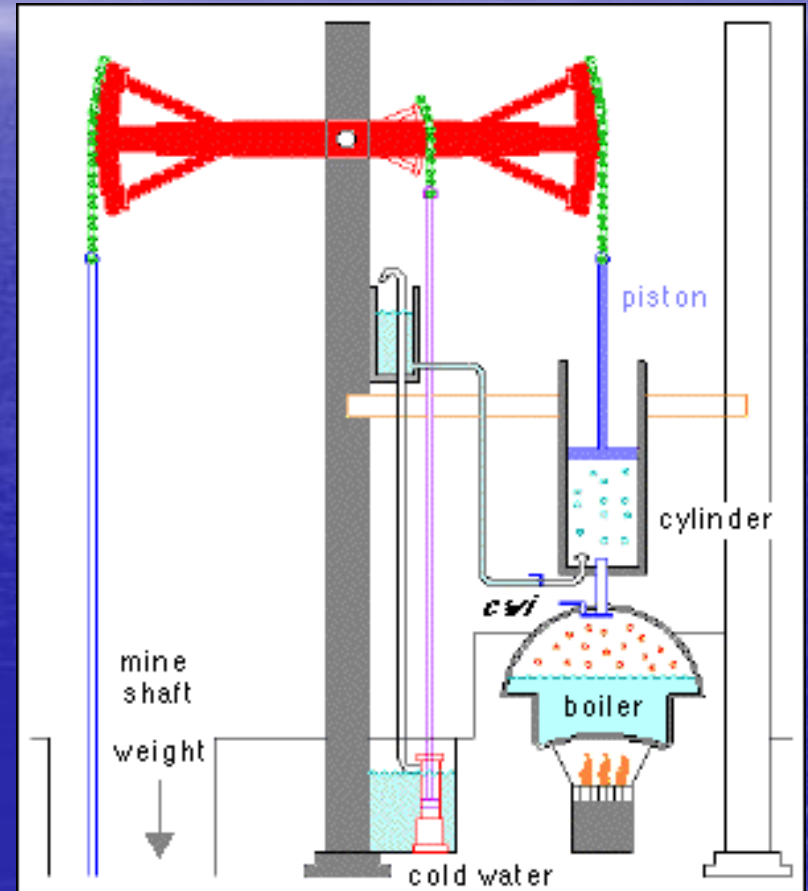
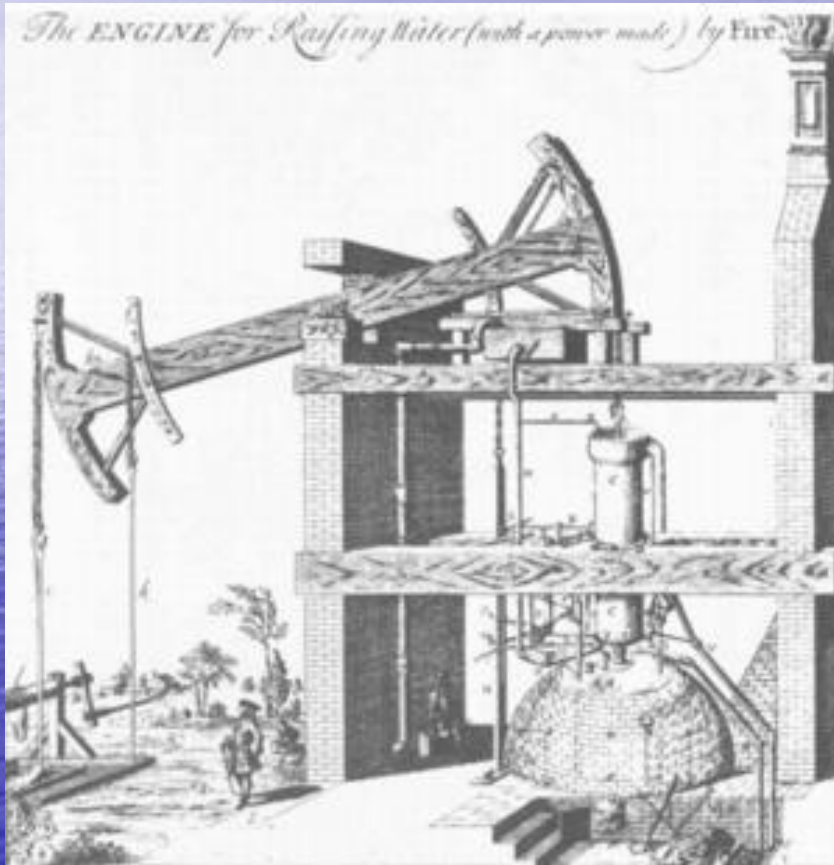


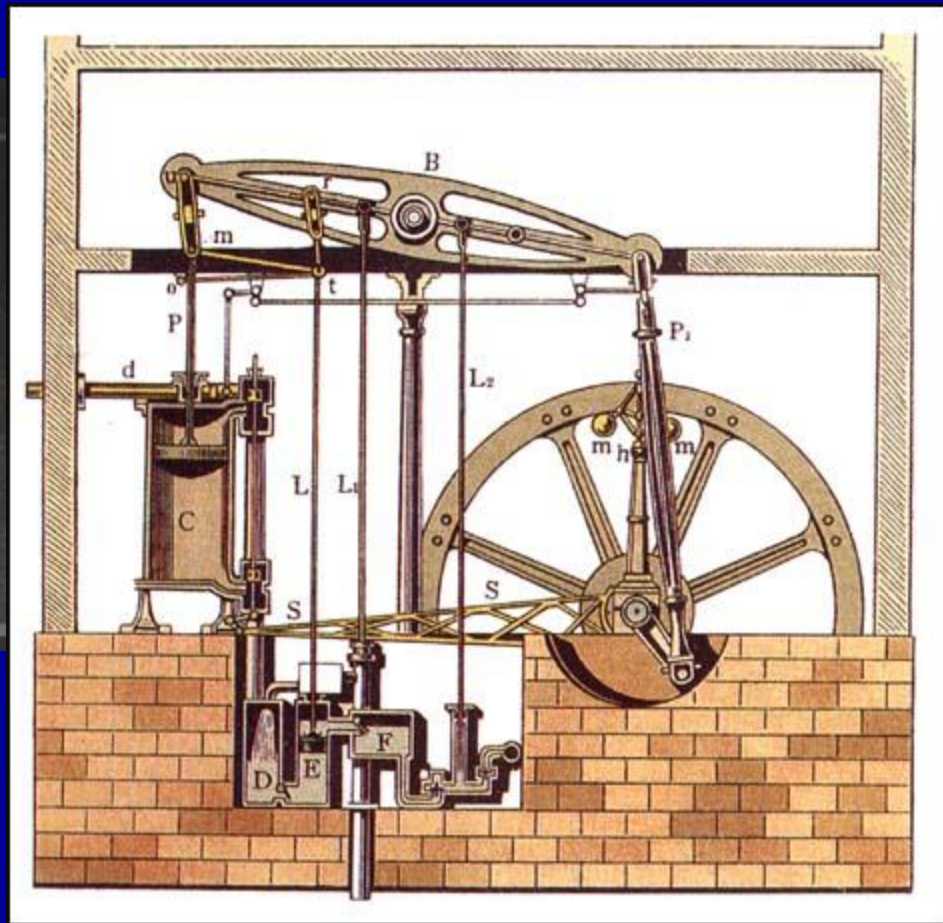
Natural process tend to move toward a state of greater disorder

Maxwell's demon



The invention of Heat machine





A useful engine exhibits two important features:

1 an engine must work in cycles

2 a cyclic engine must include more than one thermal reservoir

The efficiency of heat machine(热机效率)

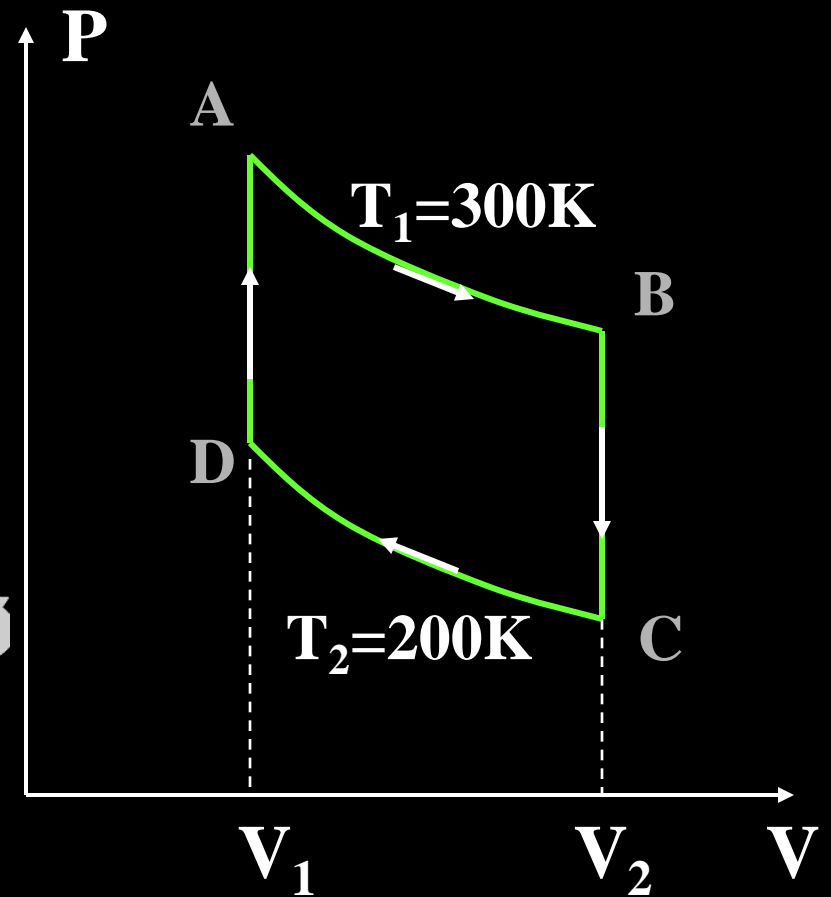
The ratio of the work done to the total positive heat flow provided by the thermal reservoir

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Some oxygen with mass 3.2×10^{-2} kg goes a cycle ABCD. A \rightarrow B, C \rightarrow D are isothermal processes, $T_1 = 300\text{K}$, $T_2 = 200\text{K}$, $V_2 = 2V_1$. Find the efficiency.

$$Q_{AB} = W_{AB} = \frac{m}{M} R T_1 \ln \frac{V_2}{V_1}$$

$$Q_{BC} = \Delta E_{BC} = \frac{m}{M} (5/2) R (T_2 - T_1)$$



The carnot cycle (卡诺循环)

the carnot cycle is consisted two isothermal processes and two adiabatic processes.

For AB:

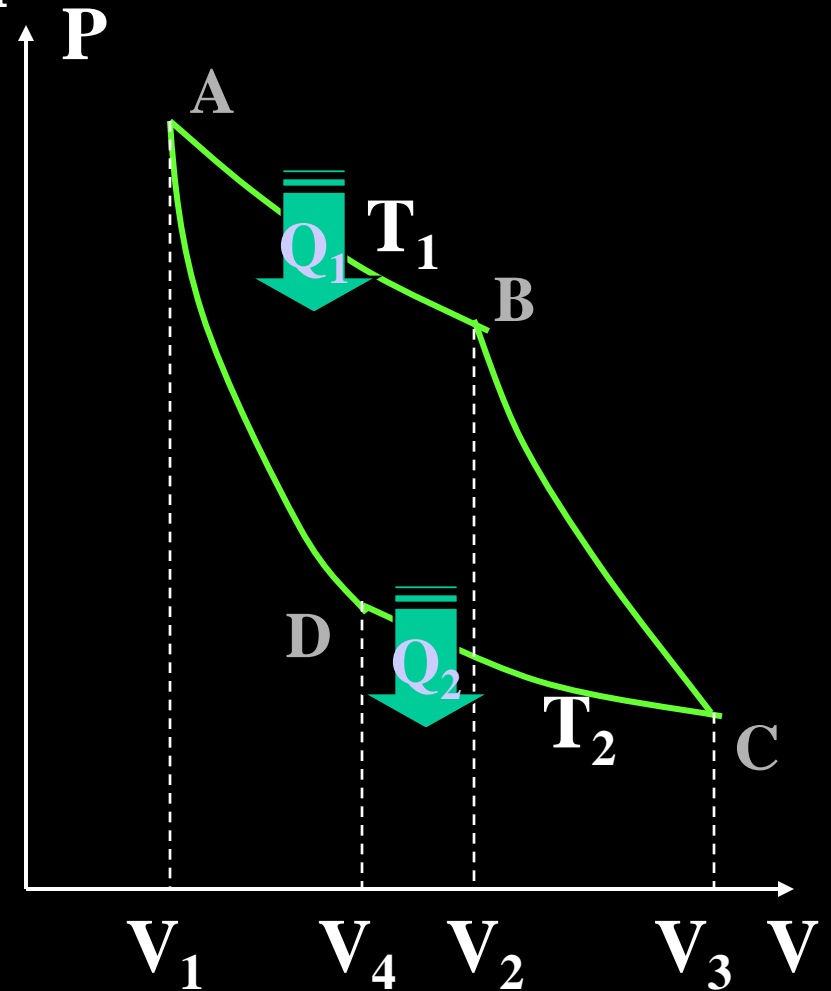
$$Q_1 = \frac{m}{M} RT_1 \ln \frac{V_2}{V_1}$$

CD:

$$Q_2 = \frac{m}{M} RT_2 \ln \frac{V_3}{V_4}$$

BC, DA:

$$Q = 0$$



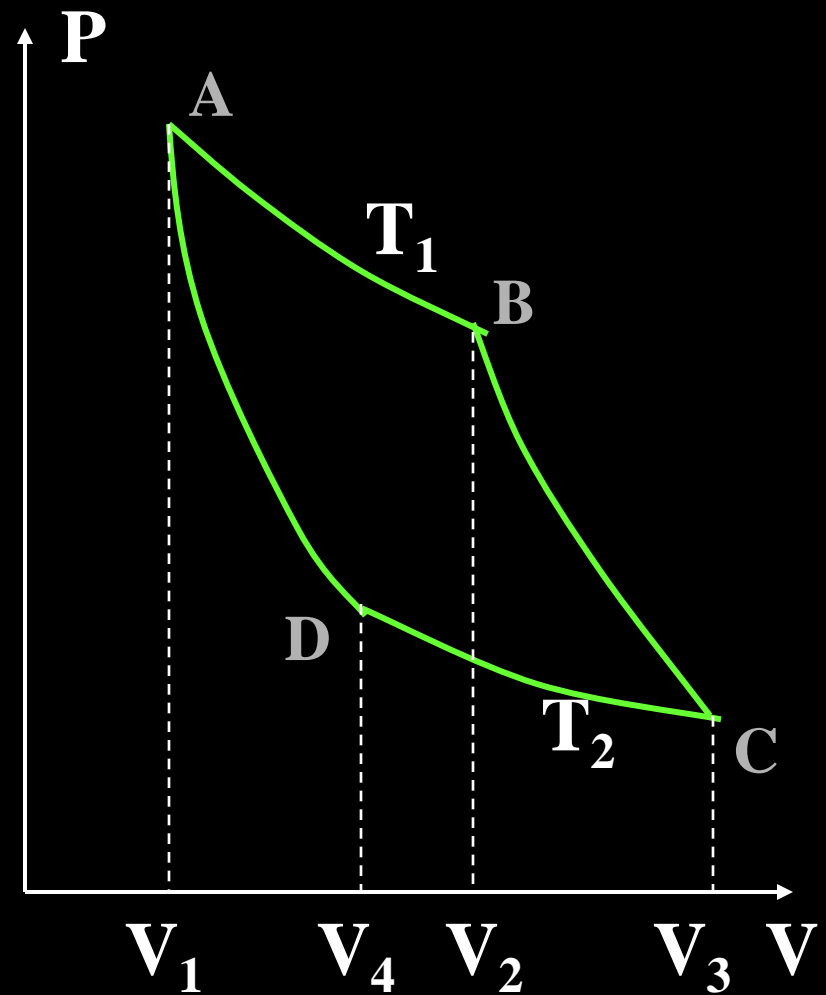
$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{T_2 \ln V_3/V_4}{T_1 \ln V_2/V_1}$$

$$\therefore T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\therefore \frac{V_2}{V_1} = \frac{V_3}{V_4}$$



The efficiency of carnot cycle:

$$\eta = 1 - \frac{T_2}{T_1}$$

All carnot cycles working between the same two temperature has the efficiency

The carnot engine is the most efficient machine working between two heat reservoir

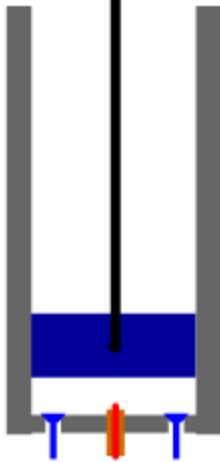
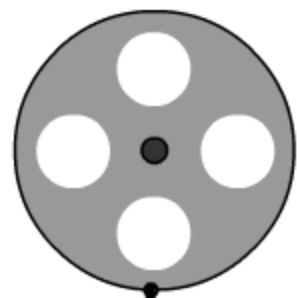
Heat pump and refrigerator

Coefficient of performance(致冷系数)

$$\varepsilon = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

For carnot cycle

$$w = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$



起始位置



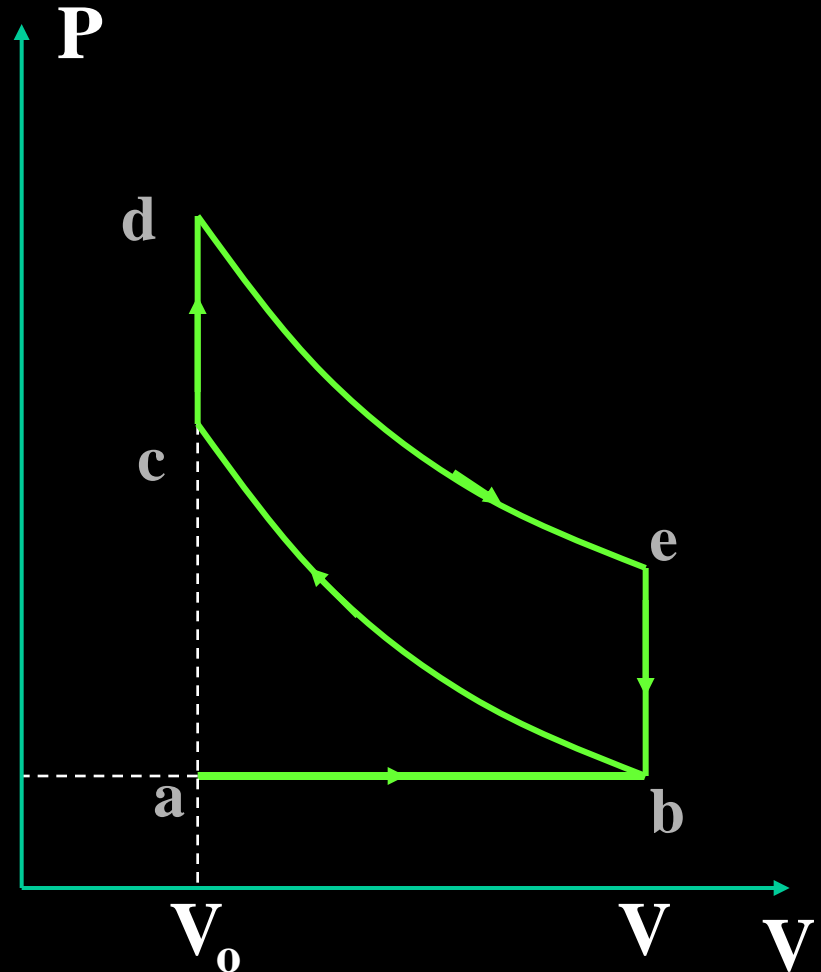
Find the efficiency of Otto's cycle

solution:

$$Q_1 = \frac{m}{M} C_V (T_d - T_c) \quad \text{吸热}$$

$$Q_2 = \frac{m}{M} C_V (T_e - T_b) \quad \text{放热}$$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_e - T_b}{T_d - T_c}$$



$$T_e V^{\gamma-1} = T_d V_o^{\gamma-1}$$

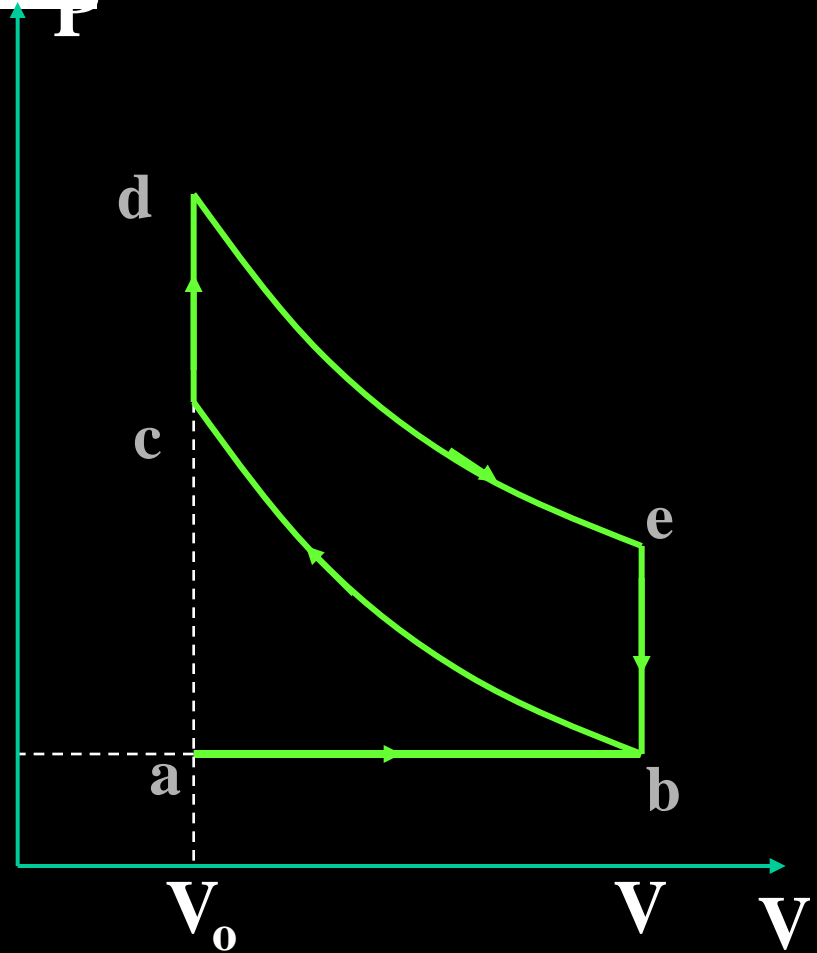
$$T_b V^{\gamma-1} = T_c V_o^{\gamma-1}$$

$$(T_e - T_b) V^{\gamma-1} = (T_d - T_c) V_o^{\gamma-1}$$

$$\frac{T_e - T_b}{T_d - T_c} = \left(\frac{V_o}{V} \right)^{\gamma-1}$$

$$\eta = 1 - \frac{1}{(V/V_o)^{\gamma-1}}$$

$$= 1 - \frac{1}{r^{\gamma-1}}$$



All natural processes are irreversible process

Carnot cycle is reversible cycle

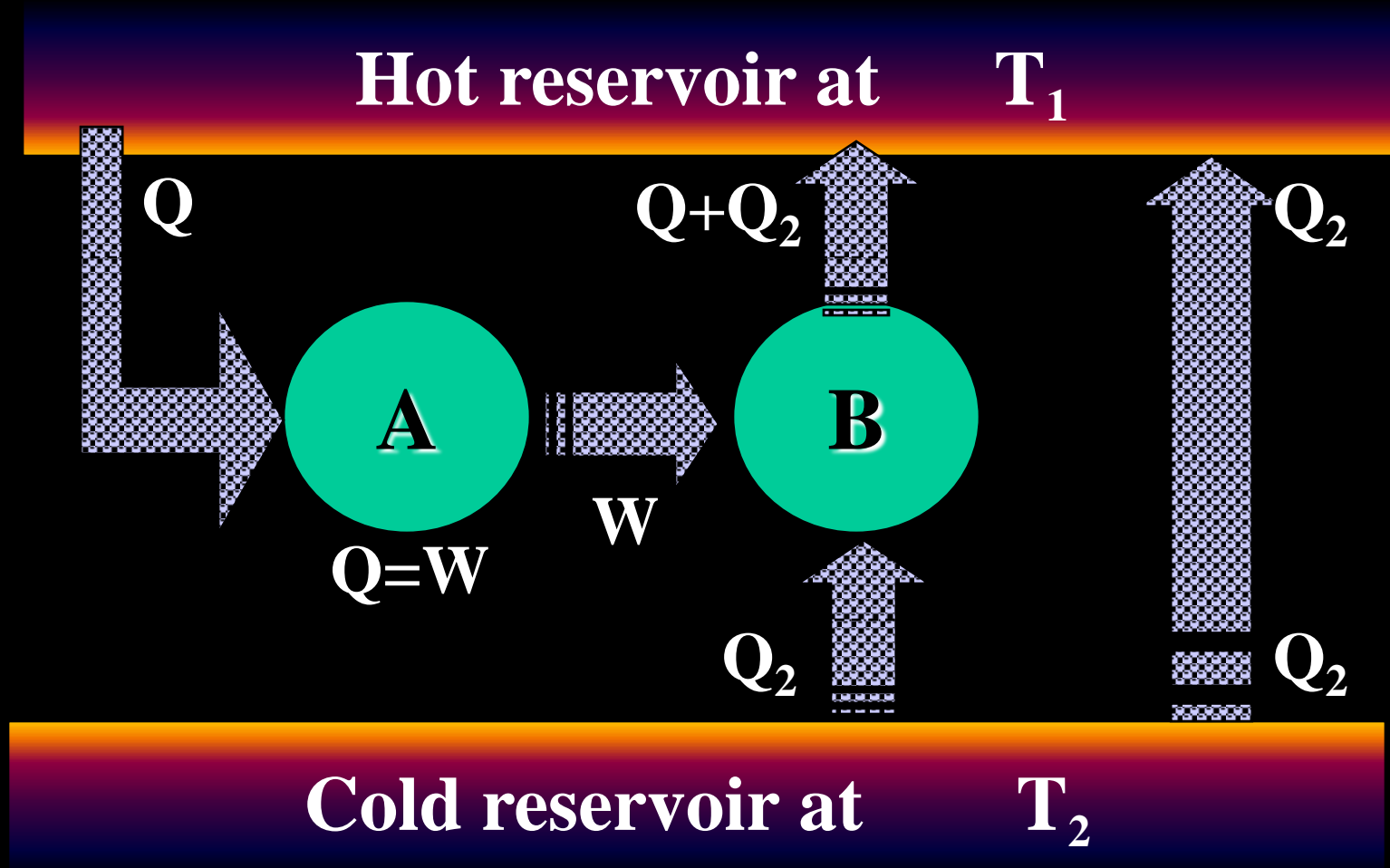
The Clausius statement for the second law of thermodynamics(热力学第二定律的克劳休斯叙述)

It is impossible for heat to flow from a cold body to a hot body automatically

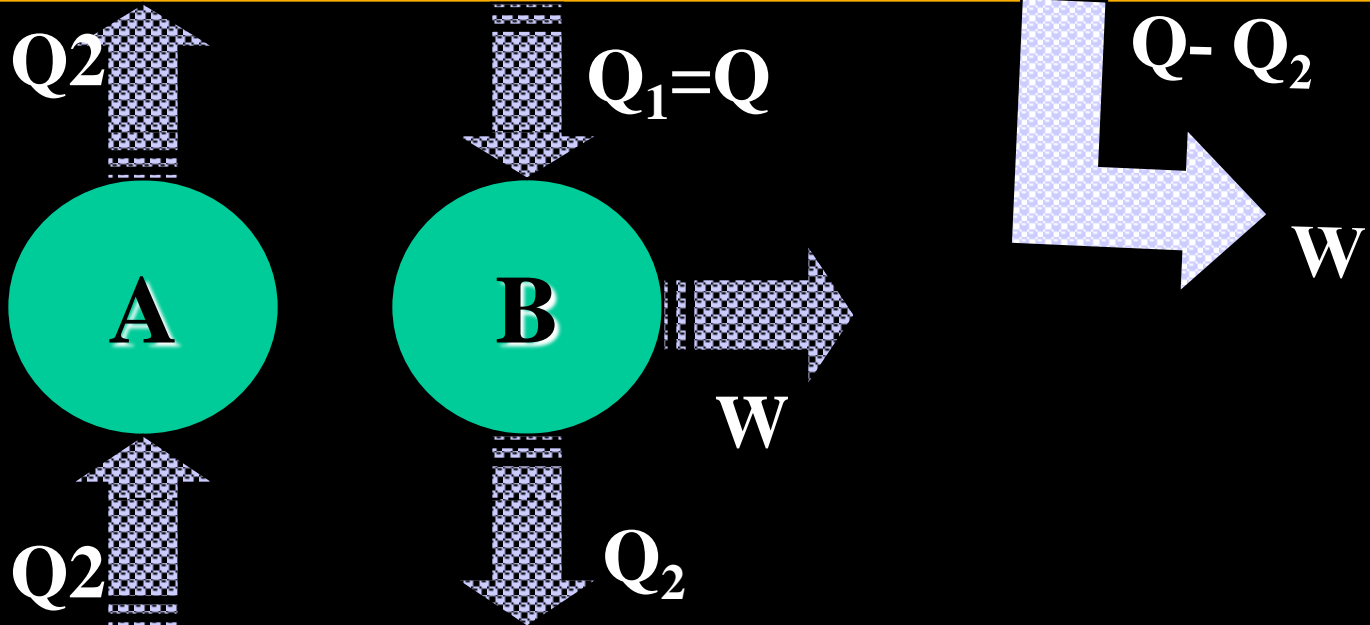
The Kelvin-Planck statement of the second law of thermodynamics(热力学第二定律的开尔文叙述)

It is impossible for a heat engine working in a cycle to produce no other effect than that of extracting heat from a reservoir and performing an equivalent amount of work.

Equivalence of the two statements



Hot reservoir T_1



Cold reservoir T_2

Carnot' s law (卡诺定律)

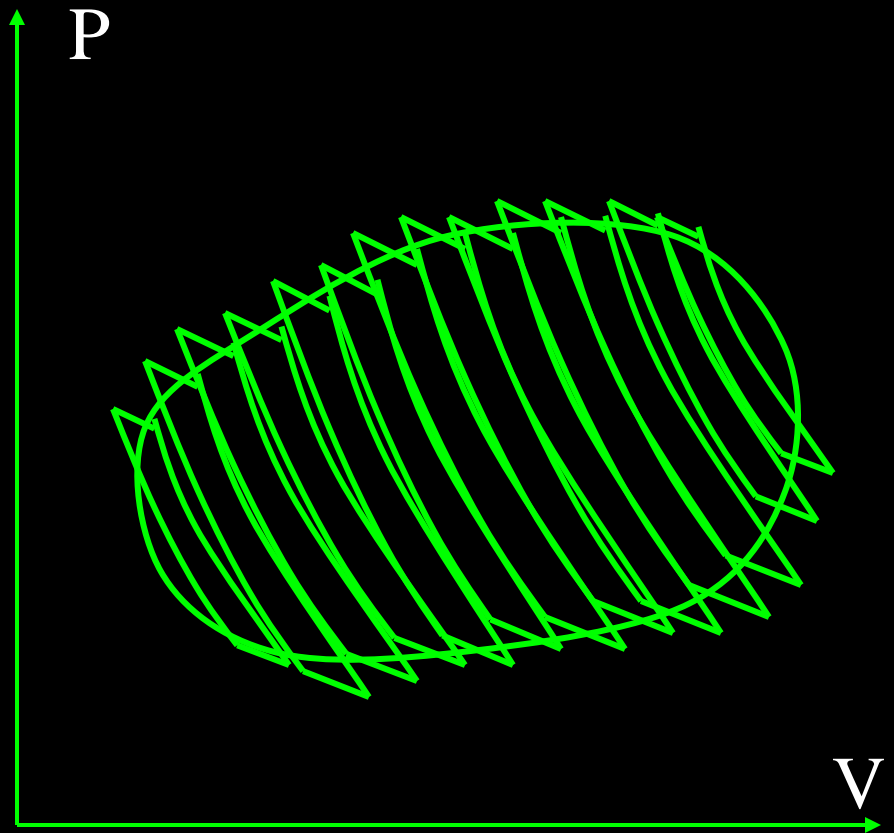
All the reversible engines have the same efficiency, which is the efficiency of Carnot cycle.

All the irreversible engines have efficiency less than that of Carnot cycle.

Entropy (熵)

Any reversible cycle can be substituted by a series of carnot cycles

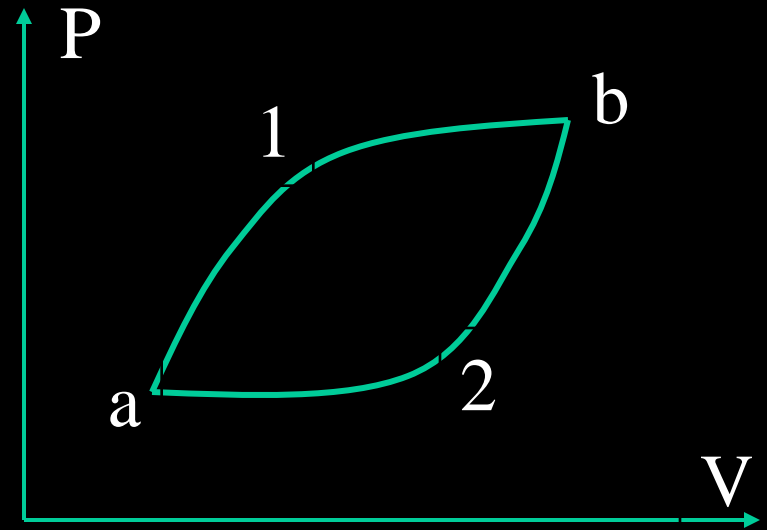
$$\oint \frac{dQ}{T} = 0$$



$$\oint \frac{dQ}{T} = \int_{a1b} \frac{dQ}{T} + \int_{b2a} \frac{dQ}{T} = 0$$

$$\int_{b2a} \frac{dQ}{T} = -\int_{a2b} \frac{dQ}{T}$$

$$\int_{a1b} \frac{dQ}{T} = \int_{a2b} \frac{dQ}{T}$$



Entropy is a state variable, the difference in entropy is independent of the path between a and b

For reversible process

$$S_2 - S_1 = \int_a^b \frac{dQ}{T}$$

The entropy of the universe do not change in reversible process

Statement of the second law of thermodynamics in general form

For irreversible process the entropy of the isolated system increases

Estimate entropy change of the universe when a red hot 2.0kg piece of iron at temperature 880 k is thrown into a lake of 280K .

Solution:

$$\Delta S_{iron} = \int \frac{dQ}{T} = mc \int_{T_1}^{T_2} \frac{dT}{T} = mc \ln \frac{T_2}{T_1} = -1100 J / K$$

$$\Delta S_{water} = \frac{\Delta Q}{T} = 1900 J / K$$

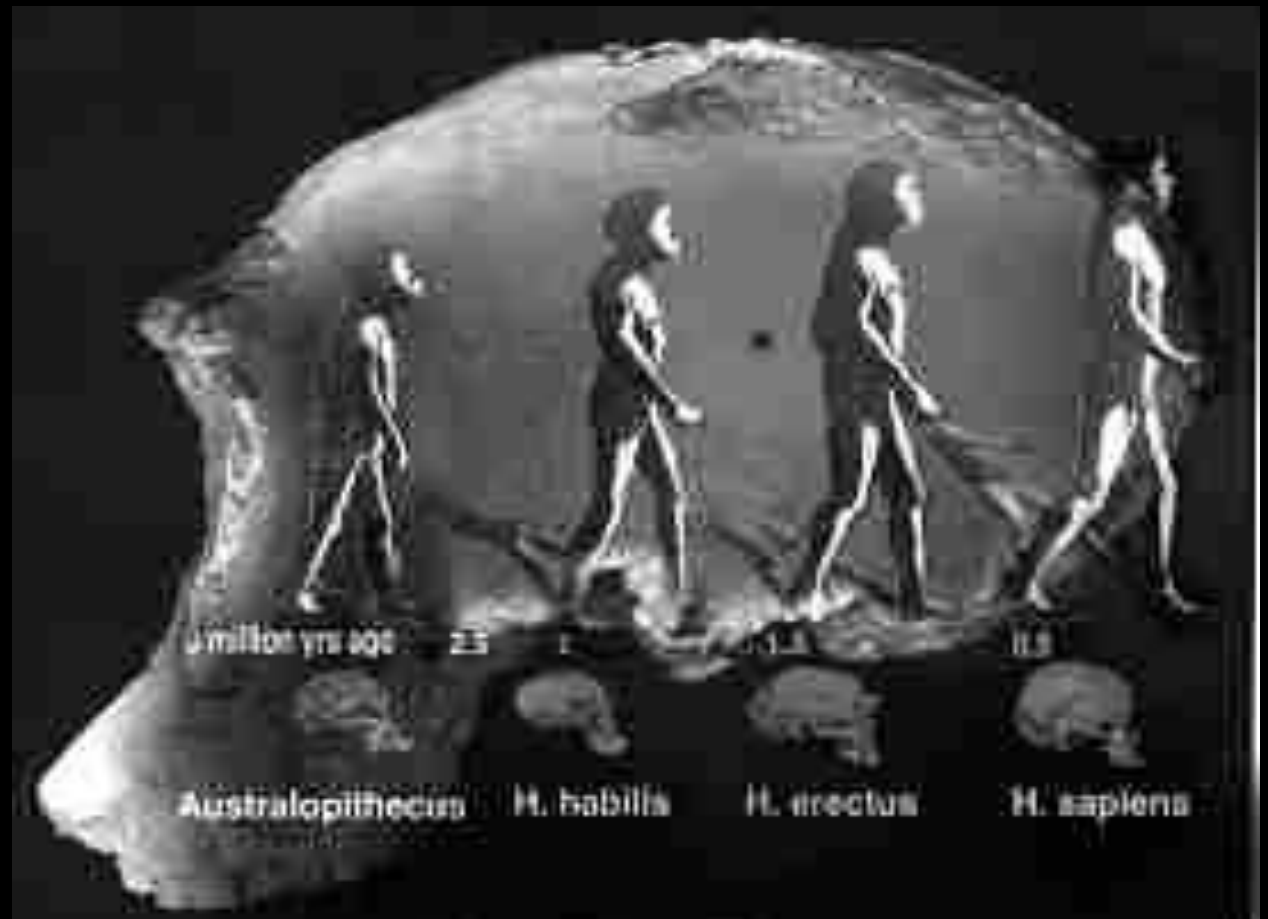
$$\Delta S = 800 J / K$$

The entropy change of ideal gas

For ideal gas from state (V_1, T_1) to (V_2, T_2) , the change in entropy is:

$$S(T_2, V_2) - S(T_1, V_1) = \frac{m}{M} C_v \ln \frac{T_2}{T_1} + \frac{m}{M} R \ln \frac{V_2}{V_1}$$

The arrow of time:



The heat death

