Thermodynamics lecture 5.

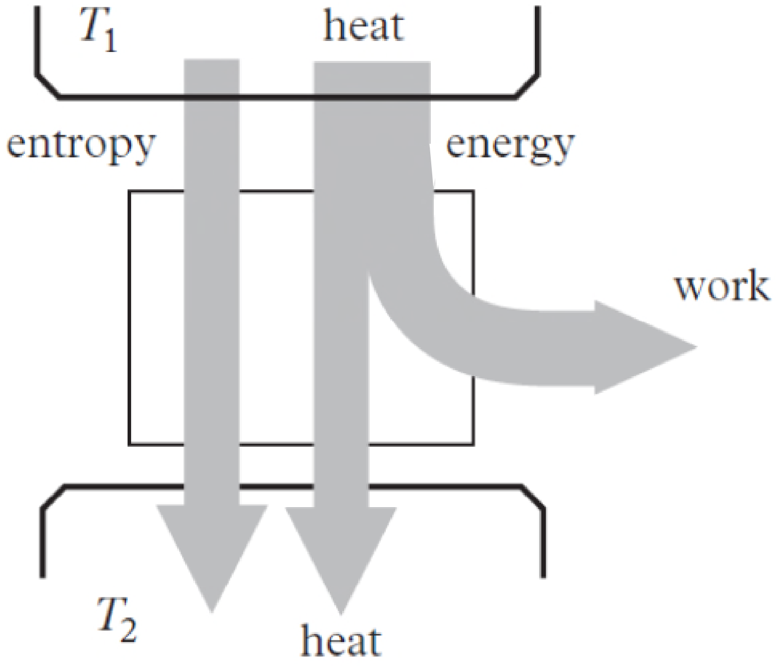
# W.A.L.T.

- How to calculate entropy changes
- Gaining familiarity and intuition about entropy
- Gibbs paradox and entropy of mixing
- Maxwell daemon and other thought-experiments
- Some practical heat engines

Heat engine:

Entropy out = entropy in

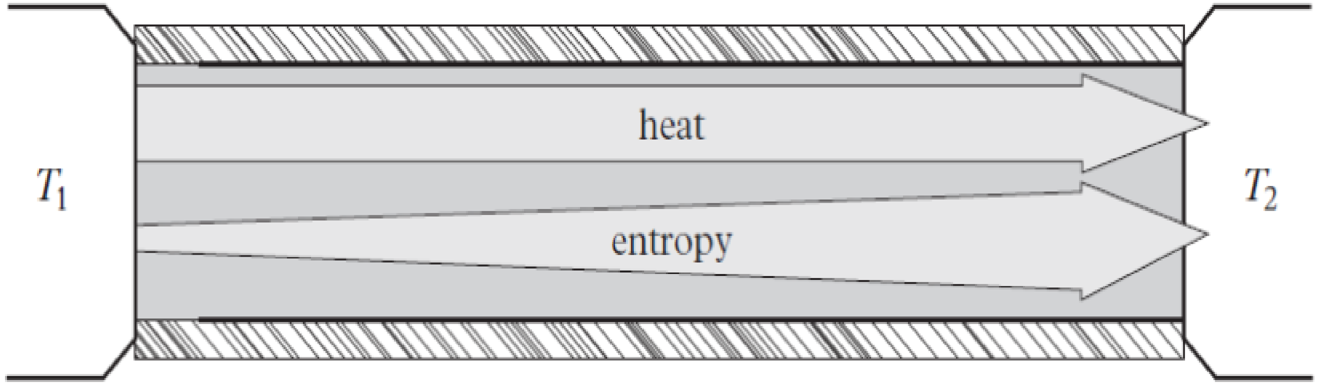
hence reversible




Heat conduction across a finite temperature difference:

(Entropy out ) > (entropy in)

hence irreversible



# But what is it?

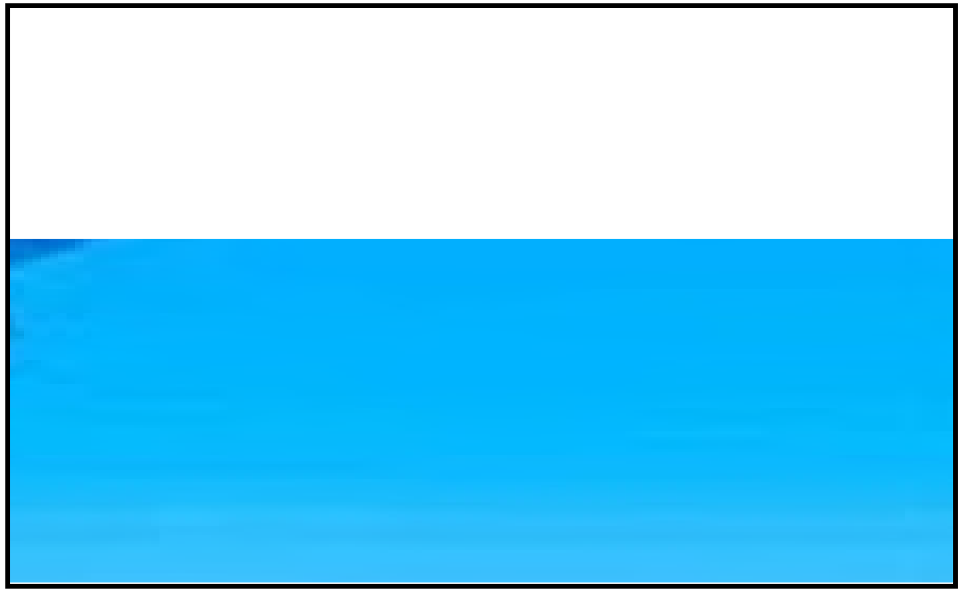
(1) Entropy is *the absence of structure.*

(2) Entropy is *freedom to explore.*

(3) Entropy increase is the *dispersal of energy.*

(4) Entropy is that which separates the future from the past.

To understand (1), consider also (2).
The ‘freedom’ here is the fact that many internal microscopic rearrangements correspond to the same macroscopic parameters (e.g. energy, volume) and only the latter are constrained by the environment.



# Entropy change in free expansion

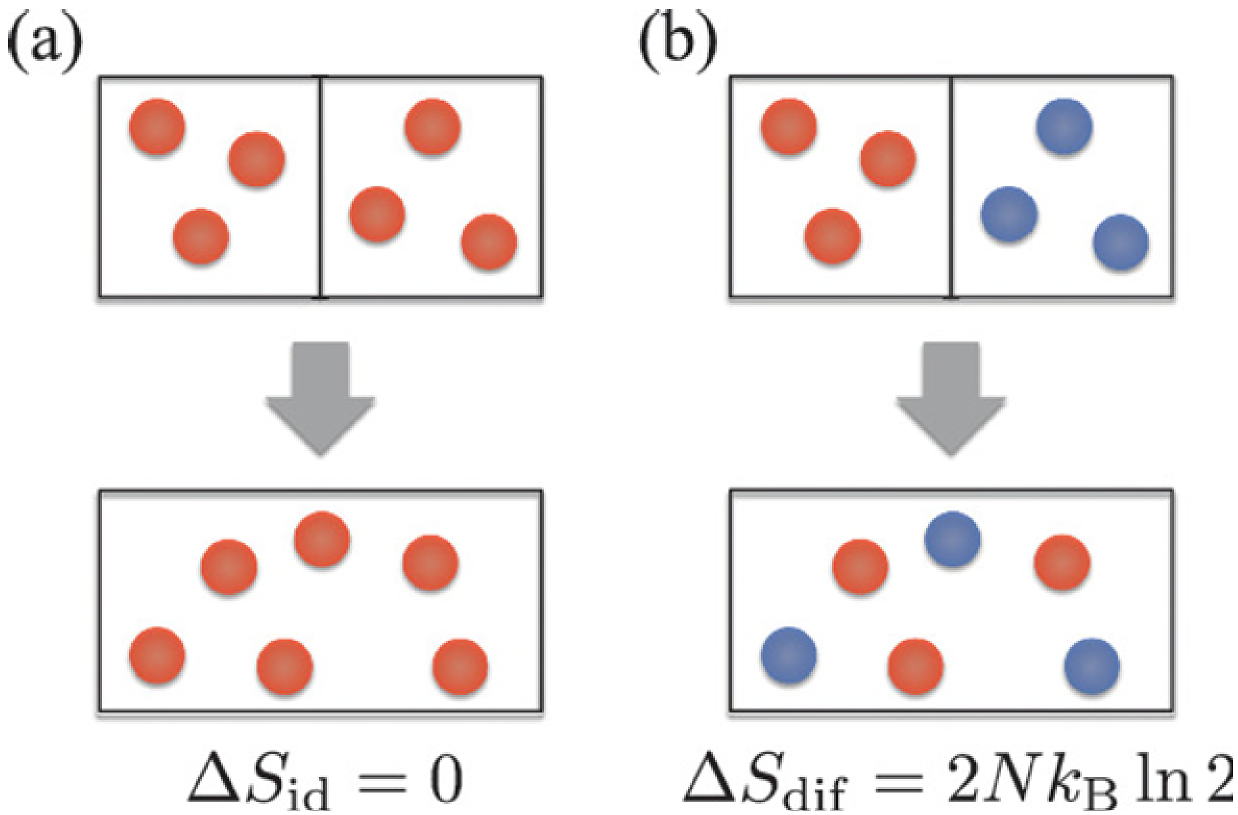
# The Hammers

*Noise of hammers once I heard,*
*Many hammers, busy hammers,*
*Beating, shaping, night and day,*
*Shaping, beating dust and clay*
*To a palace; saw it reared;*
*Saw the hammers laid away.*

*And I listened, and I heard*
*Hammers beating, night and day,*
*In the palace newly reared,*
*Beating it to dust and clay:*
*Other hammers, muffled hammers,*
*Silent hammers of decay.*

Ralph Hodgson

# Gibbs paradox

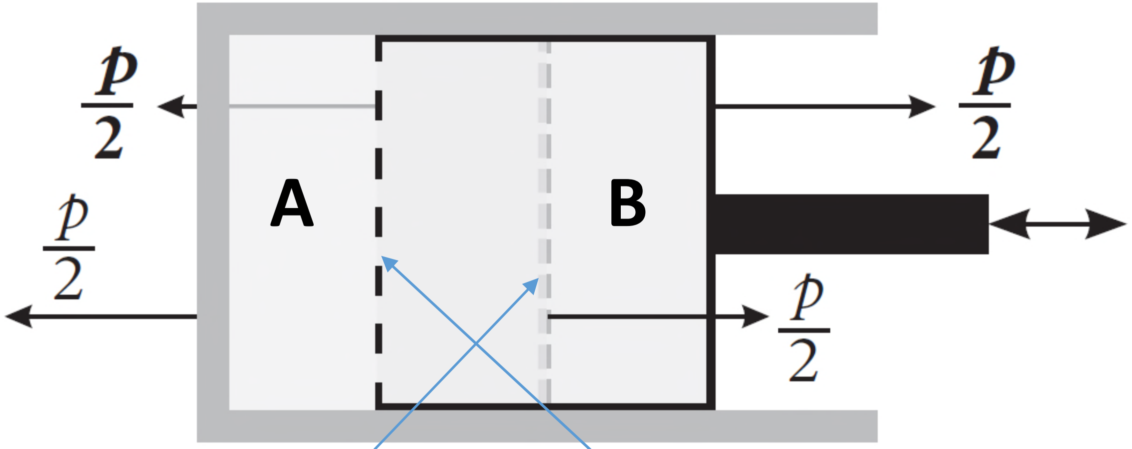



The issue is, why is the mixing in (a) not an increase in entropy?

Answer requires quantum theory! The notion of **genuine or absolute indistinguishability:**

- *All states of a system which differ only by a permutation of identical particles must be considered one and the same state.*

# Reversible mixing (i.e. without free expansion)



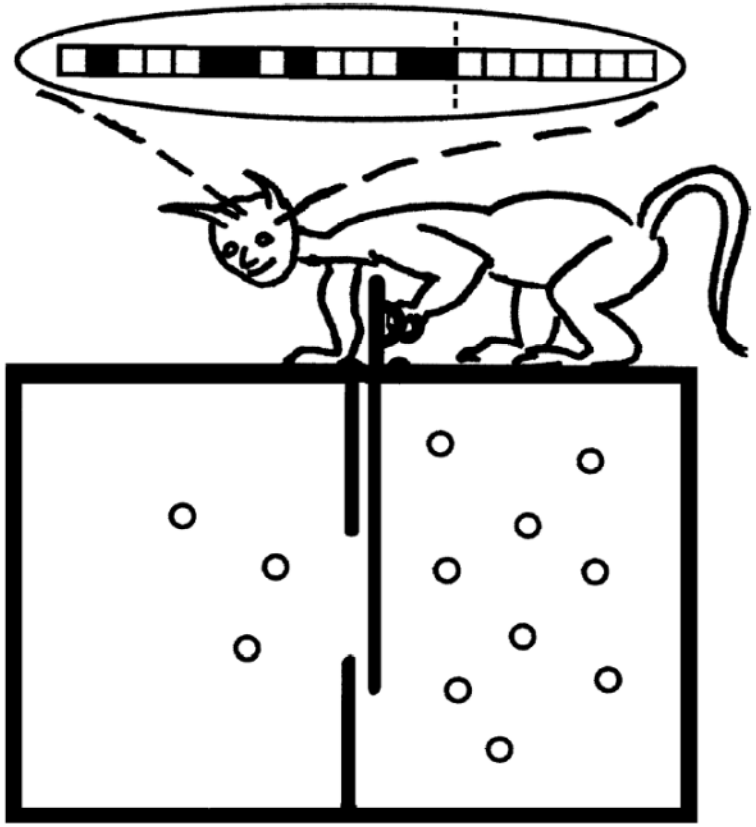

Slide in to mix;
Slide out to un-mix

*Semi-permeable membrane*

Retains gas A, lets gas B through

Retains gas B, lets gas A through

# Maxwell's daemon
# (daemon = one who enacts or mediates an interaction/process)

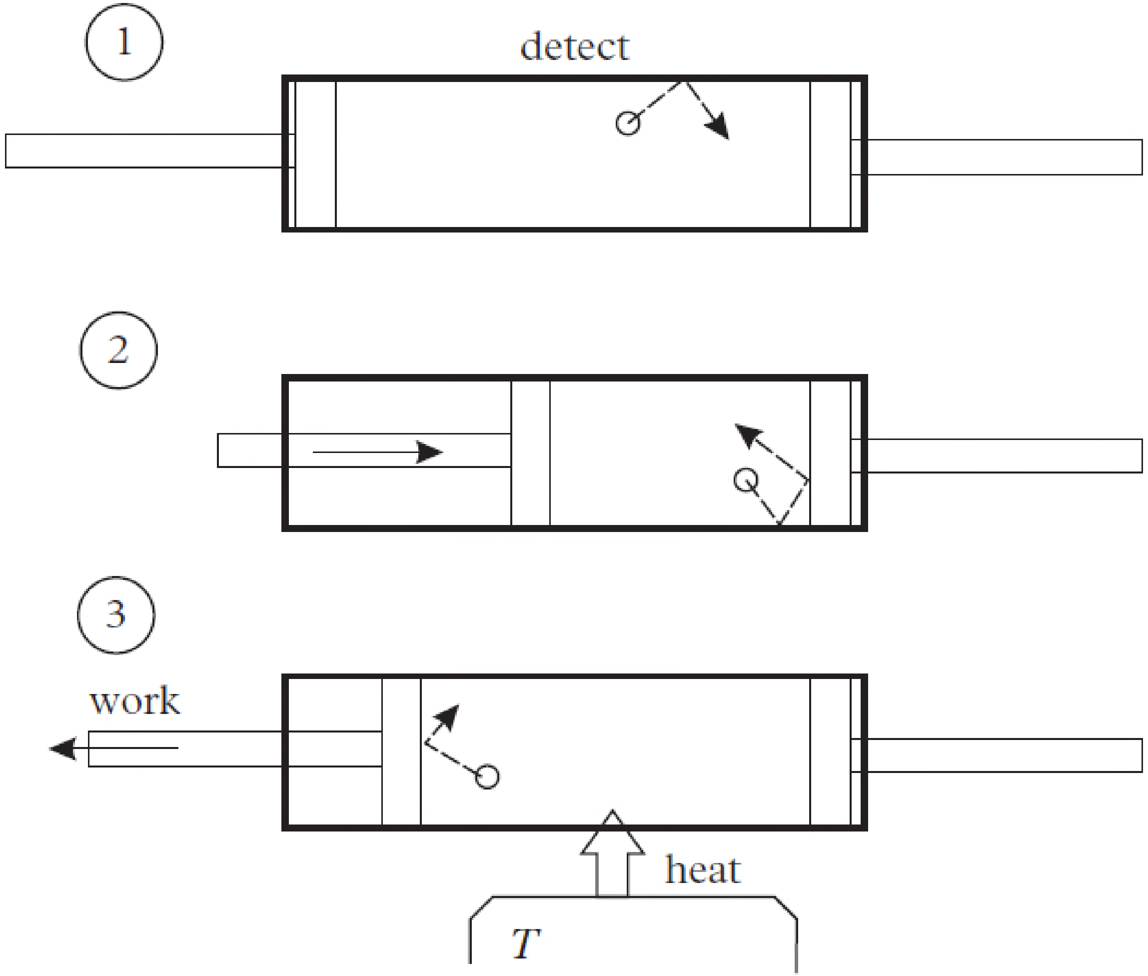


Maxwell's idea:

- Use observation to decide when to open the trap door.
- Thus separate the molecules (e.g. bring them all to one side, or separate slow from fast).
- Hence cause the entropy of the system to go down, with no net energy flow in or out.

Resolution:
The daemon is itself a physical system, and must either store the information (in which case it is not acting in a cycle) or else release it to the environment (in which case the entropy of the environment goes up).

# Szilard engine



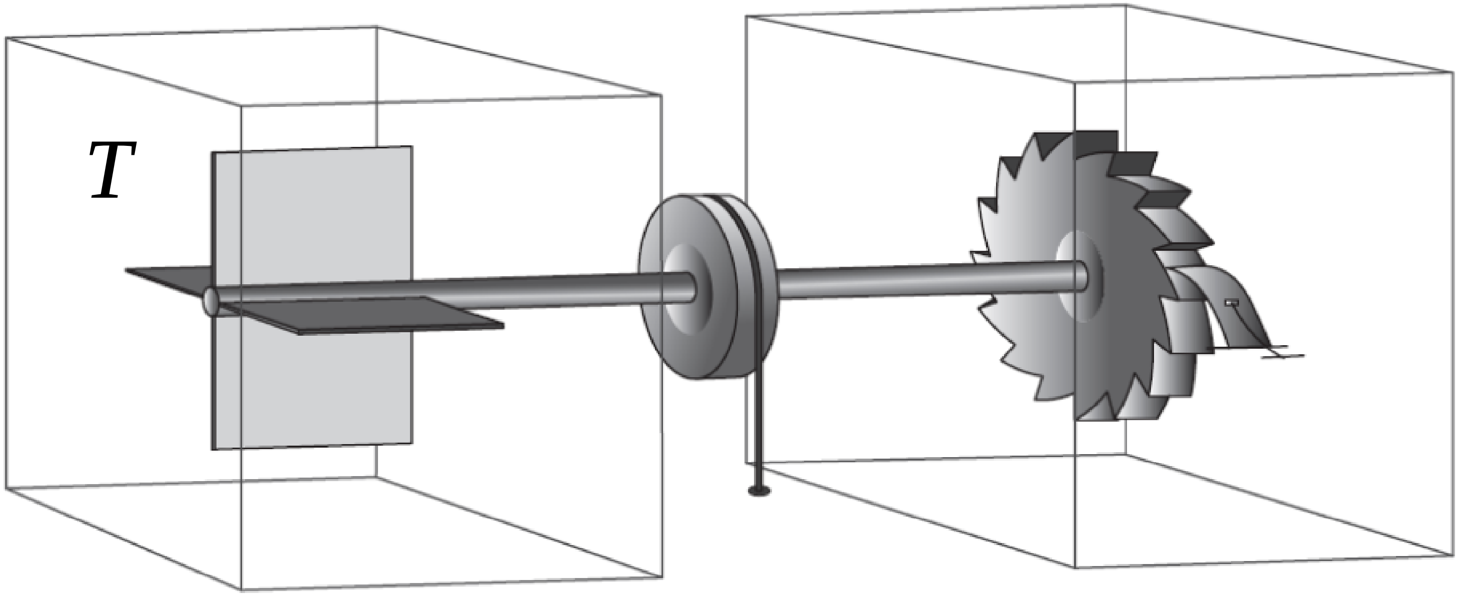

Detect where the molecule is.

Compression:
molecule is on the other side so no work needs to be supplied.

Isothermal expansion:
obtain work W while heat Q flows in.

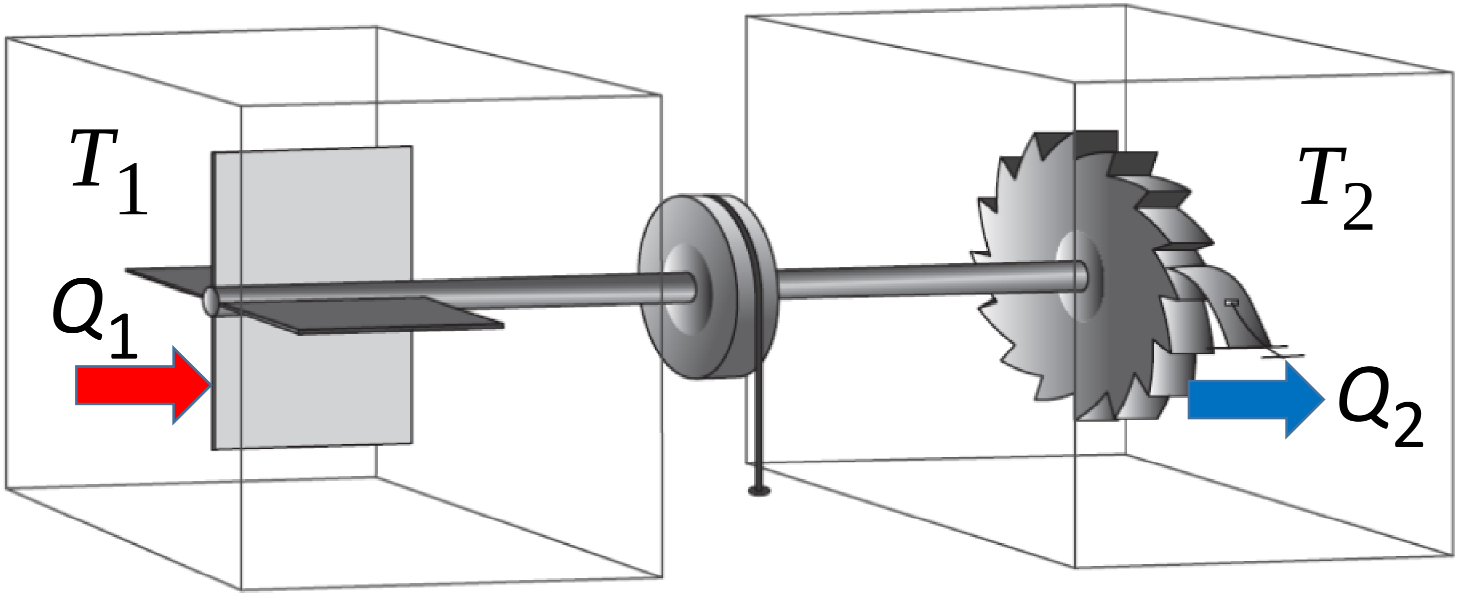
**The memory of the detector then has to be cleared**

# Feynman-Smoluchowski rachet




Exploit thermal fluctuations to raise the load.
Seems to allow violation of Kelvin statement?

# Feynman-Smoluchowski rachet



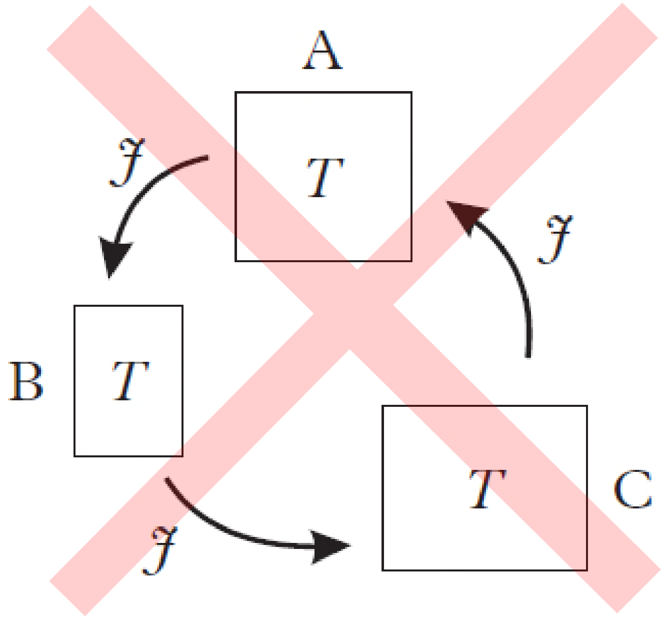

Exploit thermal fluctuations to raise the load.

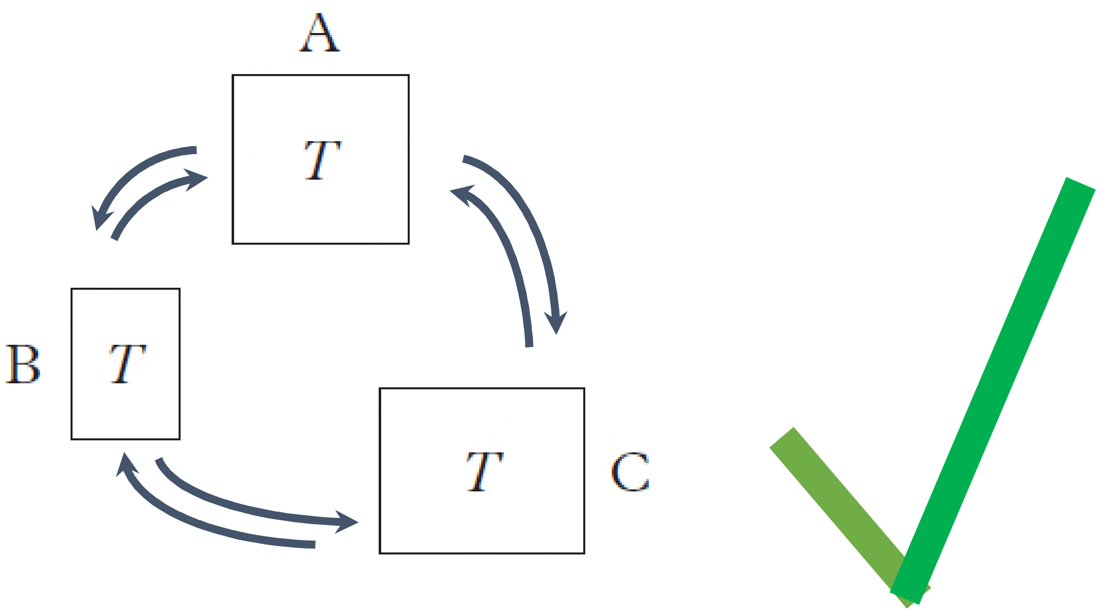
When the forward and reverse processes are balanced, we find

$$Q_1/Q_2 = T_1/T_2$$

--- it’s a heat engine obeying the Second Law.

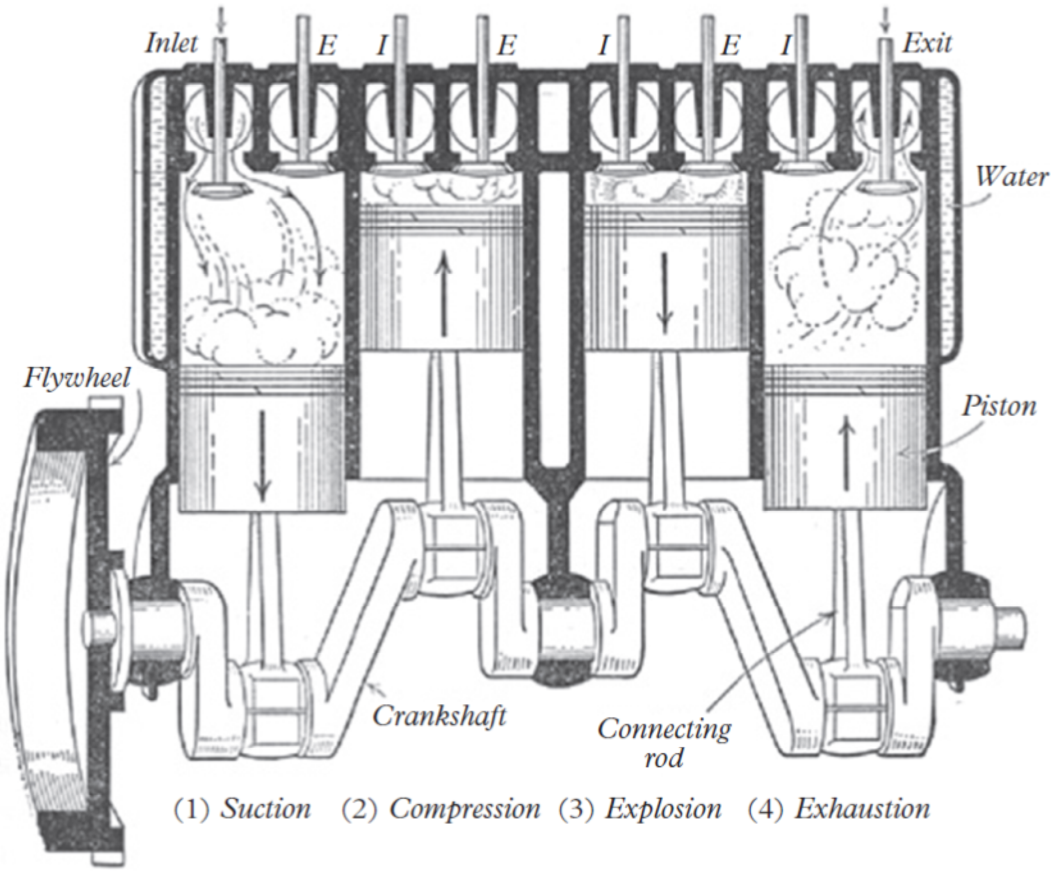
# The Principle of Detailed Balance
# (in conditions of thermodynamic equilibrium)



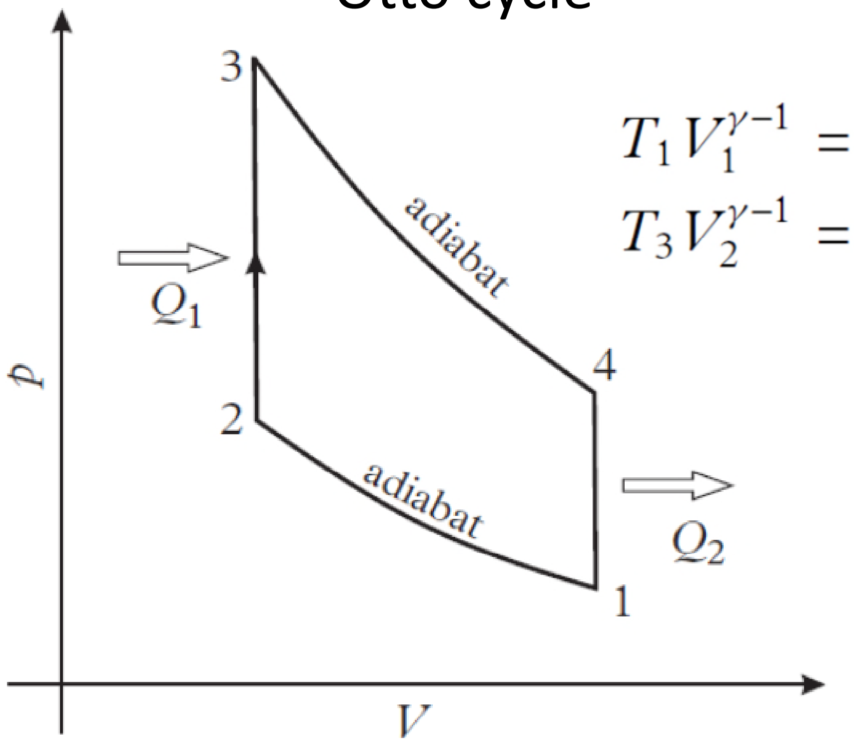




Each internal process goes at the same rate as the direct reverse process between the same two states.

# Internal combustion engine




Otto cycle




$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$$

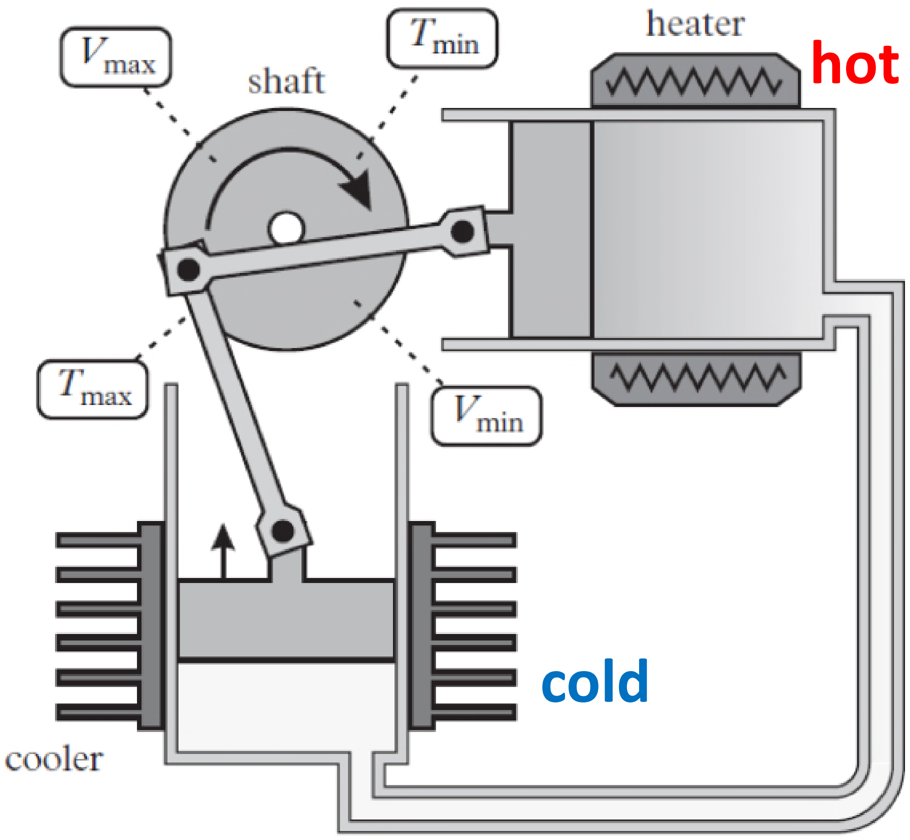
$$Q_1 = \int_{T_2}^{T_3} C_v dT = C_v(T_3 - T_2),$$

$$Q_2 = -\int_{T_4}^{T_1} C_v dT = C_v(T_4 - T_1)$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - r^{1-\gamma}$$

$r \equiv V_1/V_2$ is the *compression ratio*

Stirling engine
No valves, no explosions
→ smooth and low-maintenance

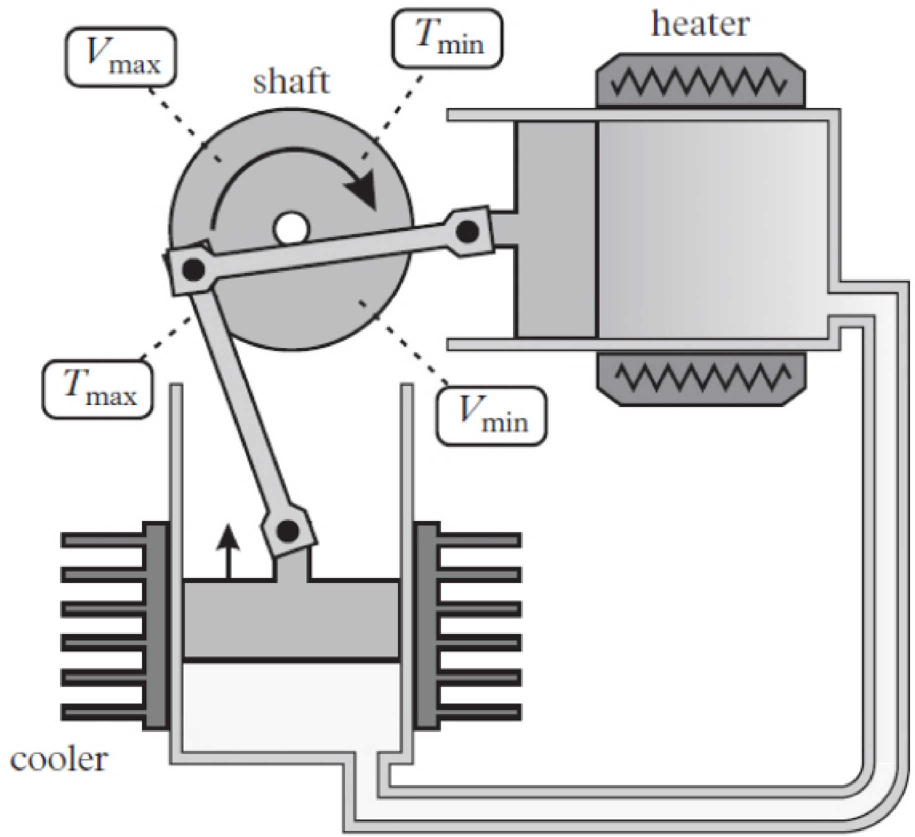



Expand while hot; compress while cold

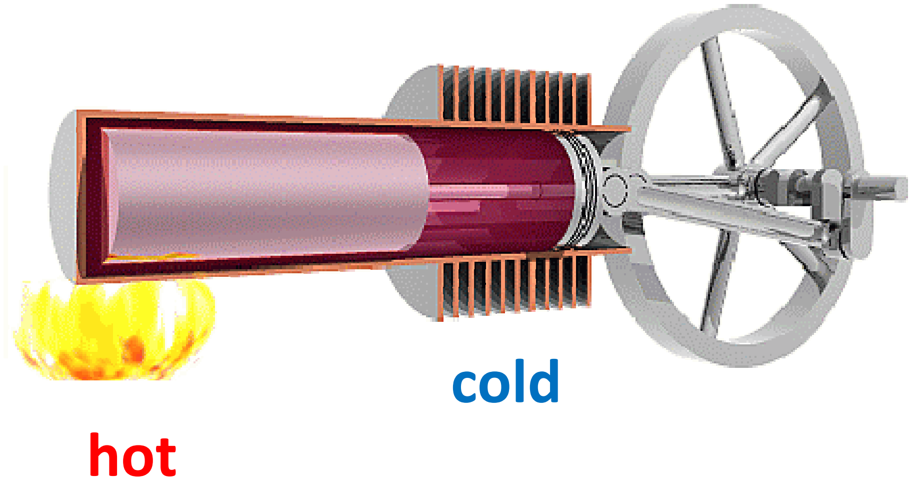
Stirling engine

No valves, no explosions

→ smooth and low-maintenance




Expand while hot; compress while cold




10 kW Solar power