



Thermodynamic Laws

The Foundation Course on Physics

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1st Law of Thermodynamics

In general, the laws of thermodynamics are ones of the most important laws in natural sciences. They are of extreme importance also for explanation of the processes in living systems.

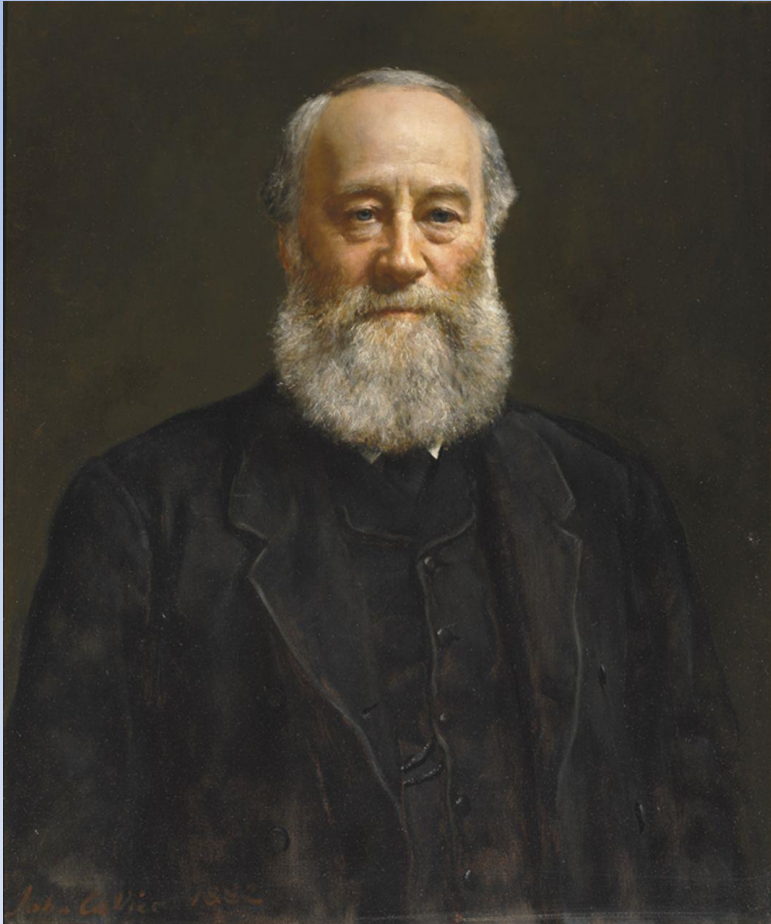
The 1st Law of Thermodynamics is a special form of the **principle of conservation of energy** and is usually written as follows:

$$\Delta U = W + Q$$

(or better $dU = dW + dQ$)

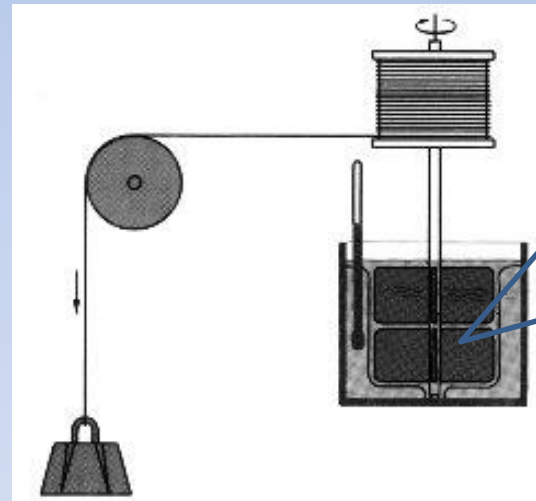
The right way of reading: **The internal energy of a thermodynamic system increases by ΔU if the surroundings does work W on the thermodynamic system and heat Q is absorbed by the system from its surroundings.**

Joule experiment



James Prescott Joule (1818–1889)

Transformation of mechanical energy in heat – one of the crucial experiments to verify energy conservation law.



Weight moves down with a constant speed

Rotating paddles in water. Temperature increase is measured.

1st Law of Thermodynamics

The following statement is another valid formulation of the 1st law of thermodynamics:

In a cyclic (reversible) process, the change in the internal energy of the system equals zero.

The 1st law of thermodynamics therefore provides a complete definition of internal energy U , one of the basic state parameters.

The absolute value of the internal energy in real systems is very difficult to determine (just think of the calculation of the potential energy of all the particles making up the system).

- As a result, classical thermodynamics only considers its changes (ΔU , dU).

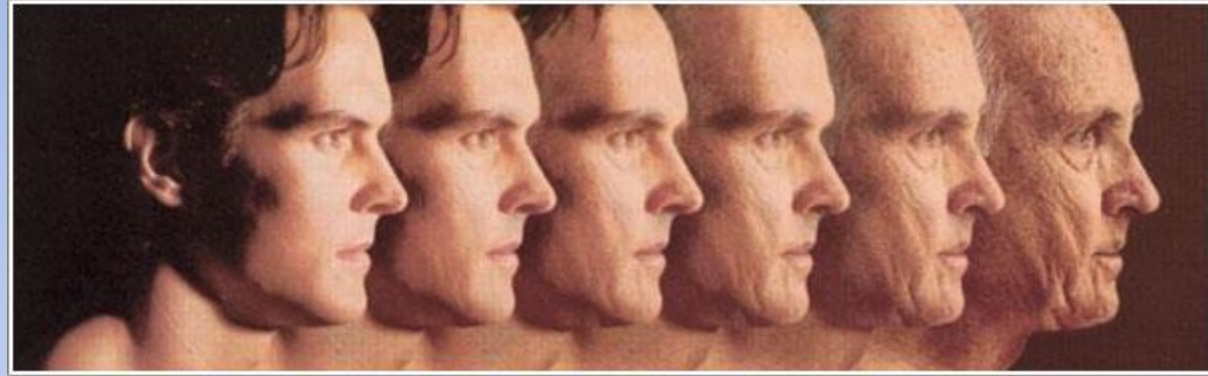
2nd Law of Thermodynamics

- One can recall many processes which are in agreement with the 1st law of thermodynamics (during which energy is conserved), of which it is however known by experience that they **cannot** happen in nature:
 - In an isolated system consisting of a colder body and a hotter one, the hotter body is never heated solely by the cooling of the colder body, i.e. at the expense of the internal energy of the colder body.
 - Gas, which leaves an enclosure and is dispersed in space, will never spontaneously return into the enclosure.
 - A wheel will not be turned by the heat from a hot brake.
 - Rubbing hands produces heat but heated palms will not start to rub mutually 😊.
 - Etc.
- These practically impossible processes are characterised by the fact that they are (better: would be) *reversed* irreversible processes, sequences of non-equilibrium states. We know already that their course *cannot be reversed*. The law determining the sense or direction of the processes running in isolated systems (and with sufficient accuracy in similar ones) is the **2nd law of thermodynamics**.

Irreversible processes once again



Dough and bread



(a)

Albumen

Water-soluble

insoluble

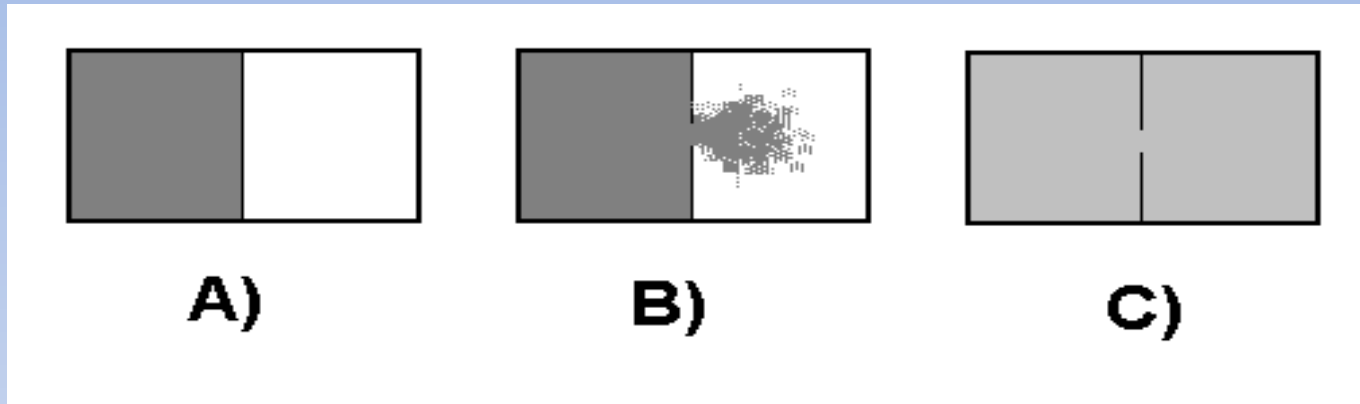
(b) Protein Thermal Irreversible Denaturation

Native albumen $\bullet \text{: -SH}$

Denaturation

Crosslinking — : S-S

Back to ideal gas: Its free expansion is a simple example of an irreversible process.



A) A box is divided into two compartments by a wall. There is compressed ideal gas in equilibrium state in the left compartment. In the right compartment, there is vacuum.

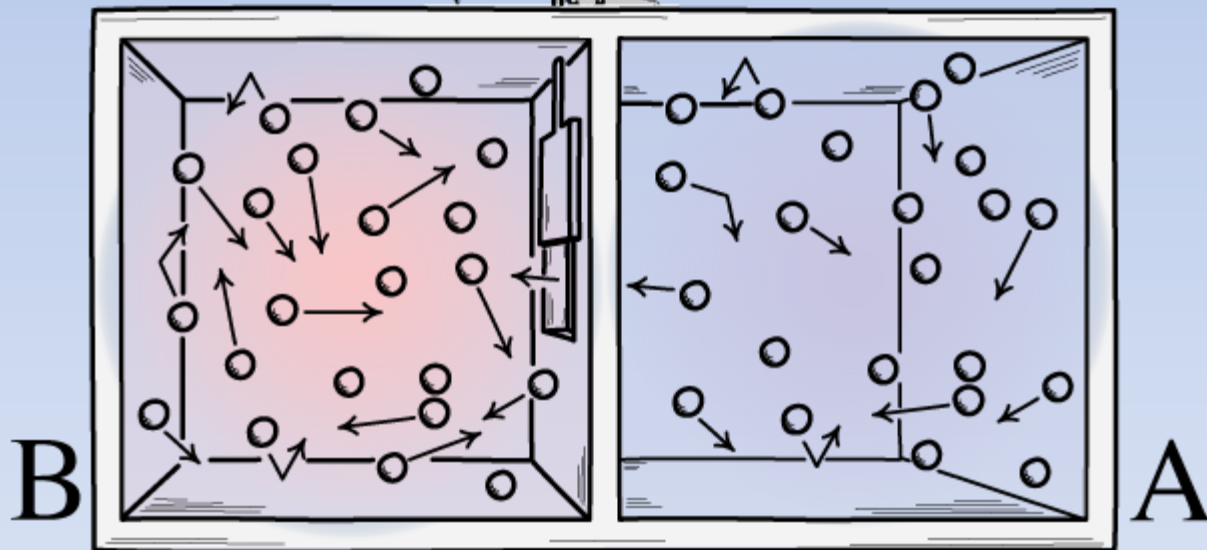
B) We make somehow an opening in the wall, the gas expands in the second part of the box – an irreversible process is in progress.

C) After certain time, in both parts of the box tmd. equilibrium is reached.

What about a change of temperature in this process?

„Ghosts“ in physics: Maxwell's Demon

How to break the 2nd law?!?!?



The ghost separates fast and slow particles, temperature difference appears. What has happened to the 2nd law?

- http://www.pitt.edu/~jdnorton/Goodies/exorcism_phase_vol/exorcism_phase_vol.html

2nd Law of Thermodynamics

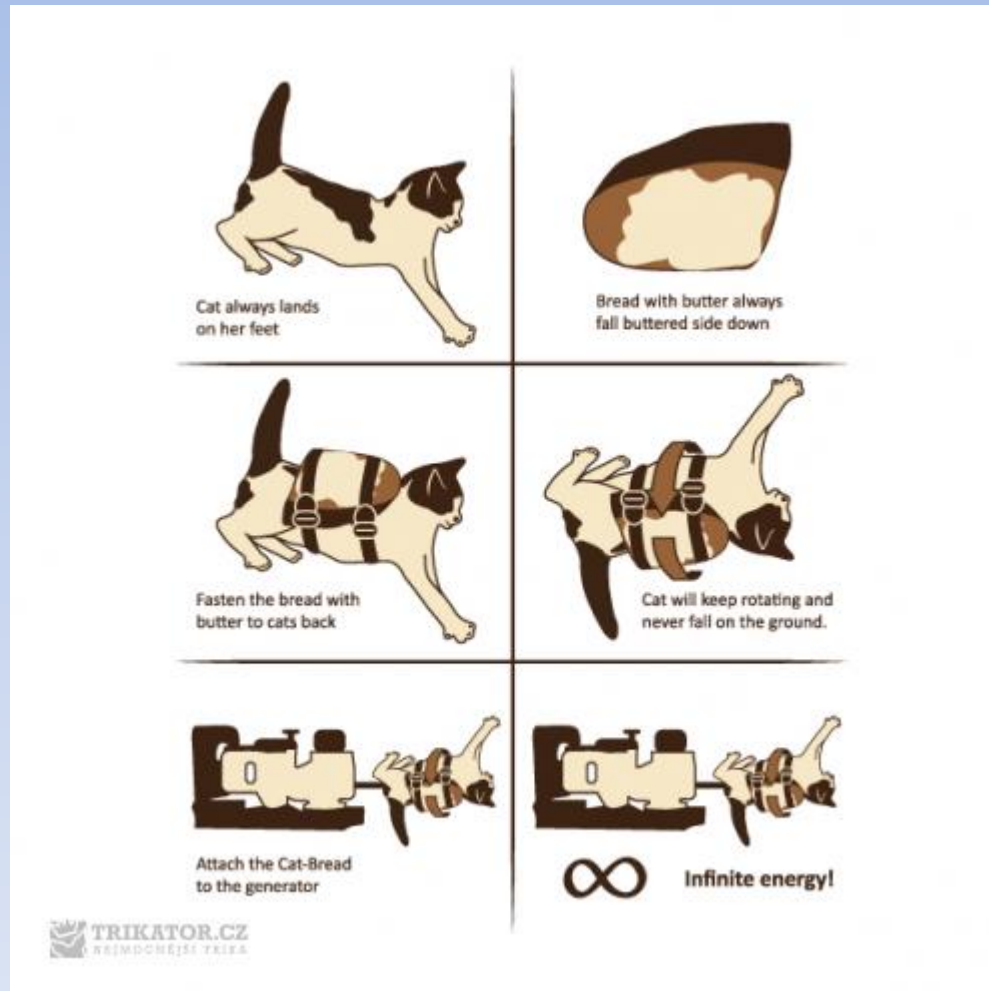
2nd Law of Thermodynamics has many mathematical formulations or wordings. We mention only four:

- 1. It is impossible to make a cyclic (working) engine that would only extract heat from a reservoir and convert it to equivalent work, without a certain amount of heat being transferred from the hotter to the colder body, i.e. it is impossible to construct the so-called *perpetuum mobile of the second kind*.

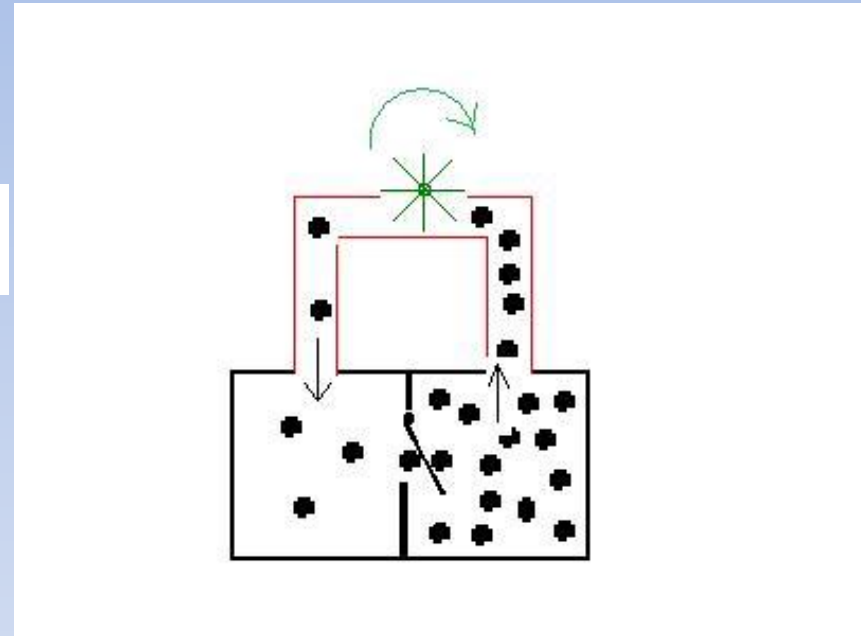
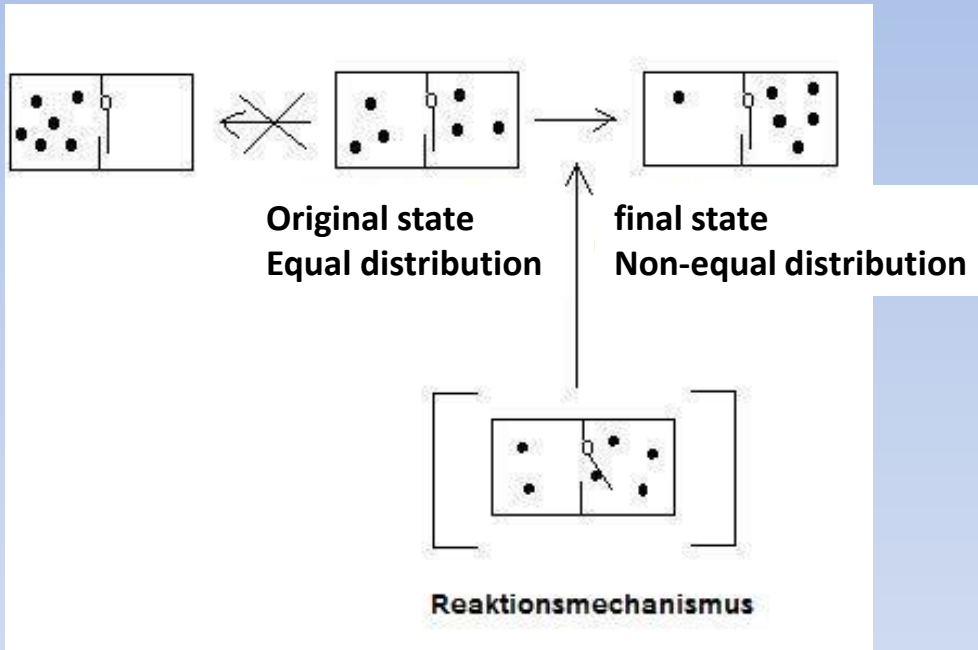
(Note: A *perpetuum mobile of the first kind* contradicts the law of conservation of energy.)

- 2. It is impossible to transfer heat from a colder to a warmer body without doing work.
- 3. Heat cannot spontaneously flow from a colder to a warmer body.

Perpetuum mobile (to relax)



Perpetuum mobile of 2nd kind „seriously“



Can it work forever? Where is the problem? Explanation will be awarded by some candy tomorrow.

Is the problem influenced by the number of particles?

Interesting vids

- <https://www.youtube.com/watch?v=Y9nOV7u8Y4A>
- <https://www.youtube.com/watch?v=Tay3-2WKQ5Y>

Entropy

4. **There is an additive* state parameter/function S , entropy, defined by the relation:**

$$\Delta S \geq \frac{Q}{T}$$

where ΔS is change in entropy and Q is the amount of heat added to the system at temperature T . The inequality applies to irreversible processes. In a reversible process:

$$\Delta S = \frac{Q}{T}$$

Entropy is the result of the efforts to find a thermodynamic quantity (a state parameter) that would include heat transferred into or outside the system. Heat is not a state function.

***Additive state parameters: we can summarise their values in individual compartments of the system. Additive/non-additive = extensive/intensive. Example: energy/temperature**

Entropy

In a thermally isolated system (e.g. during an adiabatic process, Q – amount of heat added - equals zero) the following relation applies:

$$\Delta S \geq 0$$

As a result, the second law of thermodynamics is sometimes referred to as the **increase-in-entropy law**. The change in entropy in an isolated system can be only positive, hence entropy can only increase. Processes in an isolated system tend towards establishing thermodynamic equilibrium, so that under thermodynamic equilibrium entropy reaches its **maximum**.

Combined Formulation of the 1st and 2nd law

- For a reversible process we can formulate $Q = T.\Delta S$ and $W = -p.\Delta V$ (taking into consideration only the volume work of the system). If we pass the following for Q in the first law of thermodynamics, we obtain:

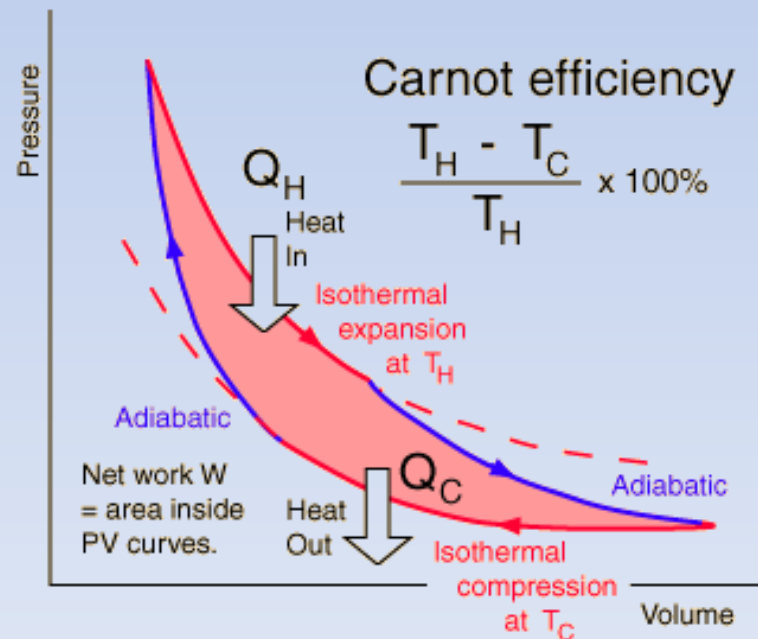
$$\Delta U = T.\Delta S - p.\Delta V.$$

- This equation is sometimes referred to as the combined formulation of the first and the second law of thermodynamics.
- **The third law of thermodynamics** is mentioned merely for the sake of completeness: No finite process can bring the system to the temperature of absolute zero.

The Carnot cycle (optional)

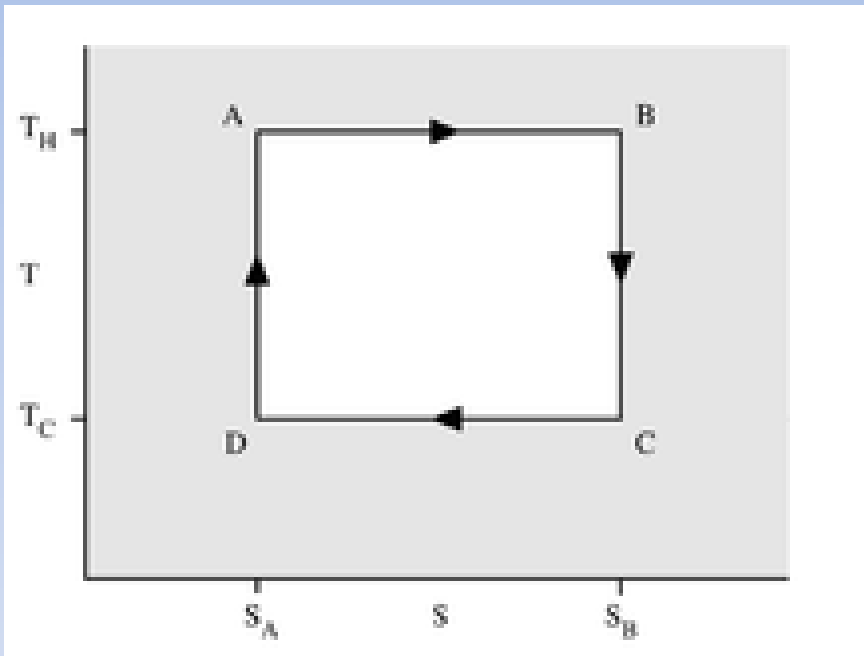
Carnot cycle – a theoretical heat engine

The most efficient heat engine cycle is the Carnot cycle, consisting of two isothermal processes and two adiabatic processes. The Carnot cycle can be thought of as the most efficient heat engine cycle allowed by physical laws. When the 2nd law of thermodynamics states that not all the supplied heat in a heat engine can be used to do work, the Carnot efficiency sets the limiting value on the fraction of the heat which can be so used.



Red area quantifies the useful work done. Heat was transformed into work

Carnot cycle in T(S) diagram



$$Q = T\Delta S$$

$$Q_H = T_H\Delta S$$

$$Q_C = T_C\Delta S$$

$Q_H - Q_C =$ heat absorbed which can be changed in useful work

Efficiency =

$$= \frac{Q_H - Q_C}{Q_H} = \frac{T_H\Delta S - T_C\Delta S}{T_H\Delta S} = \frac{T_H - T_C}{T_H}$$

Carnot cycle

- (Carnot's theorem) *The efficiency of any heat engine operating between two specified temperatures can never exceed the efficiency of a Carnot engine operating between the same two temperatures.*
- Maximum achievable efficiency of this engine η (eta) could be equal to 1 (i.e. 100%) but only if the lower temperature $T_2 = 0$ K. Efficiency of real heat engines (e.g. diesel engines) does not exceed about 50 %.
- The heat engine is a system that converts heat or thermal energy—and chemical energy—to mechanical energy, which can be used to do mechanical work.
- 25 percent for most automotive gasoline engines.
- 49 percent for a modern coal-fired power stations
- 60 percent for a steam-cooled gas turbine.

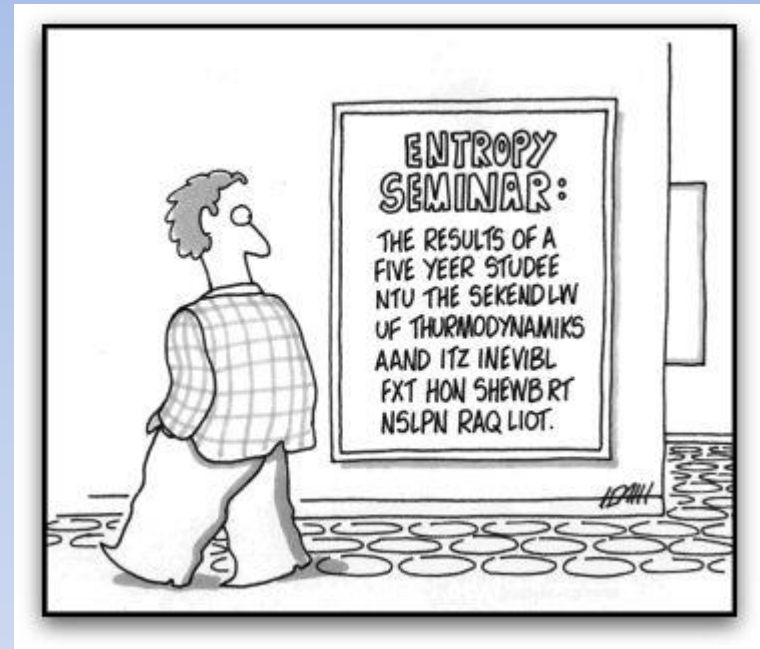
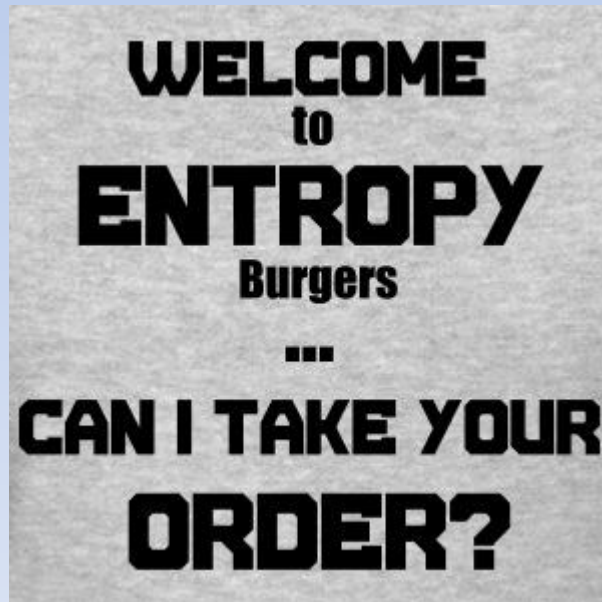
Entropy and disorder (optional)

- We can easily imagine that absorption of heat in a system can influence its structure – the increased thermal motion can disintegrate molecules, for example.
- Overmore, it can be relatively easily shown that any **increase of entropy** is connected with **increase of disorder**.
- Disorder has higher probability compared with an ordered state.
- Thus there is an equation showing relation between entropy and probability of a thermodynamic state. It is very famous formula called **Boltzmann principle**:

$$\Delta S = k \ln(P_1/P_2)$$

The 2nd Law of Thermodynamics

- How to explain these jokes?
(*Jokes of physicists are sometimes difficult to understand.*)



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