SEMMELWEIS UNIVERSITY

Lágy Anyagok Laboratóriuma

Dept. of Biophysics and Radiation Biology,
Laboratory of Nanochemistry

(Bio)thermodynamics, entropy,
Equilibrium and change

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1st law of thermodynamics

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

Conservation of energy!.

$$\Delta U = \Delta Q + \Delta W_{me\,\mathrm{ch}} + \Delta W_{k\acute{e}m} + \ldots + \Delta W_i$$

2nd law of thermodynamics

The entropy of an isolated system always increases during any spontaneous process. *The entropy does not conserve.*

3rd law of thermodynamics

The entropy of a perfect crystal is zero when the absolute temperature is zero.

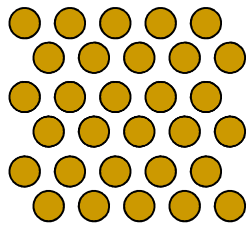
entropy

Thermal entropy *(T changes)*

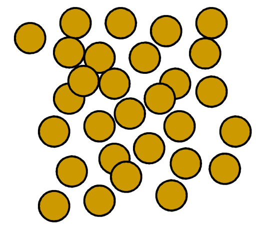
Configurational entropy *(T does not change)*

$$\boxed{\Delta S = \Delta S_{term} + \Delta S_{konf}}$$

melting:



$\Delta Q_{op} > 0$ $\xrightarrow{\;T_{op}\;}$

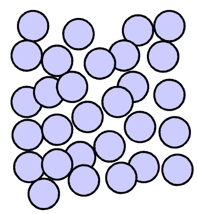


crystal melt

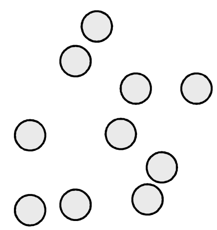
$$\boxed{\Delta S_{konf}\left(T_{op}\right) = \frac{\Delta Q_{op}}{T_{op}} > 0}$$

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

evaporation:



$\Delta Q_{fp} > 0$ $\xrightarrow{\;T_{fp}\;}$

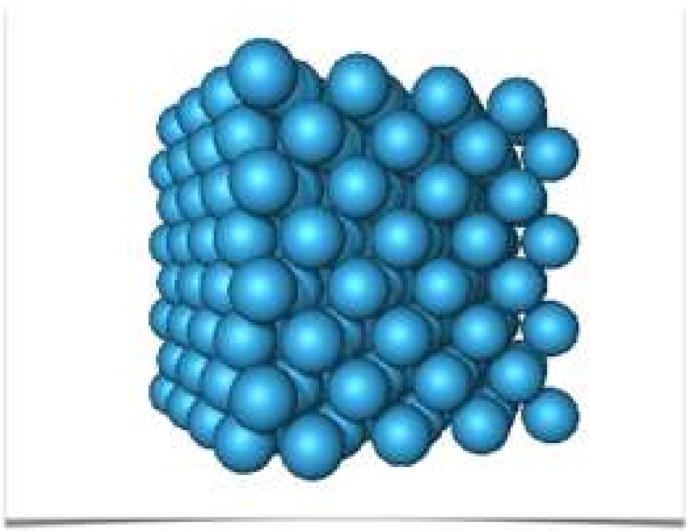


liquid vapour

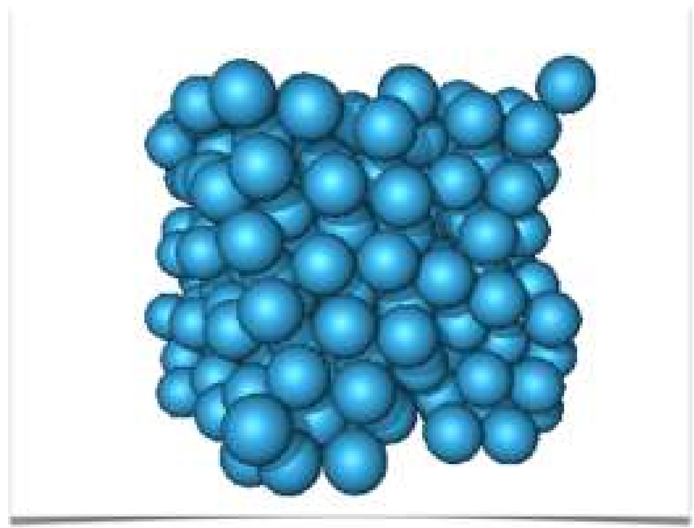
$$\boxed{\Delta S_{konf}\left(T_{fp}\right) = \frac{\Delta Q_{fp}}{T_{fp}} > 0}$$

Entropy is a measure of molecular disorder!

Entropy is the measure of disorder



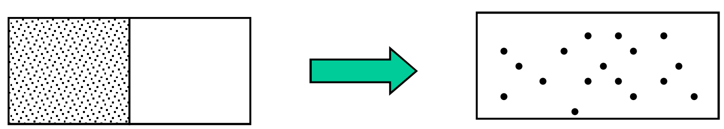
Ordered crystal:
Low entropy



Disordered liquid:
High entropy

$$\boxed{S = S_{term} + S_{konf}}$$

Adiabatic expansion of a gas: $S_{total} = const.$



$$\Delta S_{total} = 0$$

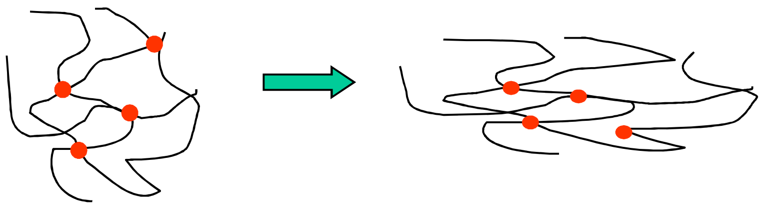
Disorder increases: $\Delta S_{konfig} > 0$

$$\Delta S = \Delta S_{konfig} + \Delta S_{term} = 0 \Rightarrow \Delta S_{konfig} = -\Delta S_{term} \Rightarrow \boxed{\Delta S_{term} < 0}$$

$$\Delta S_{term} = \frac{C_V}{T}\Delta T < 0 \Rightarrow \boxed{\Delta T < 0}$$

T decreases

Adiabatic streching of a rubber band



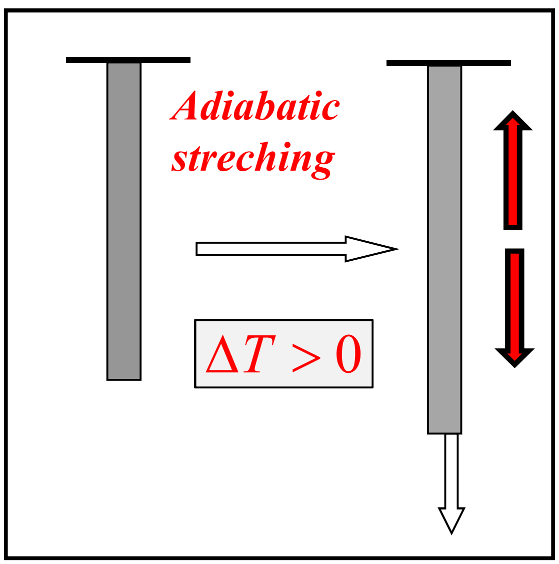
$$S_{total} = const.$$

Order increases: $\Delta S_{konfig} < 0$

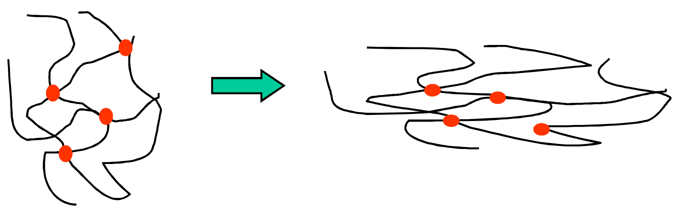
$$\Delta S = \Delta S_{konfig} + \Delta S_{term} = 0 \Rightarrow \Delta S_{konfig} = -\Delta S_{term} \rightarrow \boxed{\Delta S_{term} > 0}$$

$$\Delta S_{term} = \frac{C_V}{T}\Delta T > 0 \Rightarrow \boxed{\Delta T > 0}$$

T increases

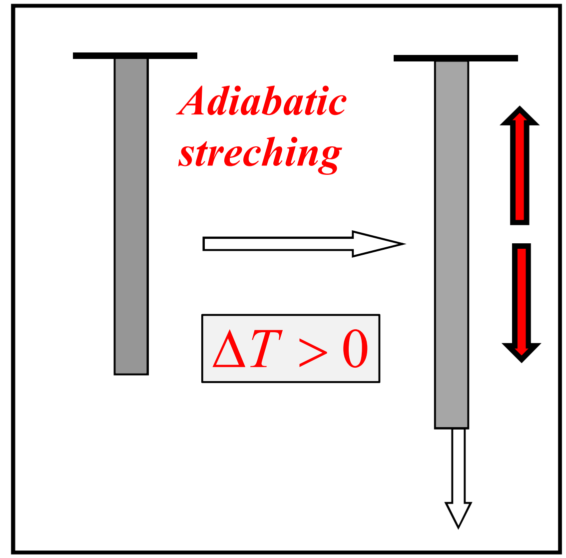


Entropy elasticity of macromolecules



$$\boxed{\Delta S_{konfig} < 0}$$

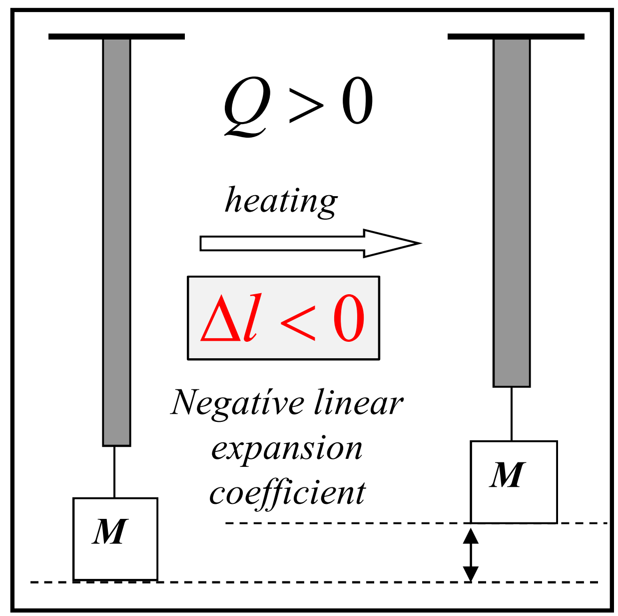
$$\Delta S = \Delta S_{konfig} + \Delta S_{term} = 0 \Rightarrow \Delta S_{term} > 0$$



$$\Delta S_{term} \Rightarrow \Delta S_{konfig}$$

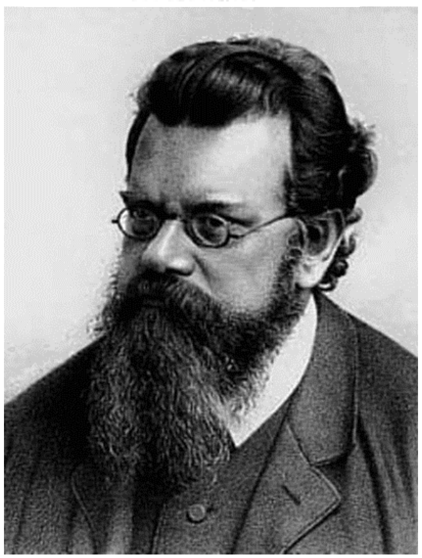
$$\boxed{\Delta S_{konfig} > 0}$$

$$\underbrace{\text{expanded} \Rightarrow \text{coiled}}_{\textbf{contraction}}$$



Is entropy the measure of disorder?

YES!

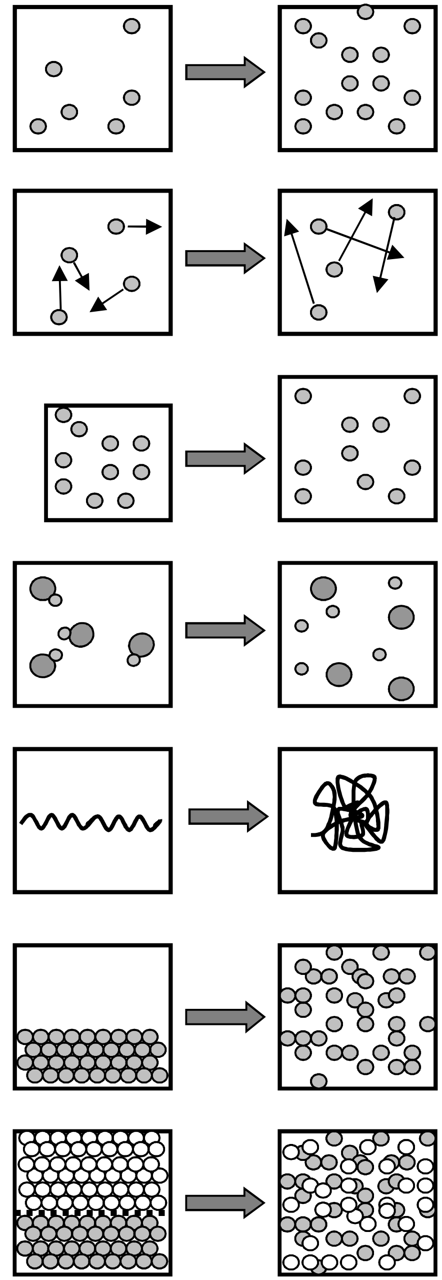


Boltzmann law:

$$\boxed{S = k_B \ln \Omega}$$

$k_B = 1.38 \cdot 10^{-23}$ J/K $\longrightarrow k_B = \dfrac{R}{N_{Av}}$

Thermodynamic probability: **Ω>>*1***



increase of particle number

Increase in temperature

Volume increase

dissociation

Coiling

melting, evaporation

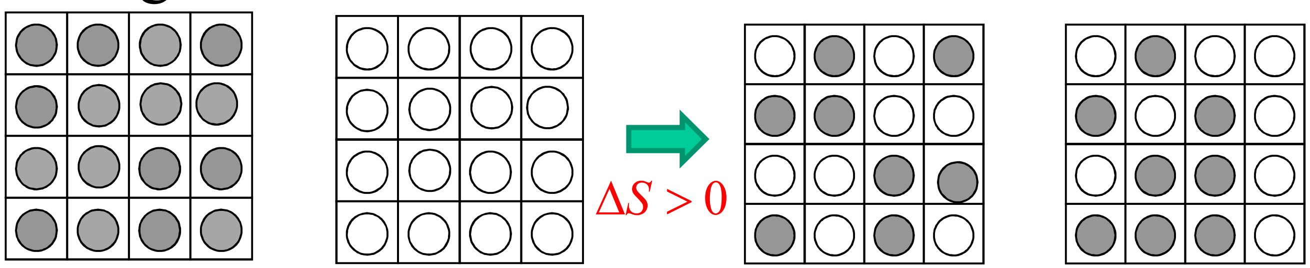
mixing

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

1. example: **macrostate**: concentration
microstate: number of possible molecular arrangements

$$\boxed{\Omega = \frac{16!}{8!8!} = 12870}$$

$$\boxed{x_A = 8/16}$$

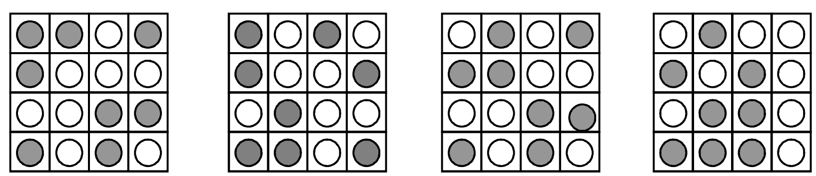


$$\boxed{S = k_B \ln \Omega}$$

$\Omega_A = 1$ $\quad$ $\Omega_B = 1$ $\quad$ $\Omega_{A,B} = 12870$

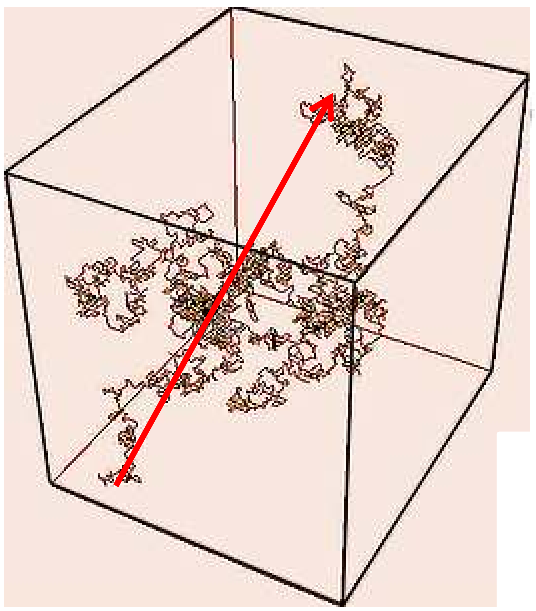
$S_A = 0$ $\quad$ $S_B = 0$ $\quad$ $S_{A,B} = k_B T \ln(12870)$

$$\boxed{\Omega_{A,B} = \frac{(N_A + N_B)!}{N_A! N_B!} = \frac{16!}{8!8!} = 12870}$$



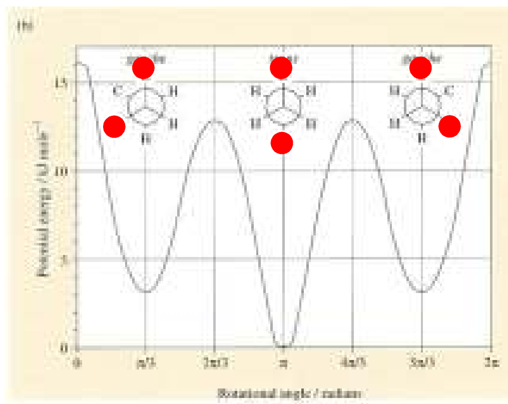
Four different microstates from the overall 12870 states.

2. example: **macrostate:** end-to-end distance
microstate: number of different conformations



coil, *g*

$$\boxed{S = k_B \ln \Omega}$$



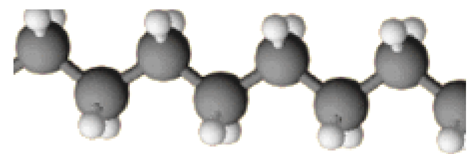
$$N_{C-C} = 10^4$$

$$\Omega_g = 3^{10000}$$

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

$$\boxed{S_g = 10^4 k_B T \ln 3}$$

streched, *ny*



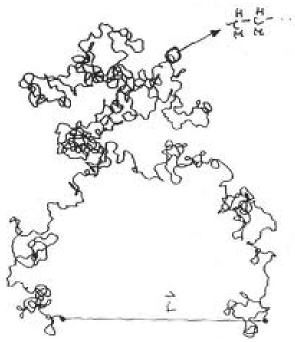
$$N_{C-C} = 10^4$$

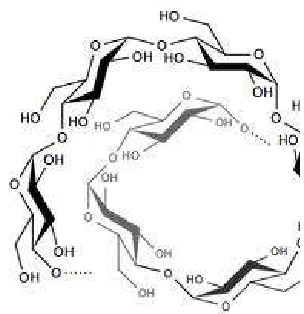
$$\Omega_{ny} = 1$$

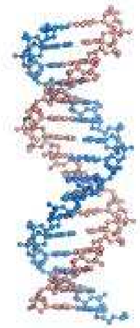
$$S_{ny} = k_B T \ln 1$$

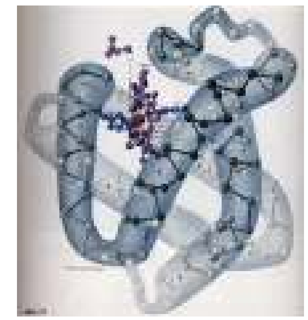
$$\boxed{S_{ny} = 0}$$

constitution - configuration - conformation







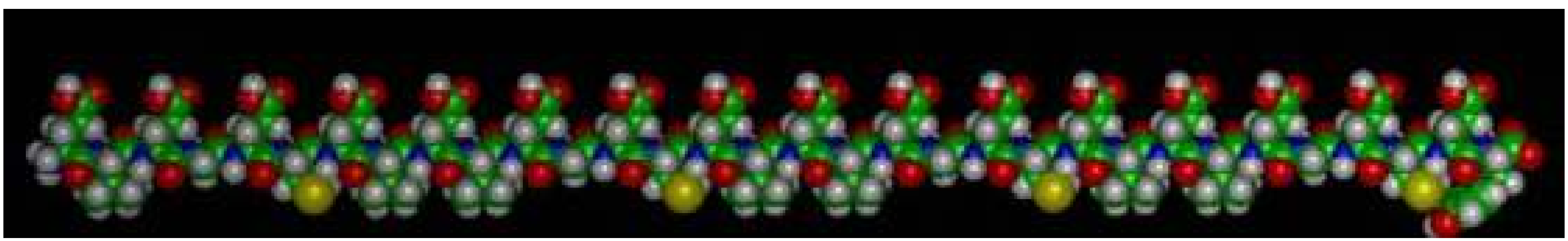


Statistical coil

Ordered structures

High entropy

Much lower entropy



$\Omega=1$

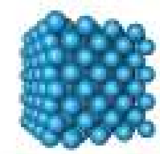
$$\boxed{S_{konf} = 0}$$

Third law of thermodynamics

The entropy of a perfect crystal is zero when the absolute temperature is zero.

→ Nernst's law from the **experiments**

→ From the **theory (**Boltzmann law)

At 0 K thermal motions halt, there are no thermal crystal faults. 

Because of mono-component system, only one type of molecular arrangement is possible., tehererefore $\Omega = 1$

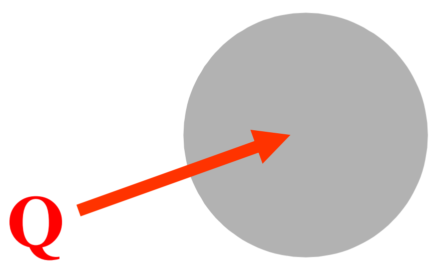
$$\boxed{S = k_B \ln 1 = 0}$$

Environmental effects

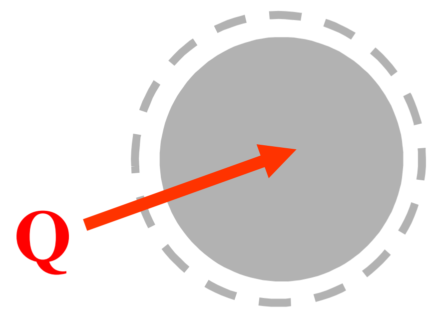
environment →
- isotherm $\quad T = const.$
- isobaric $\quad p = const.$
- izochor $\quad V = const.$
- adiabatic $\quad S = const.$

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

Usable energy $\neq$ Internal energy



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



$V = const.$ $\qquad$ $\boxed{\Delta U = \Delta Q - p\Delta V}$ $\qquad$ $p = const.$

$\Delta U = \Delta Q$ $\qquad$ $\Delta U = \Delta Q - p\Delta V$

A belső energia adott körülmények között hasznosítható része:

Isobar : **H enthalpy**

Isotherm : **F free energy**

Isotherm-isobar: **G free entalpy** (Gibbs free energy)

ENTALPY

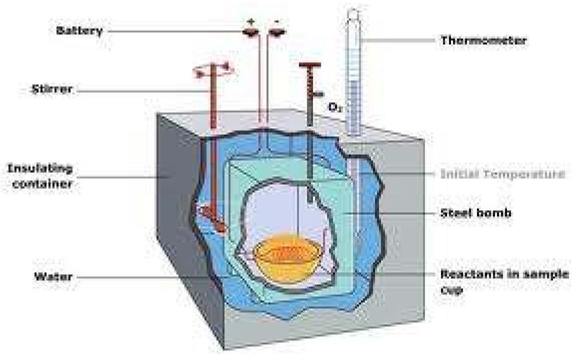
Only thermal and mechanical interactions are considered.

$$\Delta U = T\Delta S - p\Delta V \quad \text{if } p\text{=const.} \;\Rightarrow\; \Delta U = T\Delta S - \Delta\left(pV\right)$$

$$\Delta U + \Delta\left(pV\right) = \Delta\left(U + pV\right) = T\Delta S$$

$$\Delta H = \Delta\left(U + pV\right) = T\Delta S \;\Rightarrow\; \boxed{\text{heat}}$$

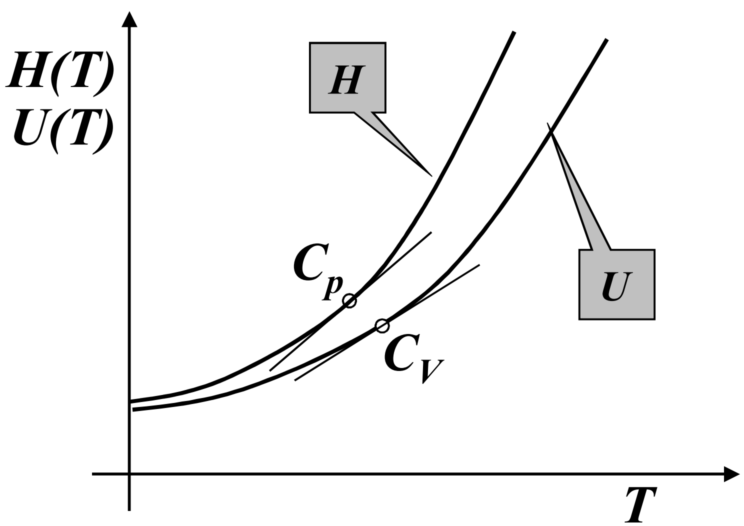
$$\boxed{H = U + pV}$$

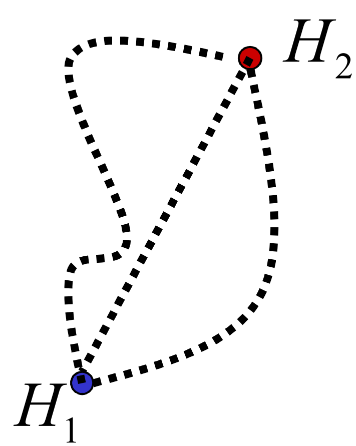


$$\boxed{H = U + pV}$$

Enthalpy is **extenzív** quantity.

state function.





$$\boxed{\Delta H = H_2 - H_1}$$

Hess law!

Free energy

Only thermal and mechanical interactions are considered.

$$\Delta U = T\Delta S - p\Delta V \quad T = \text{const.}, \quad \Rightarrow \quad \Delta U = \Delta(TS) - p\Delta V$$

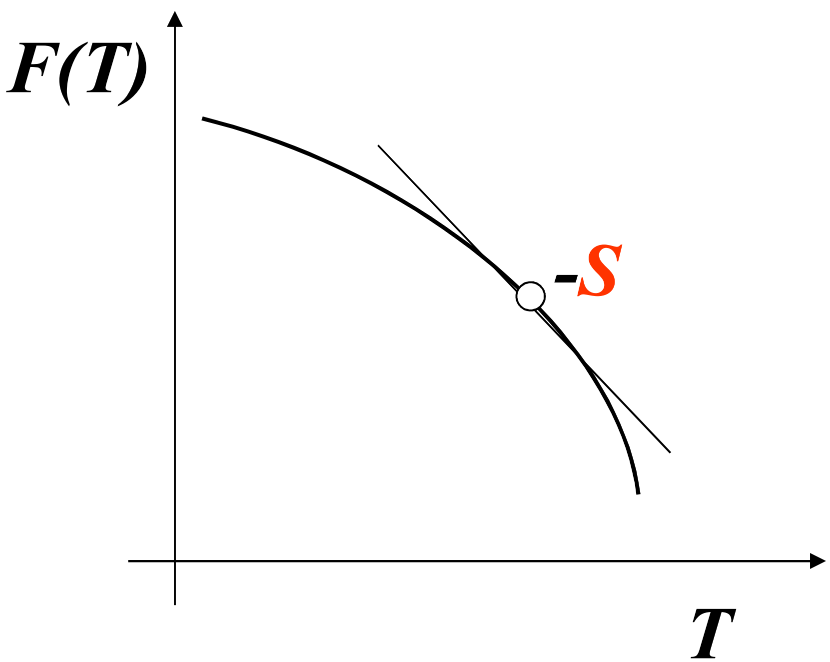
$$\Delta F = \Delta U - \Delta(TS) = -p\Delta V = \Delta W_{mech}$$

$$\Delta F = \Delta(U - TS) = -p\Delta V = \Delta W_{mech}$$

Mechanical work

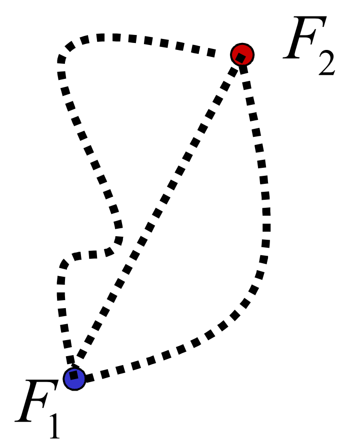
$$\boxed{F = U - TS}$$

$$F = U - TS$$



The free energy is extenzív quantity.

state function.



$$\Delta F = F_2 - F_1$$

Free enthalpy

Thermal, mechanical and chemical interactions are considered.

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

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

ha T és p=állandó, akkor $\Delta U = \Delta(TS) - \Delta(pV) + \sum_{i=1}^{K} \mu_i \Delta n_i$

$$\Delta G = \Delta U + \Delta(PV) - \Delta(TS) = \sum_{i=1}^{K} \mu_i \Delta n_i$$

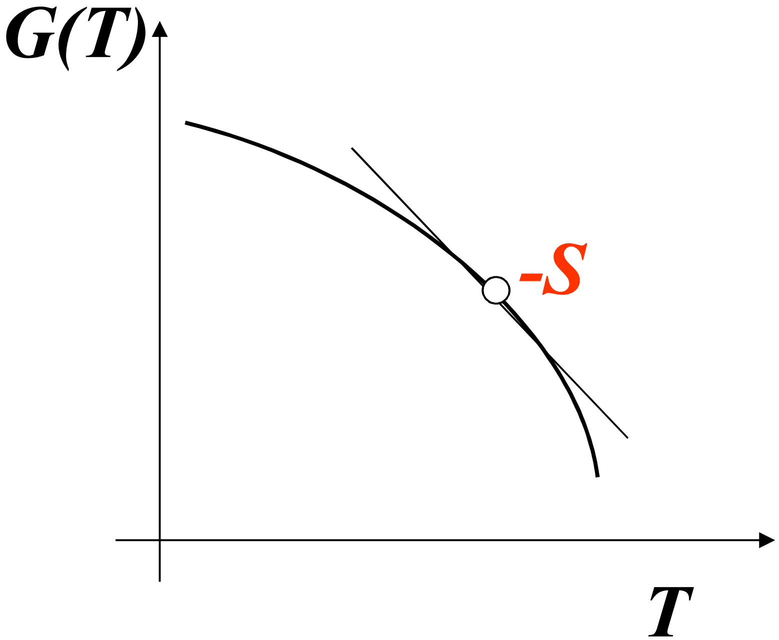
$$\Delta G = \Delta(U + PV - TS) = \sum_{i=1}^{K} \mu_i \Delta n_i$$

$$\Delta G = \Delta(H - TS) = \sum_{i=1}^{K} \mu_i \Delta n_i$$

Chemical work

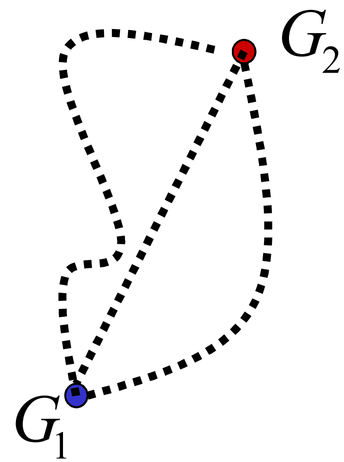
$$\boxed{G = H - TS}$$

$$G = H - TS$$



Gibbs free energy is extenzív quantity.

State function.



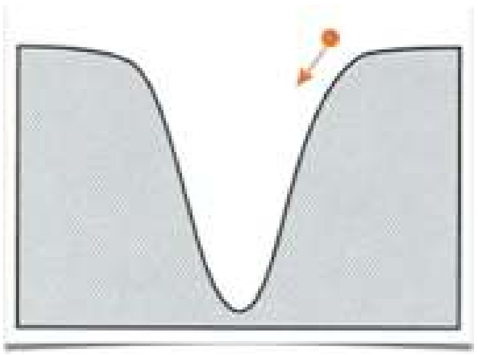
$$\Delta G = G_2 - G_1$$

p

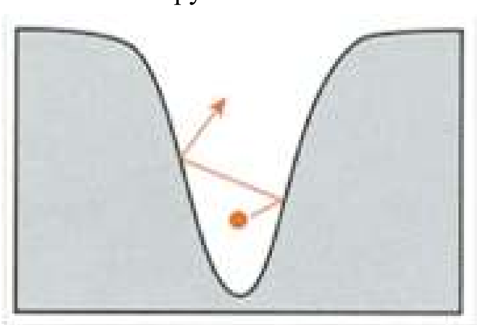
Significance of entropy and gibbs Free energy

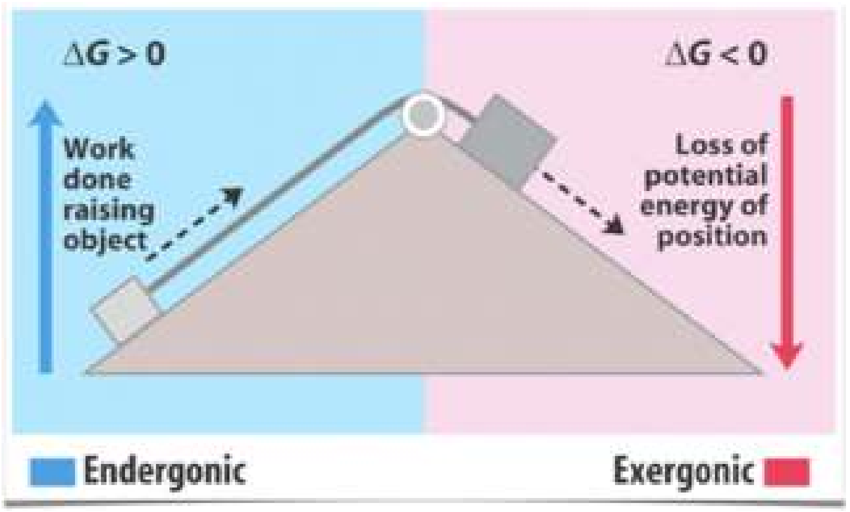
- Spontaneous processes are those, during which Gibbs free energy decreases (ΔG < 0) and the entropy of the universe increases ($S_{tot} > 0$).

Decrease in free energy: stabilizes



Increase in entropy: randomizes

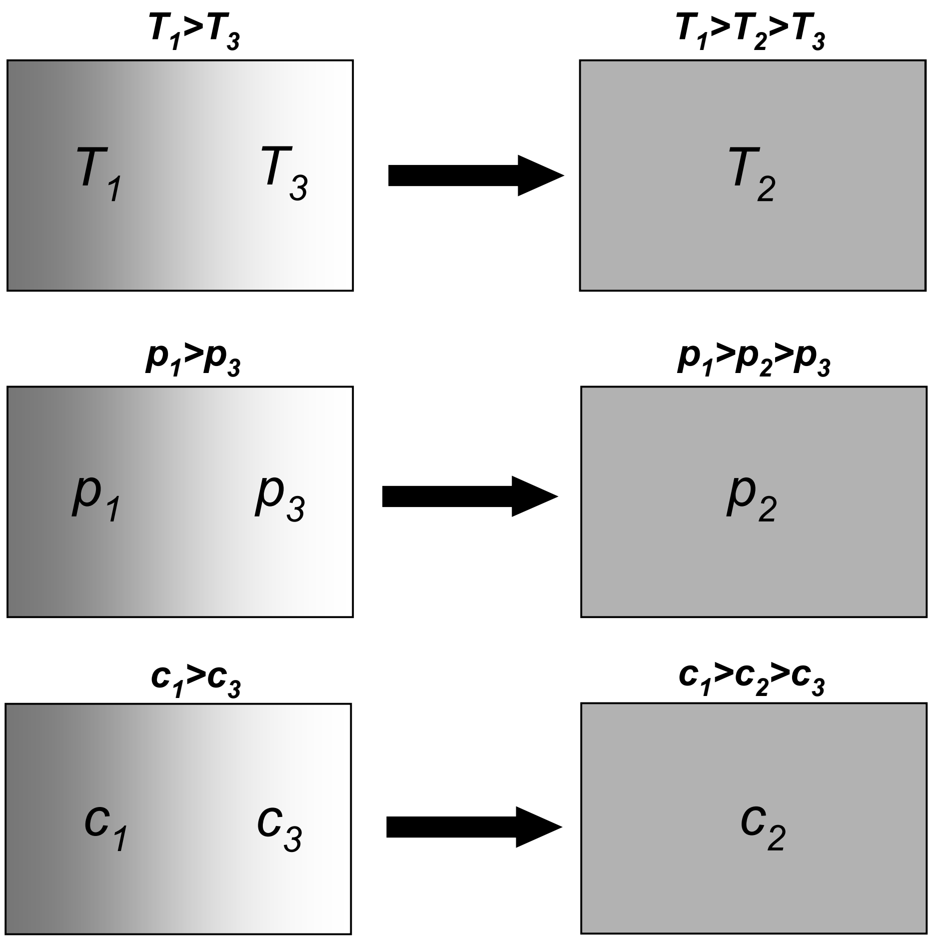




- Useful work is done by exergonic processes.
- Endergonic processes can be driven by coupling to exergonic processes.
- Entropy can be decreased locally.
- Life consumes entropy (its entropy is decreased at the expense of increasing total entropy).

ΔU does not indicate the direction of spontaneous changes!

In isolated system: $\Delta U = 0$

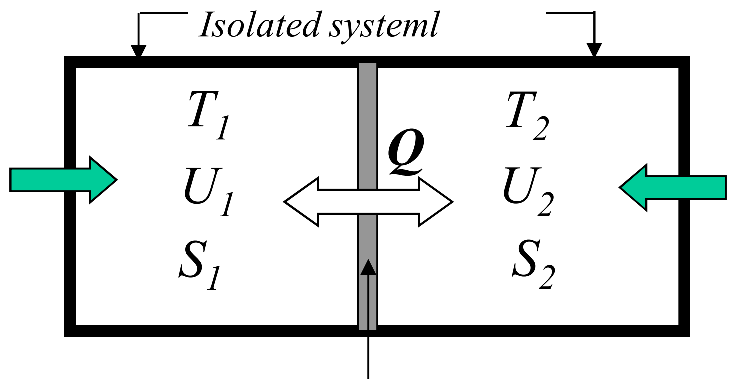


The entropy is not conserve!

Isolated system

Energy is conserv!

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



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

$$U = U_1 + U_2 = const. \qquad \Delta U = 0 \longrightarrow \Delta U_1 = -\Delta U_2$$

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

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

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

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

Direction and driving force of changes

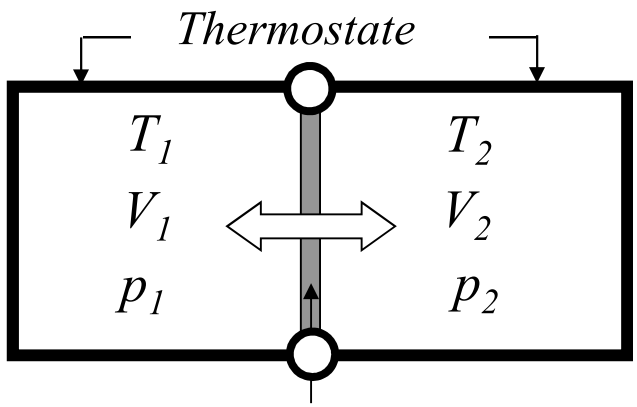
Isotherm system $\Rightarrow$ $F = U - TS$ $\Downarrow$ $\Delta F = -p\Delta V$

$\boxed{F = F_1 + F_2 = ?}$

$\Delta F = \Delta F_1 + \Delta F_2 = ?$

$\Delta F_1 = -p_1 \Delta V_1$ $\Rightarrow$

$V = V_1 + V_2 = const.$



$\Leftarrow$ $\Delta F_2 = -p_2 \Delta V_2$

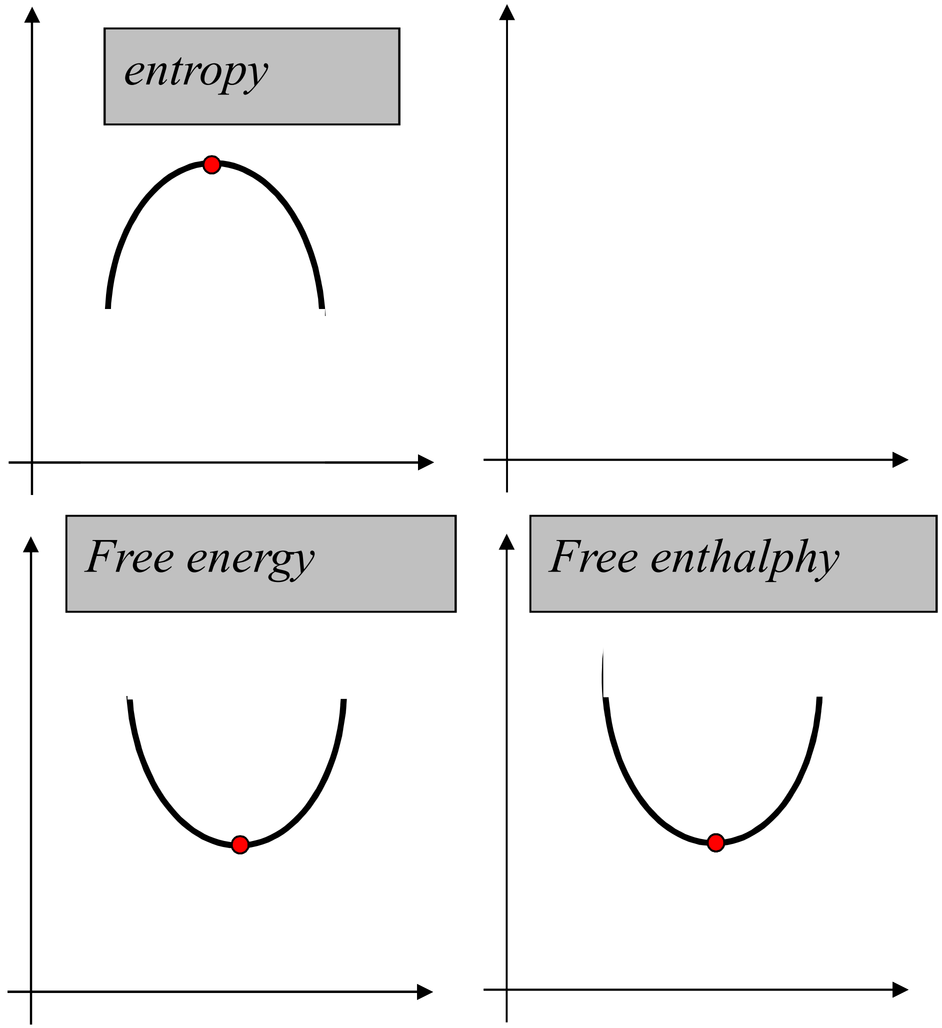
$$\Delta V_1 = -\Delta V_2$$

$$dF = -p_1\Delta V_1 - p_2 \Delta V_2 \qquad \boxed{\Delta F = (p_1 - p_2)\Delta V_2}$$

$p_1 > p_2$	$(p_1 - p_2) > 0$	$\Delta V_2 < 0$	$\Rightarrow$	$\Delta F < 0$
$p_1 < p_2$	$(p_1 - p_2) < 0$	$\Delta V_2 > 0$	$\Rightarrow$	$\Delta F < 0$
$p_1 = p_2$	$(p_1 - p_2) = 0$	$\Delta V_2 = 0$	$\Rightarrow$	$\Delta F = 0$

Direction of change: $\Delta F < 0$

Condition of thermodynamic equilibrium



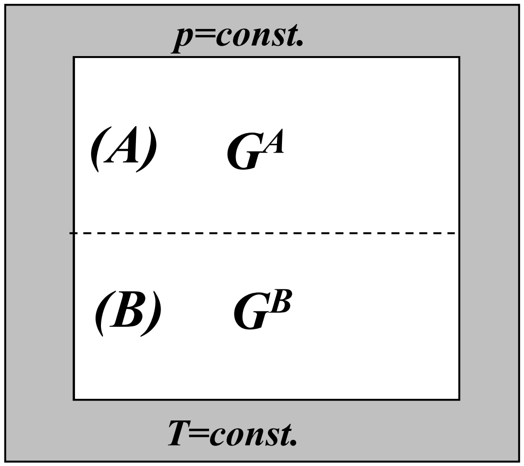
Condition of thermodynamic equilibrium

TD function	*environment*	*„isolation"*	*extremum*	*driving force*
$\boldsymbol{S}(U, V, n)$	isolated	$\boldsymbol{U, V, n}$	maximum	$\boldsymbol{S} > \mathbf{0}$
$\boldsymbol{U}(S, V, n)$	-	$\boldsymbol{S, V, n}$	minimum	$\boldsymbol{U} < \mathbf{0}$
$\boldsymbol{H}(S, p, n)$	mechanical	$\boldsymbol{S}$, **-**, $\boldsymbol{n}$	minimum	$\boldsymbol{H} < \mathbf{0}$
$\boldsymbol{A}(T, V, n)$	thermal	**-**, $\boldsymbol{V, n}$	minimum	$\boldsymbol{F} < \mathbf{0}$
$\boldsymbol{G}(T, p, n)$	Mechanical and thermal	**-**, **-**, $\boldsymbol{n}$	minimum	$\boldsymbol{G} < \mathbf{0}$

The uniform distribution of intensive variable is the necessary requirements of thermodynamic equilibrium.

Equilibrium between phases (A és B)

One component, two phases



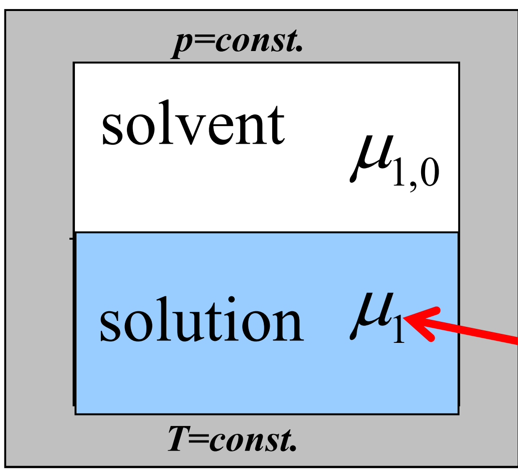
$$\boxed{G = G^A + G^B}$$

Equality of the the molar free enthalphy

(Gibbs free energy)!

$$\boxed{G_m^A \equiv G_m^B}$$

Two components, two phases



Equality of the chemical potentials

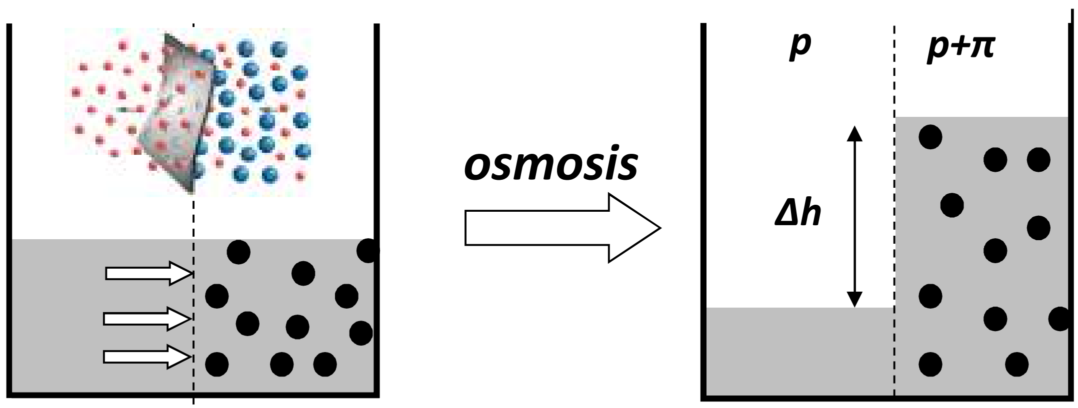
$$\boxed{\mu_1^L = G_m^S}$$

$$\Downarrow$$

$$\mu_1 = \mu_{1,0}(p) + RT \ln x_1$$

Osmosis

Movement of water across **semi-permeable** membrane from a region of high to a region of low impermeant solute concentration.



van't Hoff equation

$$\pi_{id} = RTc_m$$

Molar concentration of solute

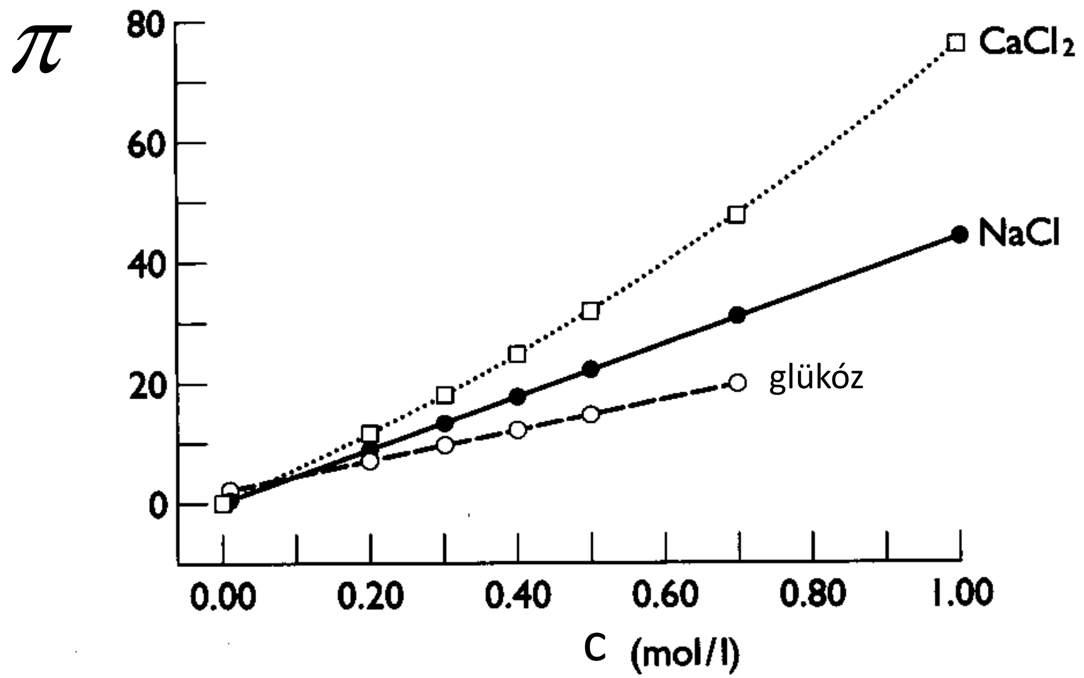
$$\pi_{id} = \frac{RT}{M_2} c_2$$

Osmosis: colligative property

$$n = n_0 \alpha \nu + n_0 (1-\alpha) = n_0 [1 + \alpha(\nu - 1)]$$

$$\boxed{\pi = \frac{RT}{M_2} c_2 \cdot i}$$

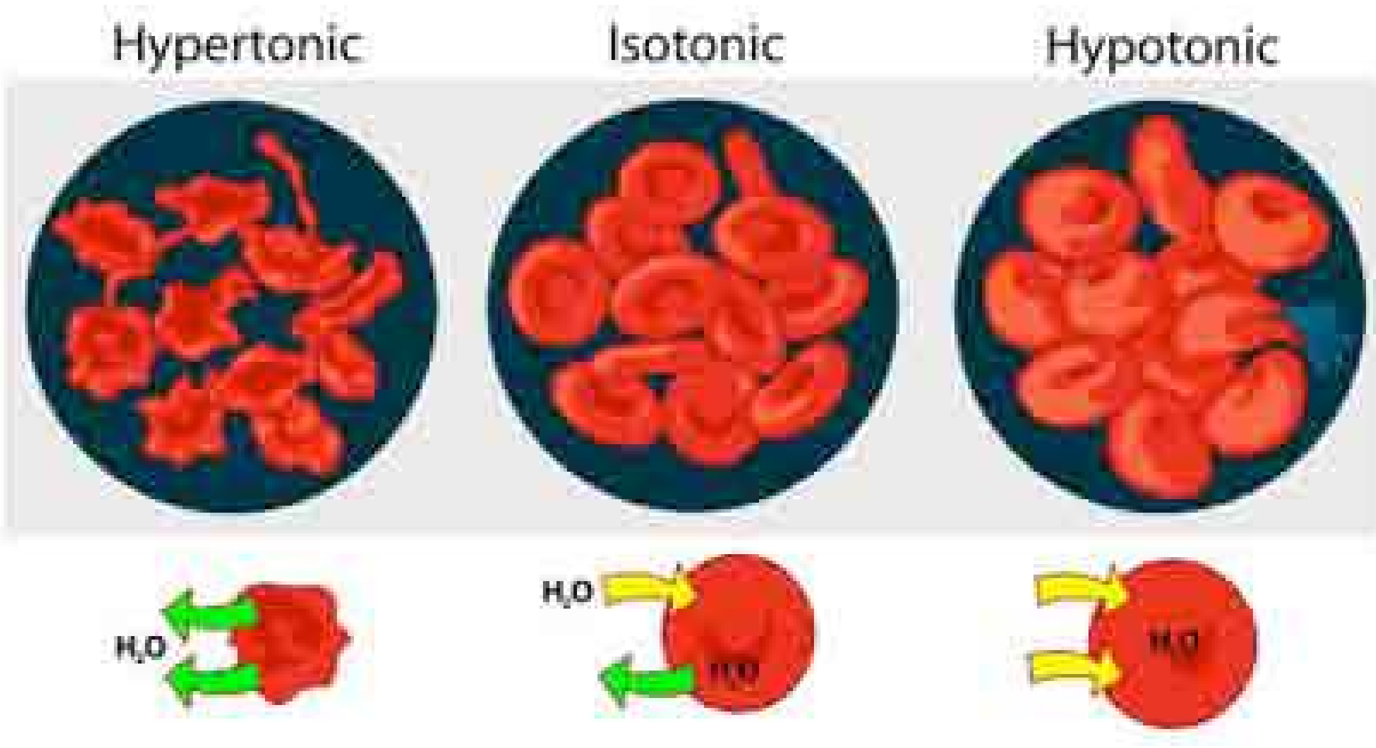
$$i = [1 + \alpha(\nu - 1)]$$



If the osmotic pressure is equal in two different solution **: isotonic solutions**

Solutions are isotonic with respect to mammalian cytoplasm

3,8 m%-os Na-citrát oldat,
5,5 m%-os glükóz oldat,
0,87 m%-os NaCl oldat.



DRIVING FORCE OF CHEMICAL REACTIONS

$$\Delta_r G = G_{prod.} - G_{react.}$$

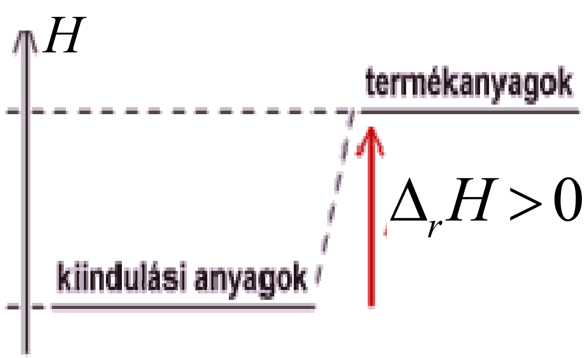
$$\boxed{\Delta_r G = \Delta_r H - T\Delta_r S}$$

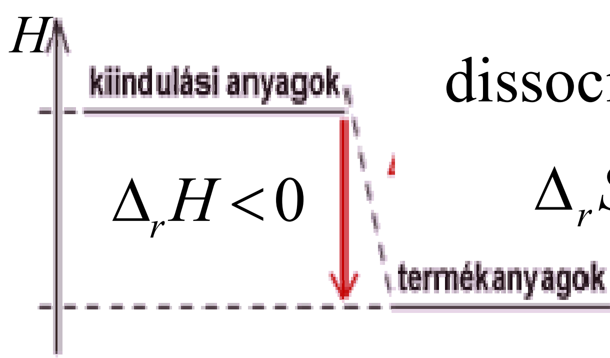
Heat of rection

Entropy of rection

endotherm

exotherm





Change in molecular order

dissociation

ring formation

$\Delta_r S > 0$

$\Delta_r S < 0$

Reaction and chemical equilibrium

Reaction

$$\boxed{\Delta_r G < 0}$$

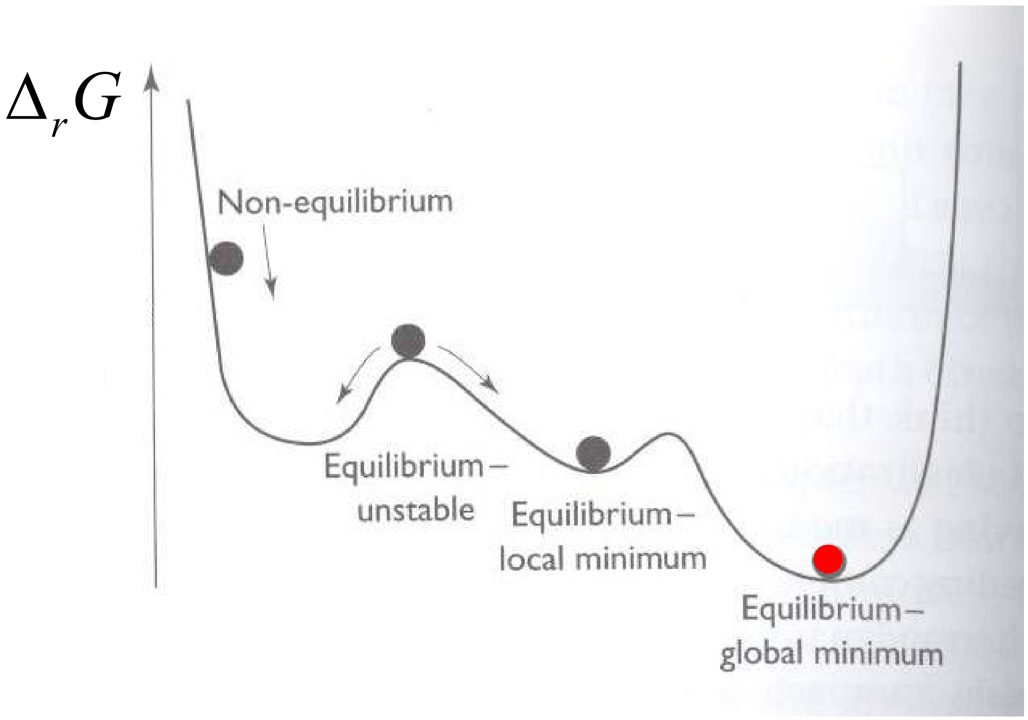
$$R_e \rightarrow T_e$$

equilibrium

$$\boxed{\Delta_r G = 0}$$

$$R_e \rightleftarrows T_e$$

$$\underbrace{\nu_A A + \nu_B B}_{R_e} = \underbrace{\nu_C C + \nu_D D}_{T_e}$$



Reaction and chemical equilibrium

reaction

$$\boxed{\Delta_r G < 0}$$

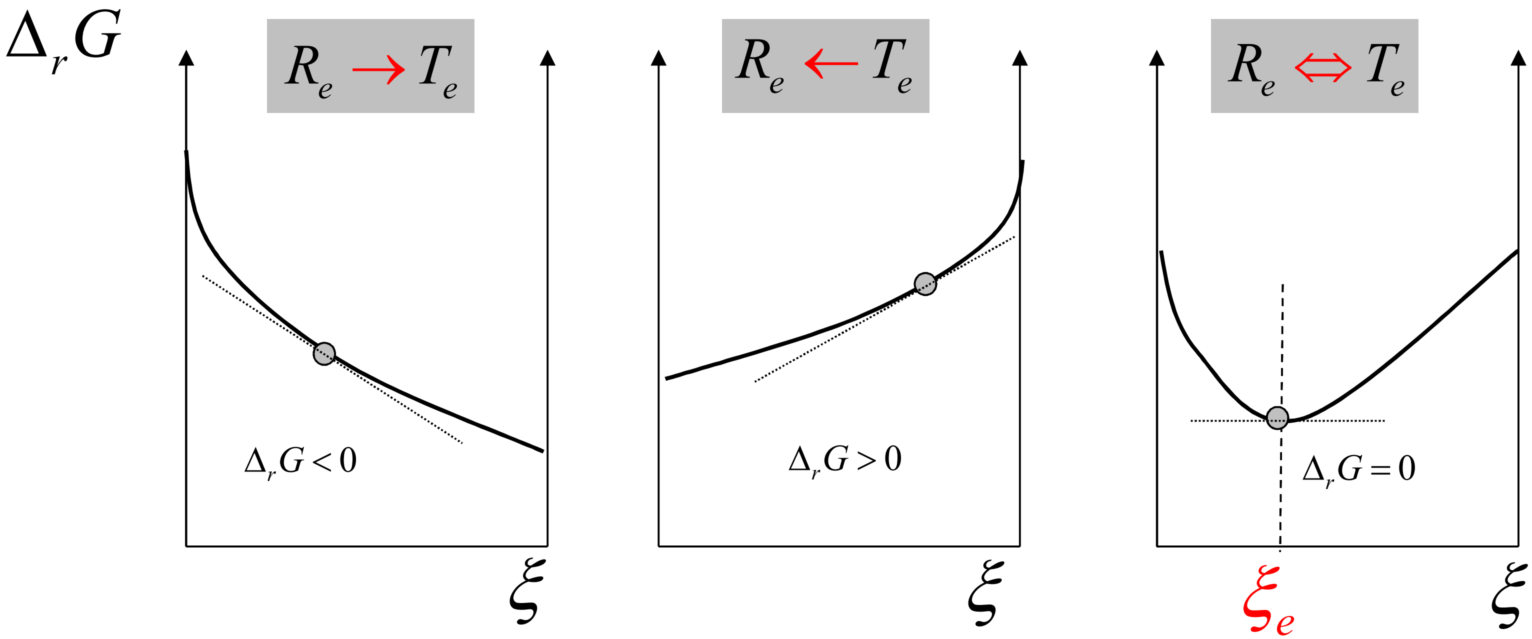
$$R_e \rightarrow T_e$$

equilibrium

$$\boxed{\Delta_r G = 0}$$

$$R_e \Leftrightarrow T_e$$

$$\underbrace{\nu_A A + \nu_B B}_{R_e} = \underbrace{\nu_C C + \nu_D D}_{T_e}$$

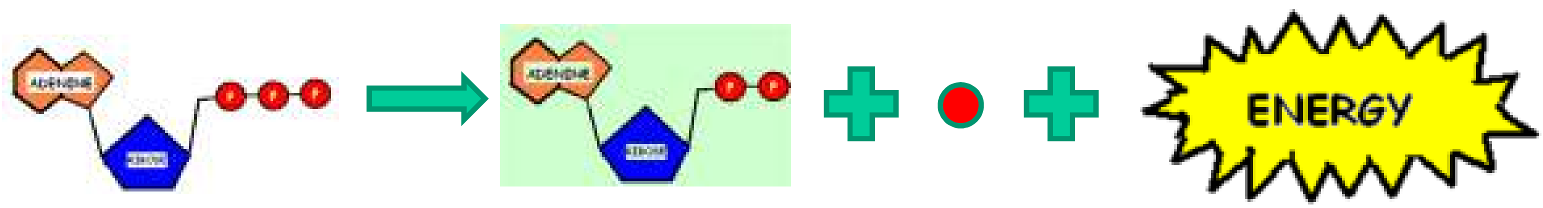


Coupled reactions

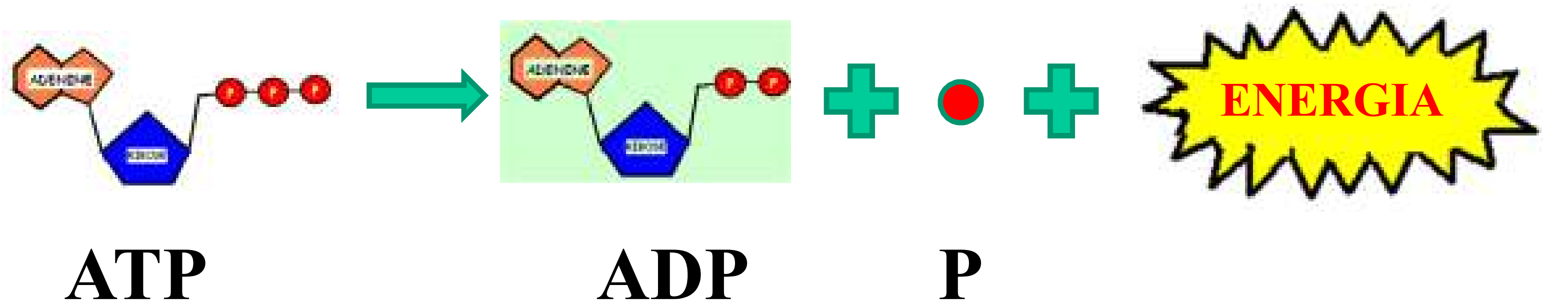
$$A + B \rightleftharpoons C + D \qquad \Delta_r G^o = +20 \text{ kJ/mol}$$

$$C \rightleftharpoons E \qquad \Delta_r G^o = -30 \text{ kJ/mol}$$

$$A + B = E + D \qquad \Delta_r G^o = -10 \text{ kJ/mol}$$



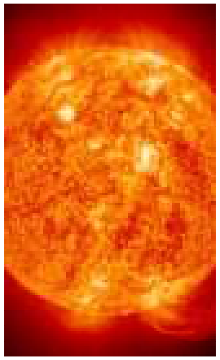
ATP **ADP** **P**



ENERGY

- Synthesis of cellular macromolecules
- Synthesis of membranes, phospholoipids and metabolites
- Cellular movements
- Transport of molecules against concentration gradient
- Generation of an electric potential across membrane
- Heat

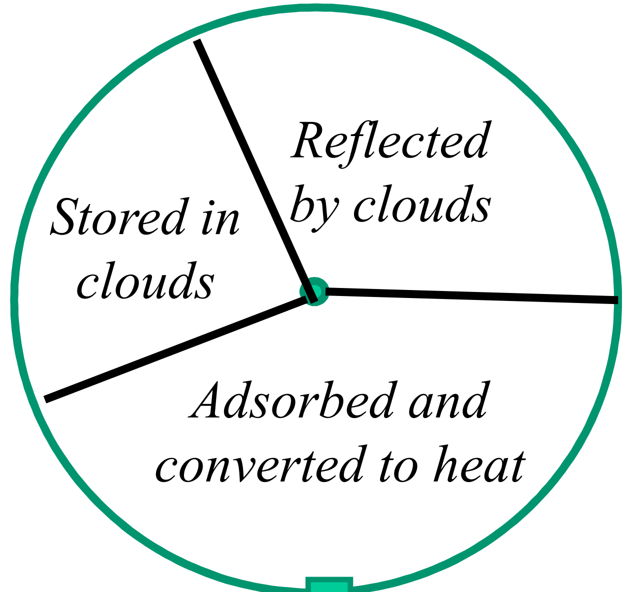
Energy transformation



$5 \cdot 10^{18}\ MJ / év$

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

earth



photosynthesis
0,025%

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

starch *glycogen* **cellulose**

Biological macromolecules

First law of bio-thermodynamics

Change in internal energy

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

Heat of metabolism

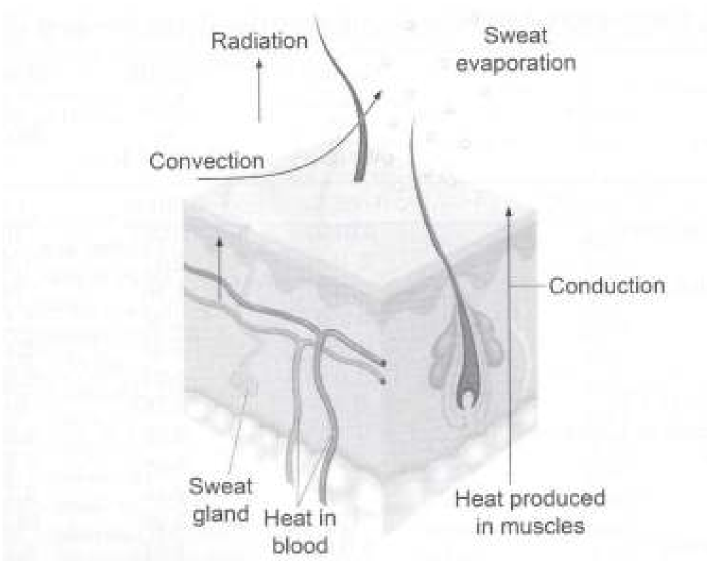
Heat lost

Mechanical work

bio-synthesis

external

internal



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

Measuring of metabolic heat

Direct calorymetry

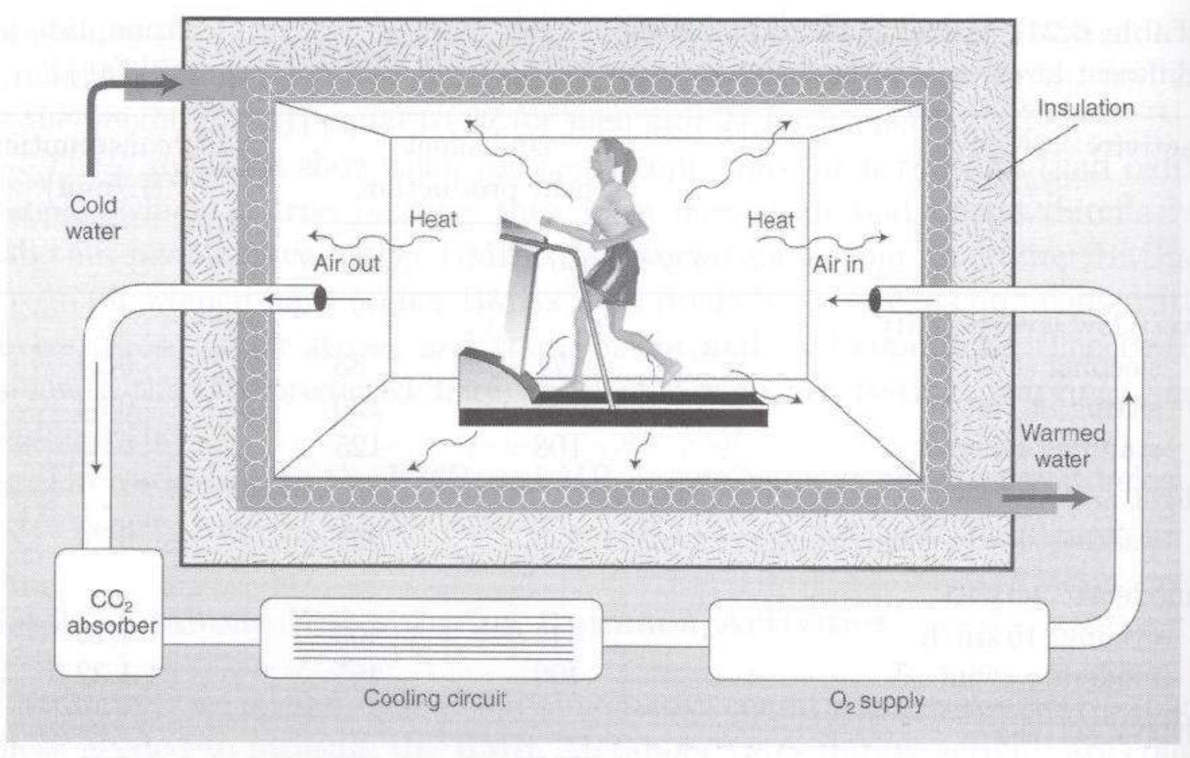
$$\boxed{\Delta Q = Q_{metabolism} + Q_{lost}}$$

Indirect calorymetry

Oxygen consumption or
release of CO2
Both can be related to heat
production

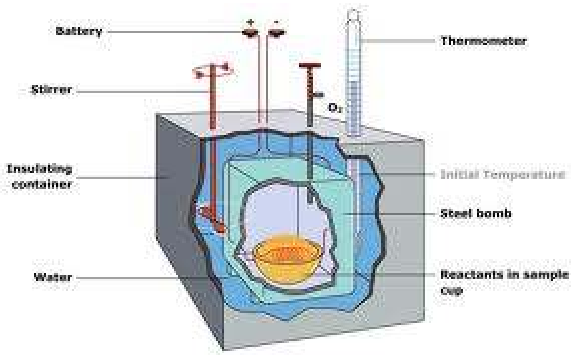
Bond energies → heat
→ movement
→ (end)products

Direct calorymetry

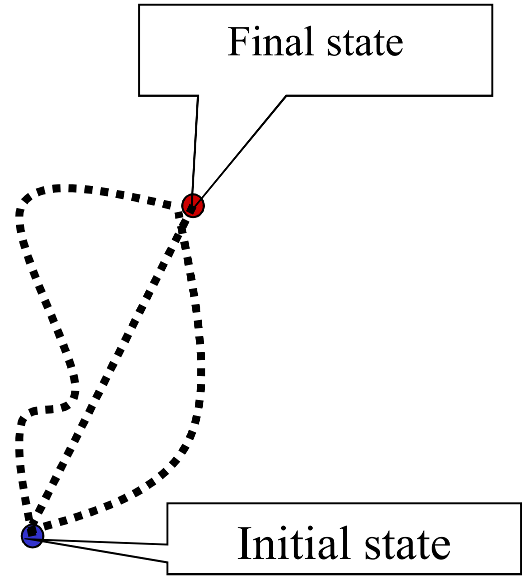


Metabolic rate is determined by the measured temperature change in the air and the water flowing through the chamber

Indirect calorymetry



Hess law:



$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O \qquad \Delta H = +2817 \text{ kJ}$$

$$C_6H_{12}O_6 + 36ATP = 36ADP + P_i \qquad \Delta H = +1757 \text{ kJ}$$

$$\eta = 61 - 65\,\%$$

Oxidation of 1 mol glucose requires 6 mol=134,46 *L* oxygen and release $\Delta H = +2817$ kJ heat.

Consumption of 1 L oxygen corresponds to 21 kJ energy.

Basal metabolic rate: **BMR**

$$BMR = \left.\frac{\Delta Q}{\Delta t}\right|_{rest}$$

$$BMR \propto m_b^{3/4}$$ Kleiber law

BMR *decreases with age!*

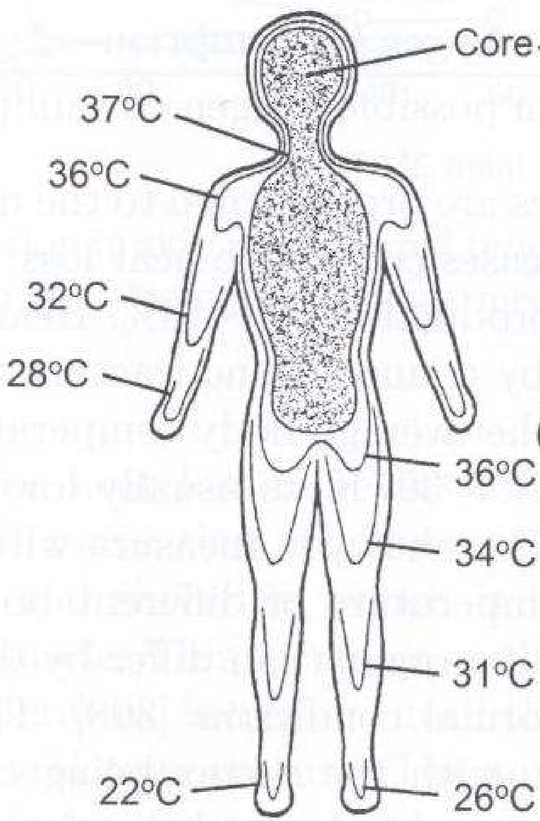
$m_b = 70$ kg 7029 kJ/day 293 kJ/hour 81 W man

60 W women

Energy and oxygen consumption:(MR)

sleeping	83 W	O_2 :	0,24 L/min
walking	265 W	O_2 :	0,76 L/min
cycling	400 W	O_2 :	1,13 L/min

Temperature distribution in body → Far from thermodynamic equilibrium!



(a) Cold room (~5°C)

Formation of metabolic heat at rest

brain	*25%*
heart	*15%*
skeletal muscle	*25%*
abdominal viscera	*25%*
kidney	*6%*
skin	*4%*

Thermal characterisation of an average body:

Specific heat: 3,47 kJ/kgK

heat capacity (70 kg) : 243 kJ/C^o

$$\color{red}{\Delta Q = C \cdot m_b \cdot \Delta T}$$

$$\frac{\Delta Q}{\Delta t} = C \cdot m_b \cdot \frac{\Delta T}{\Delta t}$$

$$\frac{\Delta T}{\Delta t} = \frac{1}{C \cdot m_b} \cdot \frac{\Delta Q}{\Delta t} = \frac{1}{C \cdot m_b} \cdot BMR$$

$$\boxed{\frac{\Delta T}{\Delta t} = \frac{BMR}{C \cdot m_b}} \Rightarrow \frac{\Delta T}{\Delta t} = 1.2 \ C^o/\mathrm{h}$$

Without heat lost!

$$\boxed{Q_{lost} = \underbrace{Q_{radiation}}_{54\text{-}60\ \%} + \underbrace{Q_{convective} + Q_{conductive}}_{25\ \%} + \underbrace{Q_{evaporation}}_{7\ \%} + \underbrace{Q_{breathing}}_{14\ \%}}$$

In case of training

$$\frac{\Delta Q}{\Delta t} = f \cdot BMR$$

$$\frac{\Delta T}{\Delta t} = f \cdot \frac{BMR}{C \cdot m_b} \approx 1,2\, f\, C^o / h$$

$$\underset{activity}{0 < f < 20}$$

activity	*f*
sleeping	1
sitting	1.5
standing	1.7
walking	4.7

Fizikai aktivitás esetén

$$\frac{\Delta Q}{\Delta t} = f \cdot BMR$$

$$\frac{\Delta T}{\Delta t} = f \cdot \frac{BMR}{C \cdot m_b} \approx 1,2\, f C^o / h$$

$$0 < f < 20$$

Fizikai aktivitás

aktivitás	*f*
alvás	1
ülés	1,5
állás	1,7
gyaloglás	4,7