SEMMELWEIS UNIVERSITY

Lágy Anyagok Laboratóriuma

Dept. of Biophysics and Radiation Biology,
Laboratory of Nanochemistry

THERMODYNAMICS

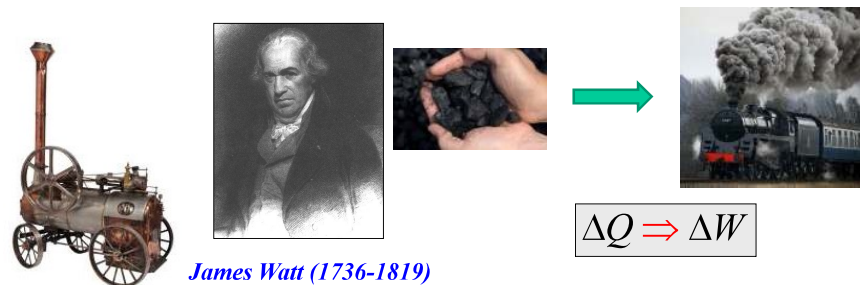The science of energy flow

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2019

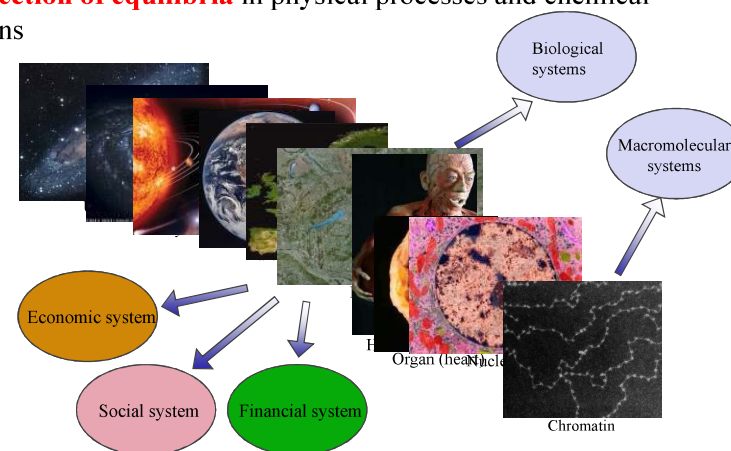
Thermodynamics

Early definition:

Thermodynamics is the study of thermal processes in macroscopic systems.

James Watt (1736-1819)

$$\Delta Q \Rightarrow \Delta W$$

Classical thermodynamics was developed in the first half of the nineteenth century by Carnot, Clausius, Joule, Kelvin, and Mayer (and others), is a *phenomenological* theory, dealing with thermal phenomena.

Prescott Joule
(1818–1889

Lothar Mayer
(1814 – 1878)

Hermann Helmholtz
(1821 – 1894)

École Polytechnique	Glasgow school	Berlin school	Edinburgh school
Sadi Carnot (1796-1832)	William Thomson (1824-1907)	Rudolf Clausius (1822-1888)	James Maxwell (1831-1879)
Vienna school	Gibbsian school	Dresden school	Dutch school
Ludwig Boltzmann (1844-1906)	Willard Gibbs (1839-1903)	Gustav Zeuner (1828-1907)	Johannes de Waals (1837-1923)

Thermodynamics today

General theory of energetic interactions providing useful relationships developed from the laws, that describe the **interchange of energy** and the **direction of equilibria** in physical processes and chemical reactions

Biological systems

Macromolecular systems

Economic system

Social system
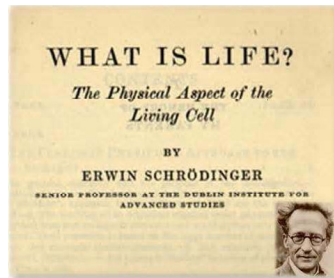
Financial system

Organ (heart)

Nucleus

Chromatin

Bio-thermodynamics (bioenergetics) dealts with how the energy is produced and transformed in living creatures.
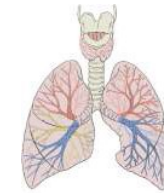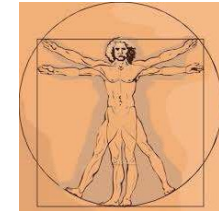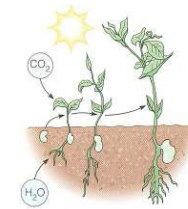
Themodynamics laws can be applied for living organisms too. **Rubner 1894.**

(A.L. Lavoisier 1743-1794)

"…respiration is nothing but a slow combustion of carbon and hydrogen…"

WHAT IS LIFE?

The Physical Aspect of the Living Cell

BY

ERWIN SCHRÖDINGER

SENIOR PROFESSOR AT THE DUBLIN INSTITUTE FOR ADVANCED STUDIES
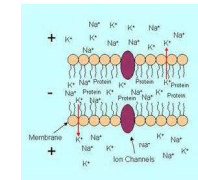
Biological exploitation of energy
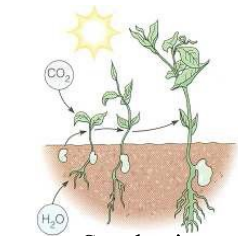
Synthesis

Physical work
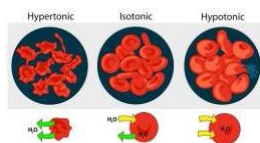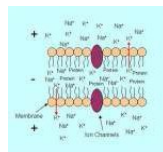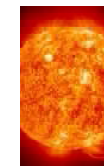
Muscle work

Osmotic work

Electrochemical work
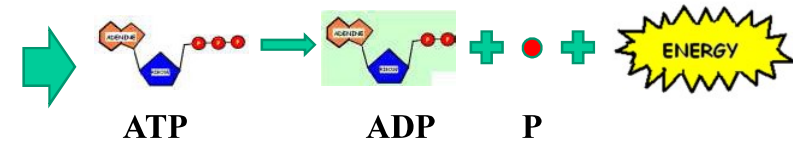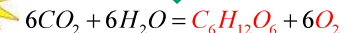
Photochemical work

Where does the energy come from?
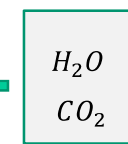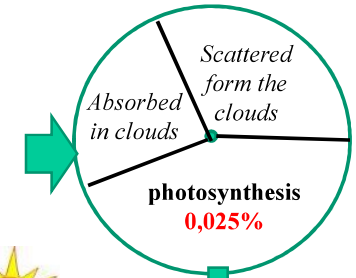
The primary energy source is the SUN

$5 \cdot 10^{18} \ MJ/year$

$1,7 \cdot 10^{17} \ J/s$

LIFE

Scattered form the clouds

Absorbed in clouds

photosynthesis 0,025%

H_2O
CO_2

$6CO_2 + 6H_2O = C_6H_{12}O_6 + 6O_2$

ENERGY

ATP   **ADP**   **P**

ATP ⟷ ADP

DISTRIBUTION OF INTERNAL ENERGY

- Synthesis of cellular macromolecules
- Synthesis of membranes
- Celuláris movements
- Transport of molecules
- Generation of electric potentials accross membranes
- Heat

Thermodynamics can provide a useful way of thinking about many different processes including biological processes.

Some examples:

What reactions and/or physiological processes are possible?
What are the allowed mechanism in protein synthesis?
What are the necessary conditions required for proteins, nucleic acids and membranes to assume their active structures?

The beauty of thermodynamics is that a **relatively small number of postulates** are used to develope the description of rather complex systems and utilization of internal energy,

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Thermodynamic system

Interactions within the system

TERMODINAMIKAI RENDSZER

Material and/or energy flow through interface

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energy   matter

isolated   **closed**   **open**

Biological systems

energy

| isotherm T=const. | isobaric p=const. | adiabatic $\Delta Q = 0$ |

BODY

metabolism

O_2

heat

food

work *(movement)*

heat

end products

Heat and temperature play essential role !

$0\ C^o \Longrightarrow T \Longrightarrow 42\ C^o$

Biological Thermodynamics

Characterization of the thermodynamic system

Macroscopic characterization: **state variables**
- explicitely determine the *state* of the system.

Pressure: p
Volume: V
Temperature: T
Concentration: c
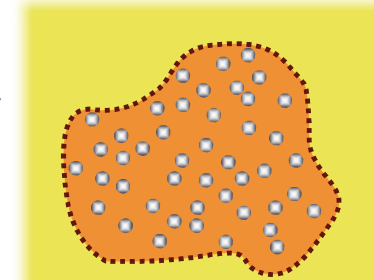
- *Thermodynamic variables* are the observable macroscopic variables of a system, such as p, V and T.
- If they are used to describe an equilibrium state of the system, they are known as *state variables*.

- *Extensive variables* depend on the size of the system; e.g. energy, mass, volume, charge, entropy,..,

- *Intensive variables* do not depend on size; e.g. pressure, temperature, concentration…,

- An *isobaric* process is one in which the pressure is constant.
- An *isochoric* process is one in which the volume is constant.
- An *isothermal* process is one in which the temperature is constant.
- An *adiabatic* process is one in which no heat enters or leaves the system; i.e. Q = 0.

change in the **internal energy**

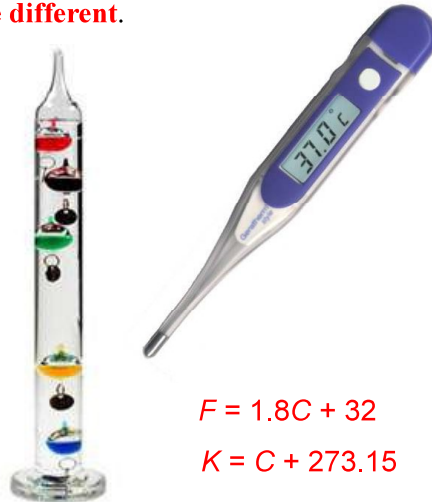- **Temperature and heat are different**.
  (**Joseph Black**)

- First thermometer
  (**Galileo Galilei**)

- First clinical thermometer
  (**Jean Rey** 1631)

- Early temperature scale
  (**Anders Celsius** 1742).

- Temperature scale
  (**Carl von Linne**)

$F = 1.8C + 32$

$K = C + 273.15$

The Kelvin scale is setup so that its zero point is the coldest possible temperature--absolute zero, at which point a substance would have zero internal energy. This is -273.15 °C. Absolute zero can never be reached, but there is no limit to how close we can get to it.

A gas exerts no pressure when at absolute zero.

P

gas A

gas B

gas C

T (°C)

-273.15 °C   0 °C
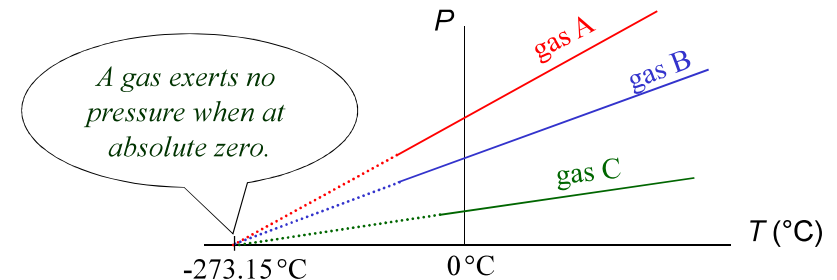
| Spontaneous process ➡ equilibrium |

that can proceed without any outside intervention

- *In equilibrium state* the properties of the system do not change with time.

- In **equilibrium state** the intensive variables are uniformly distributed throughout the system.

- A *non-equilibrium state* may contain intensive variables which vary in space and/or time.

Change in the state
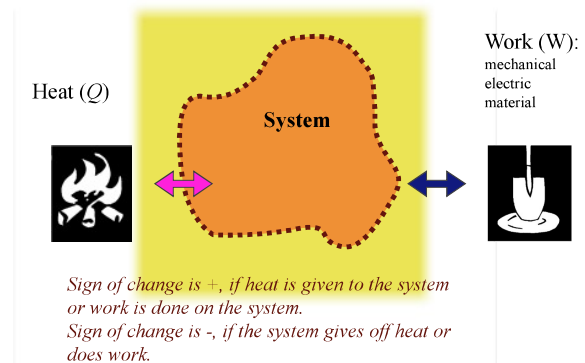
Thermodynamics is interested in the changes within the system.
Changes may be evoked by: energetic interactions
Result: **internal energy of the system changes**.

Surroundings

Work (W):
mechanical
electric
material

Heat (Q)

System

Sign of change is +, if heat is given to the system or work is done on the system.
Sign of change is -, if the system gives off heat or does work.

Internal energy

Internal energy is the energy an object or substance is due to the molecular **kinetic** and **potential** energies associated with the random motions of all the particles that make it up.

The kinetic energy is due to the motion of the particles. The potential energy is due to interactions between atoms, ions and molecules.
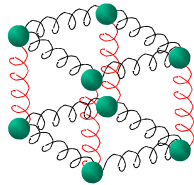
$$E = E_{pot} + E_{kin} + U$$

Microscopic characterization: **internal energy (U)**

Macroscopic potential- and kinetic energies are not included in the internal energy.
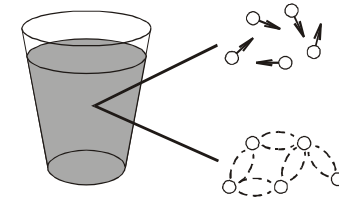
Molecular potential- and kinetic energies are in the internal energy.

Internal energy does not contain the potential and kinetic energy of the macroscopic body.

Standard internal energy (298 K)

Ideal gas with one atom

Ideal gas with severeal atoms

Liquid and solid body

rotation and vibration energy

translation energy

attractive molecular interactions

Change of internal energy

ΔT

thermal

Δp

mechanical

internal energy

chemical

n

ΔV

Δn

others
pl. surface electric

$\Delta \Phi$

Change in internal energy

$\Delta X > 0$

$\Delta X < 0$

Elementary energy exchanges

thermal | volume | surface | chemical | others

The change of internal energy is the sum of individual energy exchanges ➡ (*due to conservation of energy*)

$$\Delta U = \Delta Q + \sum_i \Delta W_i$$

Mechanical interactions (1)
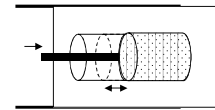
- *mechanikai work*

$$W_{mech} = -f(x) \cdot \Delta x$$

- *Volumertic work*

$$f(x) = p(V) \cdot A_s$$

$$W_{vol} = -pA_s \Delta x = -p\Delta V$$

Elementary energy exchanges: $\boxed{W_i = y_i \cdot \Delta x_i}$

Extensive variable	Intensive variable	Product: energy change
Volume (*V*) Matter (*n*) Charge (*Q*) **?????**	Pressure (*p*) Chemical potential (*μ*) Electric potential (*φ*) Temperature (*T*)	Volumetric work (pΔV) Work of material transport (μΔn) **Heat ????**

$$\Delta U = -p\Delta V + \Phi\Delta q + \mathbf{H}\Delta\mathbf{M} + \mathbf{E}\Delta\mathbf{P} + \sum_{i=1}^{K}\mu_i\Delta n_i + thermal\,???$$

The change of internal energy is the sum of individual energy exchanges

$$\Delta U = \sum_i W_i = \sum_i y_i \cdot \Delta x_i$$

$$\Delta U = -p\Delta V + \gamma\Delta A_s + \Phi\Delta q + \mathbf{H}\Delta\mathbf{M} + \mathbf{E}\Delta\mathbf{P} + \sum_{i=1}^{K}\mu_i\Delta n_i$$

volumetric

surface

electric

magnetic

electrostatic
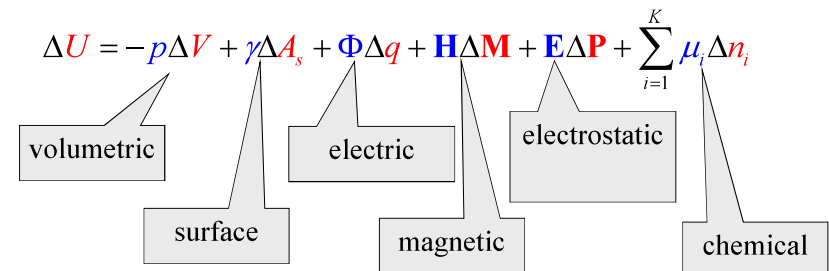
chemical

Where is the thermal interaction????

Rudolf Clausius
1822-1888

- **Thermal interactions**

$$\Delta Q = T\Delta S$$

← **entropy**

$$\Delta U = -p\Delta V + T\Delta S + \sum_{i=1}^{K}\mu_i \Delta n_i + ... +$$

Chemical potential

First law of thermodynamics

- **Law of conservation of energy**.
- Energy may be converted into different forms, but the total energy of the system remains constant. .

Work parts:

Volumetric work	Electric work:	Material transport:	Generalized:
$W_V = -p\Delta V$	$W_Q = \varphi \Delta Q$	$W_n = \mu \Delta n$	$W^i = y_{int}^i \Delta x_{ext}^i$

Negative, because in the case of work done on the system $V_2 - V_1 < 0$.

$$\Delta U = -p\Delta V + T\Delta S + \sum_{i=1}^{K}\mu_i \Delta n_i + ... +$$

chemistry

First law of bio-thermodynamics

Exploitation of internal energy

$$\Delta U = \Delta Q + \Delta W_{mech} + \Delta W_{chem}$$

metabolism   lost   bio-chemistry

work

physical   muscle

$\Delta W_{mech} < 0$
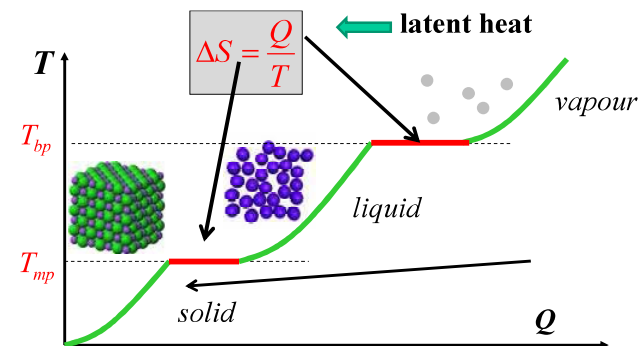$\Delta W_{term} < 0$

$\boxed{\Delta U < 0}$

$\Delta W_{kèm} > 0$

$\boxed{\Delta U > 0}$
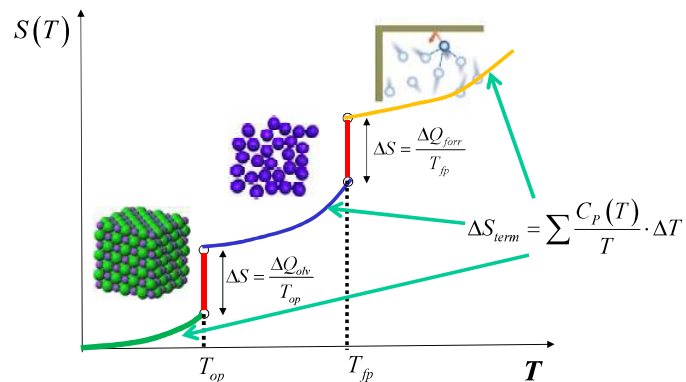

$$\Delta Q = T\Delta S$$

Thermal interactions
→ *temperature changes*
→ *temperature does not change*

$\Delta S = \dfrac{Q}{T}$ ← **latent heat**

T

T_{bp}

T_{mp}

vapour

liquid

solid

Q

heat → temperature changes ⟹ **Thermal entropy**

heat → temperature does not changes ⟹ **Configurational entropy**

Change in molecular order

$S(T)$

$$\Delta S = \frac{\Delta Q_{forr}}{T_{fp}}$$

$$\Delta S_{term} = \sum \frac{C_P(T)}{T} \cdot \Delta T$$
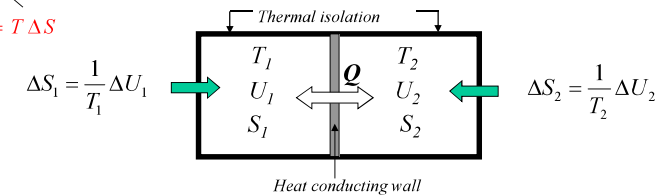
$$\Delta S = \frac{\Delta Q_{olv}}{T_{op}}$$

T_{op} T_{fp} T

Entropy change in isolated system when the temperature equalizes

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

$\Delta U = Q = T\Delta S$

Thermal isolation

$$\Delta S_1 = \frac{1}{T_1}\Delta U_1$$

T_1 U_1 S_1 Q T_2 U_2 S_2

$$\Delta S_2 = \frac{1}{T_2}\Delta U_2$$

Heat conducting wall

$U = U_1 + U_2 = állandó$ $\Delta U = 0$ $\Delta U_1 = -\Delta U_2$

$S = S_1 + S_2 = ?$ $\Delta S = \Delta S_1 + \Delta S_2 = ?$ $\Delta S = \frac{1}{T_1}\Delta U_1 + \frac{1}{T_2}\Delta U_2 = \frac{T_2 - T_1}{T_2 T_1} \cdot \Delta U_1 \neq 0$

$ha \quad T_2 \rangle T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} > 0 \quad és \quad \Delta U_1 > 0 \quad \Rightarrow \quad \Delta S > 0$

$ha \quad T_2 < T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} < 0 \quad és \quad \Delta U_1 < 0 \quad \Rightarrow \quad \Delta S > 0$

$ha \quad T_2 = T_1 \quad akkor \quad \frac{T_2 - T_1}{T_2 T_1} = 0 \quad és \quad \Delta U_1 = 0 \quad \Rightarrow \quad \Delta S = 0$

Due to temperature equalization, the entropy increases!

Entropy change in isolated system when the pressure equalizes

$$\Delta U = T\Delta S - p\Delta V + \sum_{i=1}^{K} \mu_i \Delta n_i + ... + \quad \Rightarrow \quad \Delta S = \frac{\Delta U}{T} + \frac{p}{T}\Delta V - \sum_{i=1}^{K} \frac{\mu_i}{T}\Delta n_i + ... +$$

$$\Delta S = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\Delta U_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)\Delta V_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right)\Delta n_1$$

Isotherm equalisation process :

$ha \quad p_1 > p_2 \quad akkor \quad \frac{p_1}{T} - \frac{p_2}{T} > 0 \quad és \quad \Delta V_1 > 0 \quad \Rightarrow \quad \Delta S > 0$

$ha \quad p_1 < p_2 \quad akkor \quad \frac{p_1}{T} - \frac{p_2}{T} < 0 \quad és \quad \Delta V_1 < 0 \quad \Rightarrow \quad \Delta S > 0$

$ha \quad p_1 = p_2 \quad akkor \quad \frac{p_1}{T} - \frac{p_2}{T} = 0 \quad és \quad \Delta V_1 > 0 \quad \Rightarrow \quad \Delta S = 0$
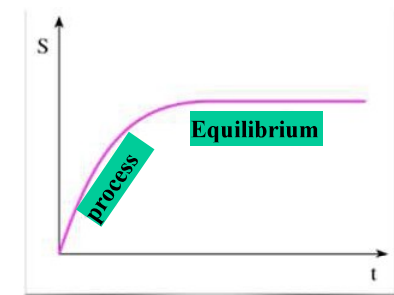
In isolated system during temperature and/or pressure equalization process the entropy increases!

Second Law of Thermodynamics

- The entropy of an isolated system never decreases; i.e.
  $$\Delta S \geq 0,$$
 approaching equilibrium, $S \rightarrow S_{max}.$

S

process

Equilibrium

t

- **Examples of real processes:**
- i.   temperature equalization;
- ii. mixing of gases;
- iii. conversion of macroscopic (ordered) KE to thermal (random)
  .

Second law of thermodynamics

- **During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.**
- Heat flows spontaneously from regions of high to low temperature.
- In an isolated system only such processes occur spontaneously which tend to equilibrate the respective intensive variables. .
- Spontaneous processes proceed towards the most probably state.

hot	hot
energy flow	
cold	cold
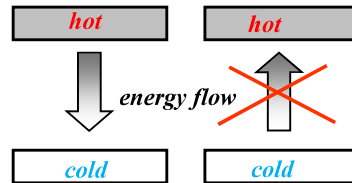
The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

entropy ➡ *arrow of time*

Second law and the refrigerator

$\Delta S_{inside} < 0$

$\Delta S_{outside} > 0$

$$\Delta S_{total} = \Delta S_{inside} + \Delta S_{outside} > 0$$

Entropy increases

Related to order − disorder transition?

YES!

Boltzmann equation:

$$S = k_B \ln \Omega$$

$k_B = 1.38 \cdot 10^{-23}$ J/K

$$k_B = \frac{R}{N_{Av}}$$

thermodynamic probability

Increase of particle number

Increase of temperature

Increase of volume

Dissociation

Helix-coil transition

Melting

Mixing

Ω thermodynamic probability gives the number of microstates for a given macrostate.

2. example:

macrostate : end-to-end distance
microstate: number of conformation

extended, e

coiled, c

$S = k_B \ln \Omega$

$N_{C-C} = 10^4$

$\Omega = 3^{10000}$

$S_g = k_B T \ln(3^{10000})$

$S_c = 10^4 k_B T \ln 3$
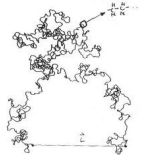
$N_{C-C} = 10^4$

$\Omega = 1$
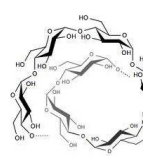
$S_{ny} = k_B T \ln 1$

$S_e = 0$

$\Delta S > 0$

Conformation and entropy

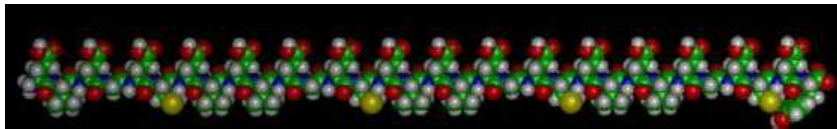*constitution - configuration - conformation*

Random coil   Ordered conformations

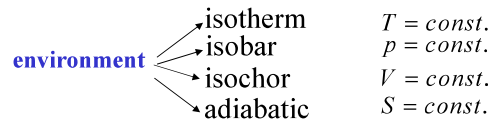| Higher conformational entropy | Much smaller conformational entropy |

$\Omega = 1$ ⟹ $\boxed{S_{konf} = 0}$

Environmental effects

environment
- isotherm $T = const.$
- isobar $p = const.$
- isochor $V = const.$
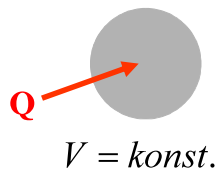- adiabatic $S = const.$

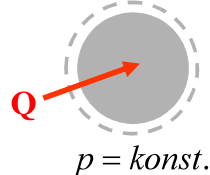**Certain part of internal energy is devoted to maintain the constancy of environment.**

| Usable energy | ≠ | Internal energy change |

$$\left(\frac{\Delta Q}{\Delta T}\right)_V < \left(\frac{\Delta Q}{\Delta T}\right)_p$$

$V = konst.$ $\boxed{C_V < C_p}$ $p = konst.$

Third law of thermodynamics

- The entropy of one-component, crystallizing material at 0 K temperature is 0.

- The 3rd Law fixes the absolute value of the entropy; i.e.
$$S \rightarrow 0 \ as \ T \rightarrow 0.$$

The unattainability of absolute zero

It is impossible to reach T = 0 in a finite number of steps.

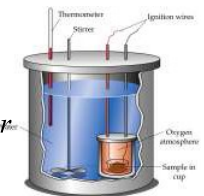## Useable part of internal energy at constant pressure:

In order to maintain the constancy of pressure in isobaric situation there is energy exchange with the environment.

The remaining useable part of internal energy is called: **enthalpy.**

H   enthalpy ⟹ $\boxed{H = U + pV}$

$$\boxed{\Delta H = \Delta U + p\Delta V}$$

calorymeter

$$\boxed{\Delta H = T\Delta S - p\Delta V + p\Delta V = T\Delta S = Q}$$ ⟸ *Heat !*

| The enthalpy is the useable part of internal energy at constant pressure. |

$$\boxed{\Delta H = Q}$$

In order to maintain the constancy of temperature in isotherm process there is energy exchange with the environment.
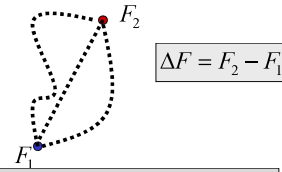
The remaining useable part of internal energy is called: **free energy**

free energy ➡ $F = U - TS$

extenzív **mennyiség**

$\Delta F = \Delta U - T\Delta S$

$\Delta F = F_2 - F_1$

$\Delta F = \cancel{T\Delta S} - p\Delta V - \cancel{T\Delta S} = -p\Delta V = W_{mech}$

The fee energy is the useable part of internal energy at constant temperature.

$\Delta F = W_{mech}$

In order to maintain the constancy of temperature and pressure of the environment, there is energy exchange with the environment.

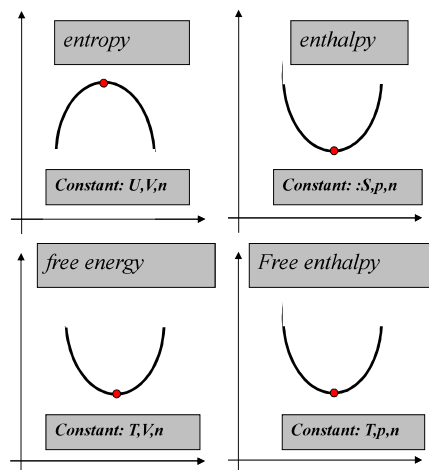The remaining useable part of internal energy is called: **free enthalpy** or **Gibbs free energy.**

free enthalpy ➡ $G = H - TS$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \sum_i \mu_i \Delta n_i == W_{kém}$

chemical potential

Conditions of thermodynamic equilibrium

entropy

Constant: U,V,n

enthalpy

Constant: :S,p,n

free energy

Constant: T,V,n

Free enthalpy

Constant: T,p,n

Thermodynamic equilibrium ⬌ Mathematical extremum problem

Stable and nonstable equilibrium condition

$\Delta_r G$

Non-equilibrium

Equilibrium− unstable

Equilibrium− local minimum

Equilibrium− global minimum

$$\Delta_e G < 0$$

$$\Delta_e G = \Delta_e H - T\Delta_e S$$

heat of mixing   entropy of mixing

endother   athermic   exotherm

$\Delta_e H > 0$ $\Delta_e H = 0$ $\Delta_e H < 0$

Change in molecular order

$$\Delta_e S > 0$$
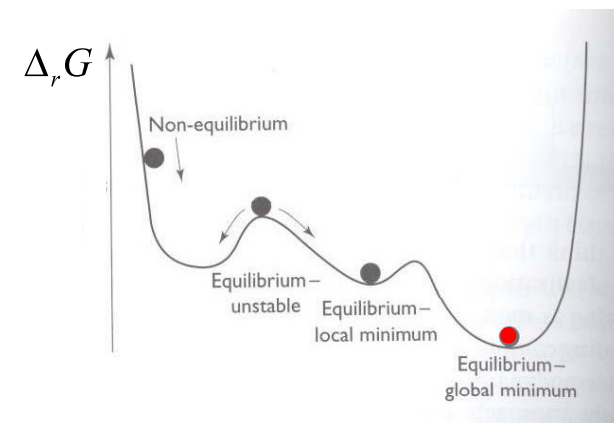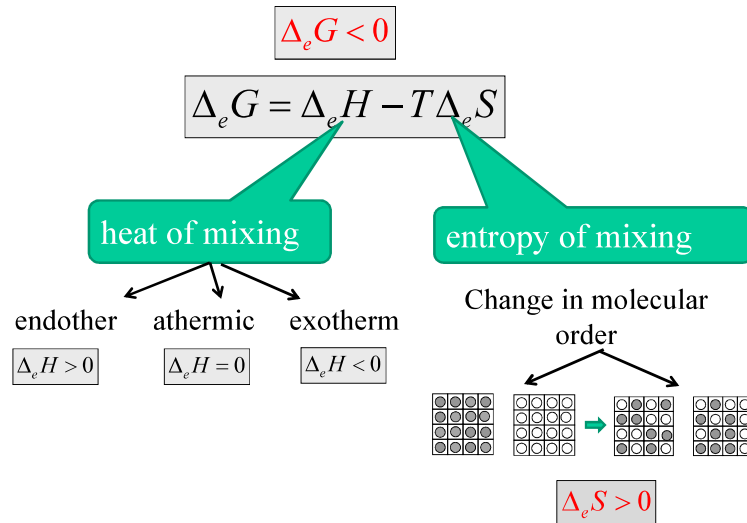
Driving force of chemical and biochemical reactions

$$\Delta_r G < 0$$

$$\Delta_r G = \Delta_r H - T\Delta_r S$$

Heat of reaction   Entropy of reaction

endotherm   exotherm

Change in molecular order

$\Delta_r H > 0$ $\Delta_r H < 0$

decomposition   ring formation

$\Delta_r S > 0$ $\Delta_r S < 0$
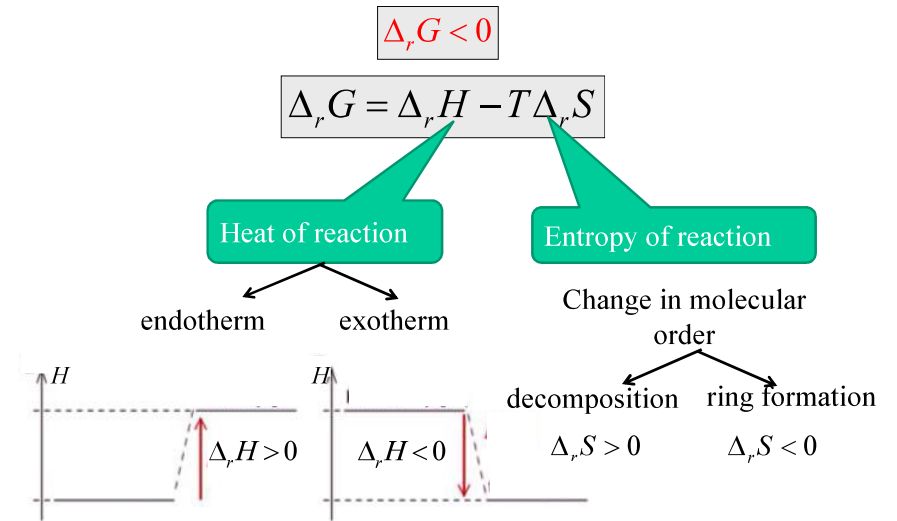
Looking back

Internal energy is the energy of an object or substance due to the molecular **kinetic** and **potential** energies associated with the random motions of all the particles that make it up.

1st law of thermodynamics:
(Conservation of energy)

$$\Delta U = T\Delta S - p\Delta V + \sum_{i=1}^{K} \mu_i\,\Delta n_i + \ldots +$$

2nd law of thermodynamics:
(Non-conservation of entropy)

During spontaneous processes entropy increases. Thermodynamic equilibrium is characterised by entropy maximum. Entropy of universe is always incresing.

3rd law of thermodynamics:
(Absolute scale of entropy)

The entropy of one-component, crystallizing material at 0 K temperature is 0

enthalpy $H=U+PV$ heat

free energy $F=U-TS$ work

free enthalpy $G=H-TS$ chemistry

(Gibbs free energy)