SEMMELWEIS UNIVERSITY

Department of Biophysics and
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Lágy Anyagok
Laboratóriuma

Thermodynamics in Biophysics
(**Bio-thermodynamics**)

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$$\Delta U = \Delta Q + \Delta W$$
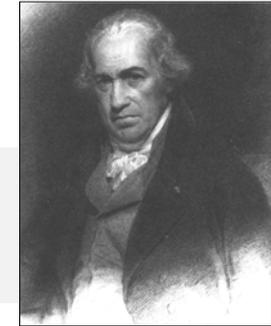
Thermodynamics, initially applied for **heat engines** to study thermal processes, has become the science of **energy exchange and equilibria**.

James Watt (1736-1819) Scot inventor

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.


(A.L. Lavoisier 1743-1794)

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

Rubner stated in 1894 for the first time that laws of thermodynamics apply to living systems.

WHAT IS LIFE?
The Physical Aspect of the Living Cell
BY
ERWIN SCHRÖDINGER
SENIOR PROFESSOR AT THE DUBLIN INSTITUTE FOR ADVANCED STUDIES
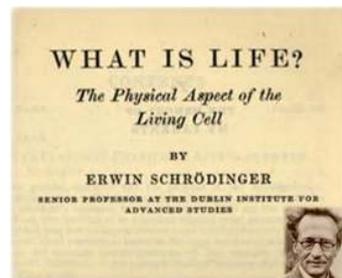
Phenomenological- and **statistical thermodynamics**

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

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,

Main issues: identification of the
- ✓ **Direction of energy exhange**,
- ✓ **driving forces**, and
- ✓ **influencing the efficiency and direction**

of changes and processes occuring during interactions of a system with its surroundings.

Generalized laws apply to
biological, societal, economical, monetary and other… systems.

Thermodynamics today

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


Biological systems

Macromolecular systems

Economic system

Social system

Financial system

Organ (heart)

Chromatin

Thermodynamic bodies in interaction

TERMODINAMIKAI RENDSZER

SURROUNDINGS

SURROUNDINGS

Permeable or isolating boundary
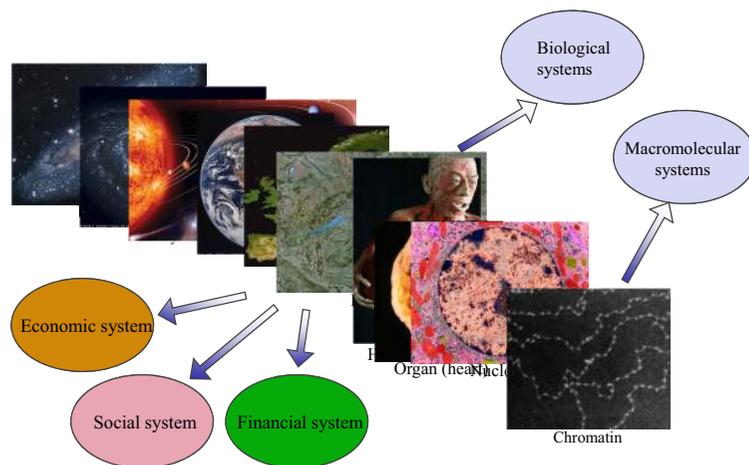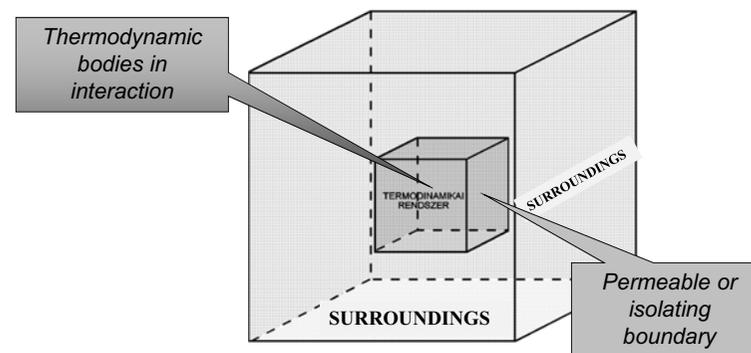
Heat and dynamics have no more primary importance today!

TYPE OF THERMODYNAMIC SYSTEMS

system

Time-independent

Time-dependent

equilibrium

stationary

Non-equilibrium

Chemical reaction

Transport processes

matter
heat
momentum

Reaction kinetics
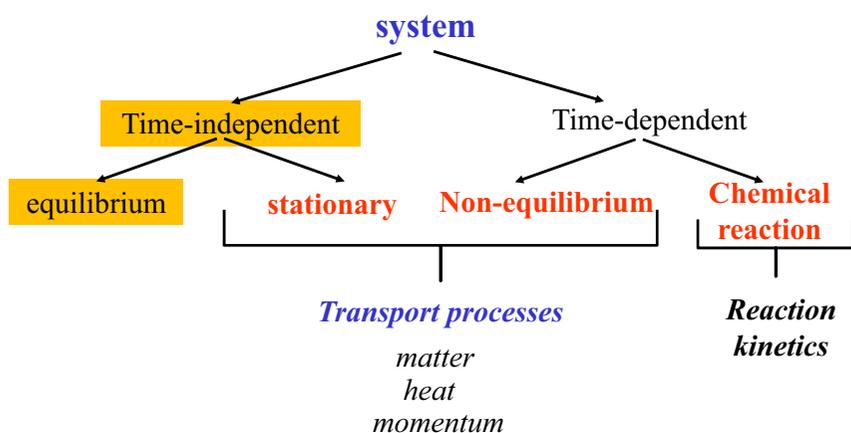
**Spontaneous process** ⟶ **equilibrium**

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

- In many cases, in **equilibrium state** the intensive variables are uniform throughout the system.

- In *non-equilibrium state* the intensive variables vary in space and/or time.

Thermodynamic systems and their surroundings

energy   matter

isolated   closed   open

Biological system

energy

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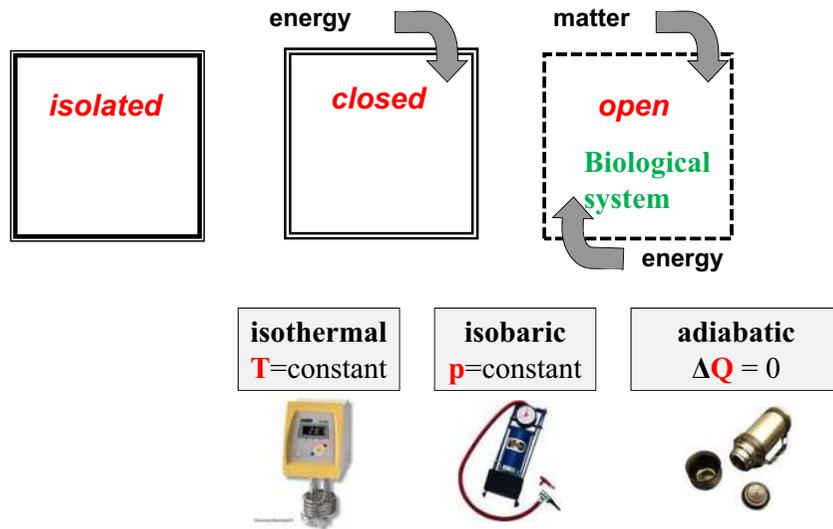
- An *isobaric* process is one in which the pressure is constant.
- An *isochoric* process is one in which the volume is constant.
- An *isothermal* process is one in which the temperature is constant.
- An *adiabatic* process is one in which no heat enters or leaves the system; i.e. Q = 0.

- *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…,

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BIOLOGICAL THERMODYNAMIC SYSTEM

O_2

heat

food

BODY

metabolism

Work *(motion)*

heat

end product

Heat plays a crucial role!

$0 \; C^o \longrightarrow T \longrightarrow 42 \; C^o$

matter

Biological system
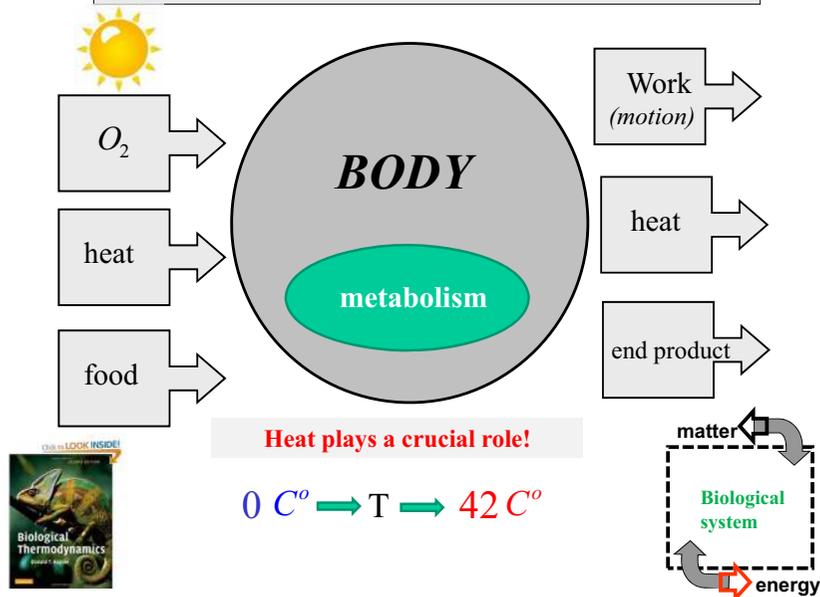
energy

Law of conservation of energy

Leibniz (1676-1689) has observed that for many mechanical systems, the kinetic energy is conserved.

*Newton* and *Descartes* have postulated the law of conservation of impulse.

Rumford has noted in 1798 that the drilling of gun barrel leads to the formation of heat: mechanical work can be transformed into heat!

Mayer realized that heat and work are two forms of energy.

Joule has carried out experiments to determine the work equivalent of heat in 1843.

*Helmholtz* has stated the law of energy conservation in 1847.

ENERGY

potential   kinetic   **internal**

$$E = E_{pot} + E_{kin} + U$$

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.
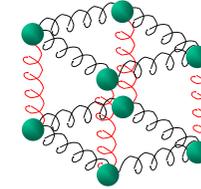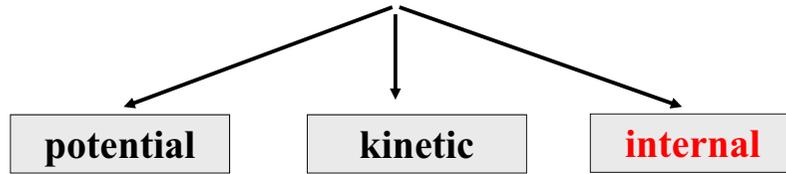

$$E = E_{pot} + E_{kin} + U$$

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

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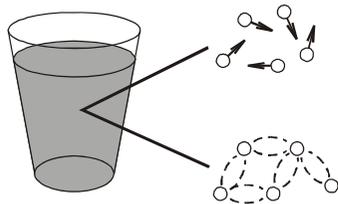
Molecular potential- and kinetic energies are in the internal energy.

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

---

internal energy

Internal energy is the sum of chemical structure-related molecular kinetic and interaction energy.

Forms of internal energy compared at equal temperature

Standardised internal energy

monoatomic ideal gas — *Ideal gas of more than one atom* — *liquid and/or solid*

Rotational and vibrational energy — *translational energy* — **Kinetic energy**

Interaction energy
Van der Waals H-bond

interactions between atoms and molecules

Basic molecular interactions

Ion-dipole — H bond — Dipole-dipole

Na⁺ / Methanol (CH₃OH) / H_2O / CH₃OH / Chloroform (CHCl₃)

Cl⁻ / Hexane (C_6H_{14}) / Acetone (C_3H_6O) / C_6H_{14} / Octane (C_8H_{18}) / C_6H_{14}

Ion-induced dipole — Dipole-induced dipole — Dispersion

Basic molecular interactions

ionic — *dipole* — *induced dipole*

indukált dipólus

Hydrophobic interactions (clustering of hydrophobic groups away from water) and van der Waals interactions

Polypeptide backbone

Hydrogen bond

Disulfide bridge

Ionic bond
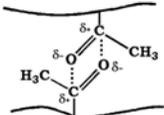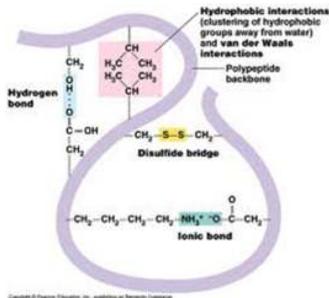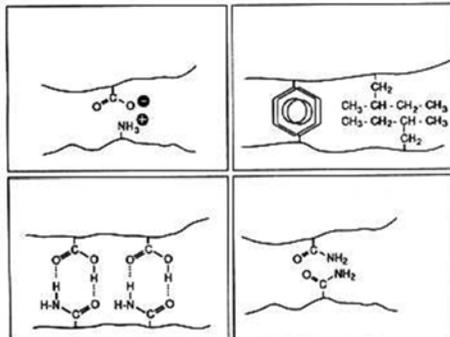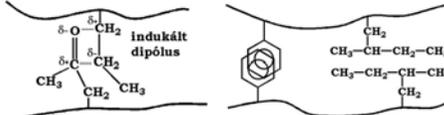
| Interaction	interaction energy in RT units
Chemical reaction	40 - 200
ion-ion	80 - 100
ion – dipole	10 - 20
H-bond	10 - 15
dipole –dipole	0.5 – 2
induced dipole – dipole	0.3 – 2
induced dipole – induced dipole	0.2 - 2

The molar internal energy of an ideal gas (in RT units):

$$U_m = \frac{3}{2}RT$$

Change of internal energy

ΔT

thermal

Δp

mechanical → internal energy ← chemical

ΔV

n

Δn

others
pl.
surface
electric

$+ + + + + + + + +$ $\Delta \Phi$
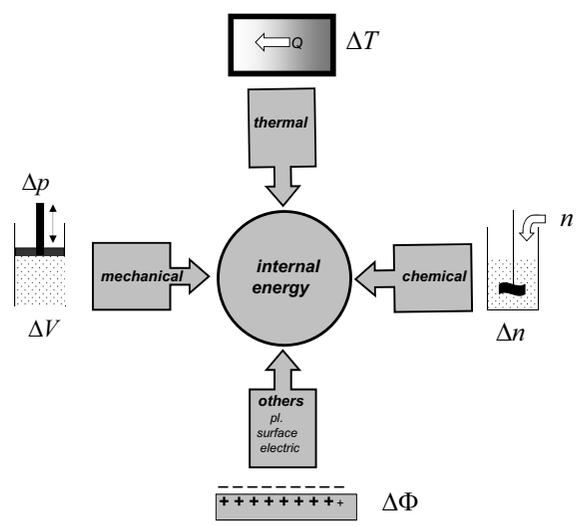
Internal energy is an extensive quantity.

Internal energy is a state function.

Final state

Initial state
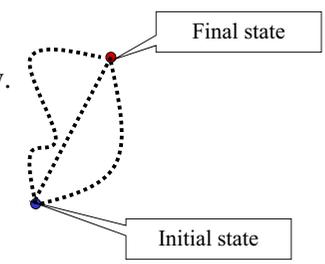
The absolute value of internal energy is unknown.

Internal energy changes when

- temperature changes,
- molecular structure or the phase changes,
- intermolecular interactions occur,
- electron orbital gets into an exited state.

Change of internal energy

Elementary energy changes

$\Delta X > 0$
$\Delta X < 0$

Sign convention!

thermal | mechanical | surface | chemical | other
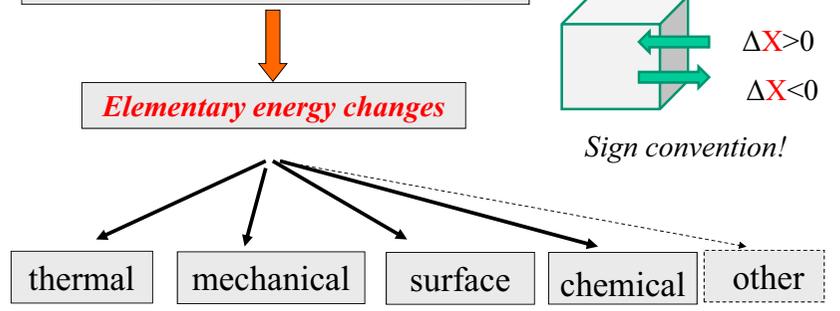
The internal energy change is the sum of individual energy changes (as many as there are interections between the body and surroundings).

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

Mechanical interactions (1)

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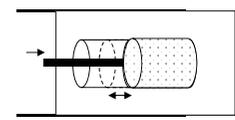
$$W_{mech} = -f(x) \cdot \Delta x$$

- Volumertic work

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

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

Slide 1 (top-left):

Each elementary energy exchange can be described asaproduct of *intensive* *and* *extensive variable.*

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

individual energy transfer

intensive variable

extensive variable

Slide 2 (top-right):
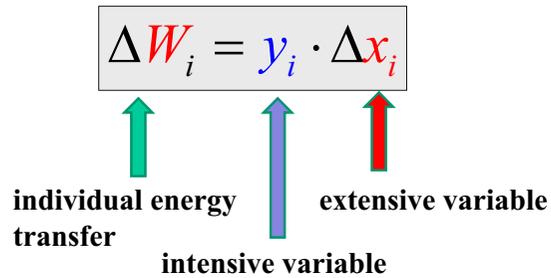
Elementary energy exchanges: $\boxed{W_i = y_i \cdot \Delta x_i}$

Extensive variable	Intensive variable	Product: energy change
Volume (V)	Pressure (p)	Volumetric work ($p\Delta V$)
Matter (n)	Chemical potential (μ)	Work of material transport
Charge (Q)	Electric potential (φ)	($\mu\Delta n$)
?????	Temperature (T)	**Hea**t **????**

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

Slide 3 (bottom-left):

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

y : intensive variable
x : extensive variable

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

volumetric

electric

chemical

mechanical

surface

magnetic
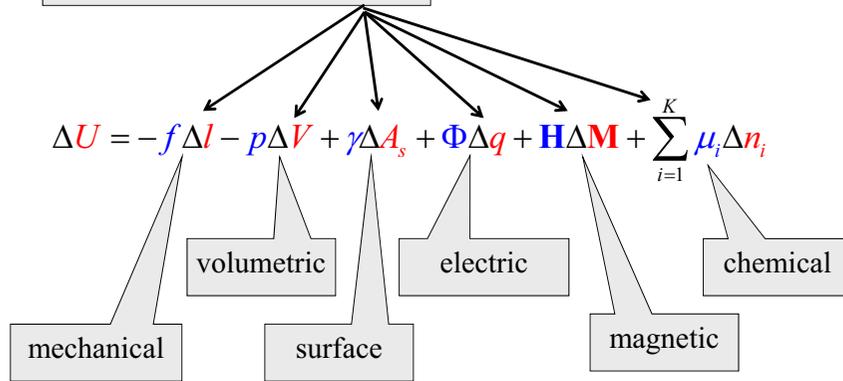
Where is thermal interaction??? y =T x = ?

Slide 4 (bottom-right):

$$\Delta U = -p\Delta V + \gamma\Delta A_s + \sum_{i=1}^{K}\mu_i\Delta n_i + ?\,\Delta\,?$$

Rudolf Clausius
1822-1888

Internal energy may also change independenly of mentioned extensive variables. This „inherent change of the internal energy" is preferably to be described similarly to previous elementary energy exchanges (product of extensive * intensive variable).

- thermal interaction $$\Delta U_Q = Q = T\Delta S$$

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

entropy
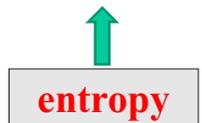
First law of thermodynamics

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

⇕

The universal form of internal energy change.

⇕

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

$$\Delta W_{mech} = \Delta U - \Delta Q - \sum_i \Delta W_i$$

A thermodynamic system is capable to work $\left(\Delta W_{mech} < 0\right)$ if it lowers its internal energy ($\Delta U < 0$), or takes heat from its surroundings ($\Delta Q > 0$), or gain other form of energy$\left(\Delta W_i > 0\right)$.

A hypothetical machine that produces work without external energy input is called, **perpetuum mobile of first kind**. According to the first law of thermodynamics, perpetuum mobile of first kind can not exist.

A smart proposition for perpetuum mobile, whose disfunction is explained by the first law.
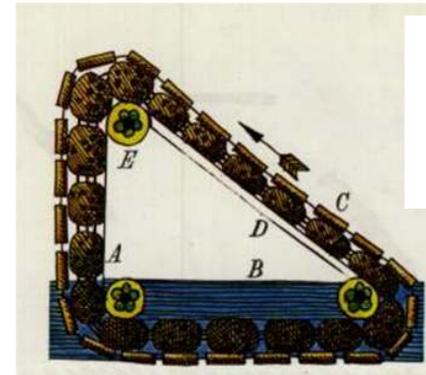
The first law of biothermodynamics

Change of the stored energy

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

metabolic heat loss biosynthesis

mechanical work

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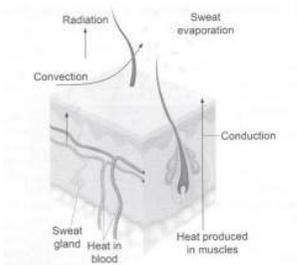
$\Delta W_{mech} < 0$
$\Delta W_{term} < 0$

$\Delta U < 0$

$\Delta W_{kém} > 0$

$\Delta U > 0$

Characteristics of thermal interactions:
### temperature and entropy

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

Characteristics of thermal interactions: temperature and entropy

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

- The notion of *temperature* derives from the sensation of warmth and cold.
- Crucial distiction: *heat and temperature are not identical*. (**Joseph Black** Scot chemist)
- First themperature sensor constructed by **Galileo Galilei** ⟶
- **Jean Rey** French doctor framed the thermometer in 1631
- Concenption of temperature scale by **Anders Celsius** (1742). Boiling point of water was 0°C, melting point was 100°C.
- Inversion of Celsius scale by **Carl von Linne**.

- 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**)
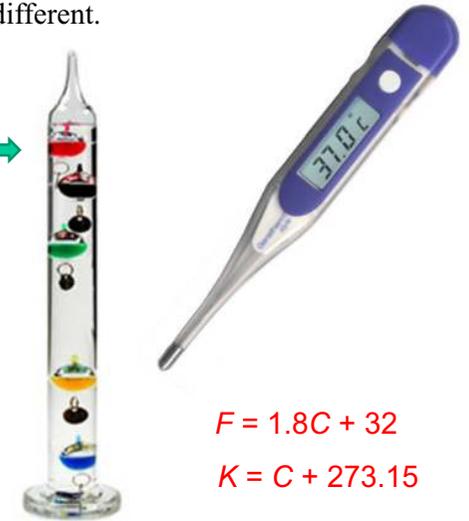
F = 1.8*C* + 32

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
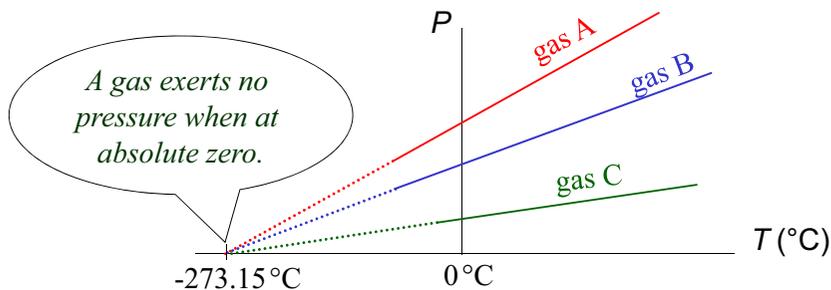
Entropy is a non-conserved extensive quantity!

Isolated system

Energy is a conserved quantity

Thermally and mechanically isolating wall

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

$$\begin{array}{|c|c|} \hline T_1 & T_2 \\ U_1 & Q \quad U_2 \\ S_1 & S_2 \\ \hline \end{array}$$

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

Heat transfer allowed

$U = U_1 + U_2 = cons\tan t$ $\boxed{\Delta U = 0}$ ⟹ $\boxed{\Delta U_1 = -\Delta U_2}$

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

$if \quad T_2 \rangle T_1 \quad then \quad \dfrac{T_2 - T_1}{T_2 T_1} > 0 \quad and \quad \Delta U_1 > 0$ ⟹ $\Delta S > 0$

$if \quad T_2 < T_1 \quad then \quad \dfrac{T_2 - T_1}{T_2 T_1} < 0 \quad and \quad \Delta U_1 < 0$ ⟹ $\Delta S > 0$

$if \quad T_2 = T_1 \quad then \quad \dfrac{T_2 - T_1}{T_2 T_1} = 0 \quad and \quad \Delta U_1 = 0$ ⟹ $\Delta S = 0$

Due to temperature equilibration, the total entropy of the system increases!

Entropy change in isolated system when the pressure equalizes

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

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

Isotherm equalisation process :

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

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

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

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, $S \to S_{max}$.
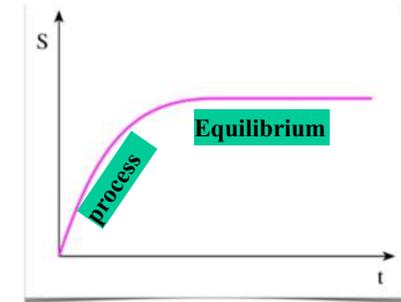
- **Examples of real processes:**
- i.   temperature equalization;
- ii. mixing of gases;

Direction and driving force of spontaneously occurring processes

The internal energy is not necessarily minimized during spontaneously ocurring thermodynamic processes!

Expamle: Melting of ice. The internal energy of water at nearly 0°C is larger than that of ice. However, ice at 1°C is spontaneously melting at atmospheric pressure. The energy change of the melting is +4,2 *kJ/mol*.

Direction of sponteneous processes

In isolated system $\boxed{\Delta S > 0}$

Second law of thermodynamics

- **During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.**
- Heat flows spotaneously 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.
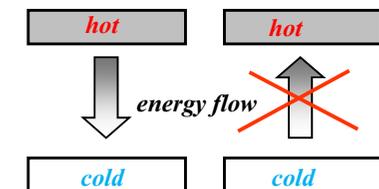
The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

entropy $\Longrightarrow$ *arrow of time*

Top-left panel:

Entropy was introduced through the changes in temperaure, but…….

two forms of heat effects

upon heating
- *temperature changes*
- *temperature remains constant* **latent heat!**

$\Delta Q = \int C \cdot dT$

T, T_{fp}, T_{op}, *vapour*, *liquid*, ΔQ_{op}, *solid*, **Q heat**

T, cooling down, **time**

Top-right panel:
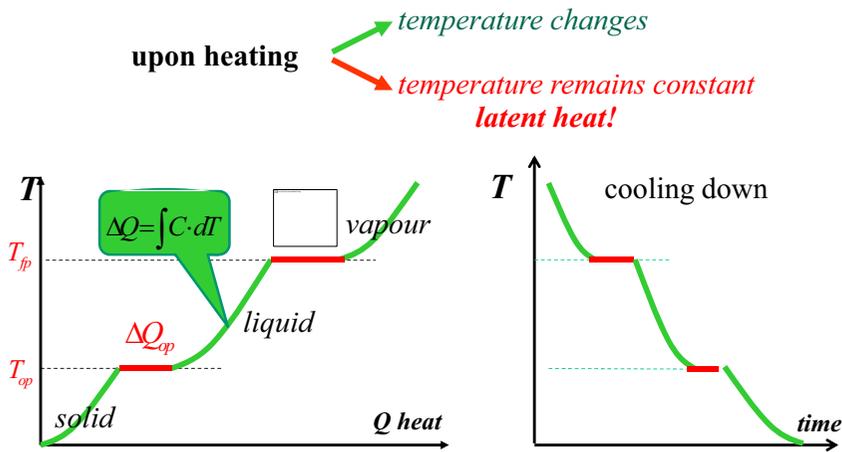
Entropy was introduced through the changes in temperaure, but…

Two forms of heat ➡ **Two forms of entropy**

HEAT
- *temperature changes* ➡ **thermal entropy**
- *T remains consant* ➡ **configurational entropy**

Change in the molecular order

$S(T)$

ΔS_{konf}

ΔS_{term}

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

T_{op}, T_{fp}, T

Bottom-left panel:
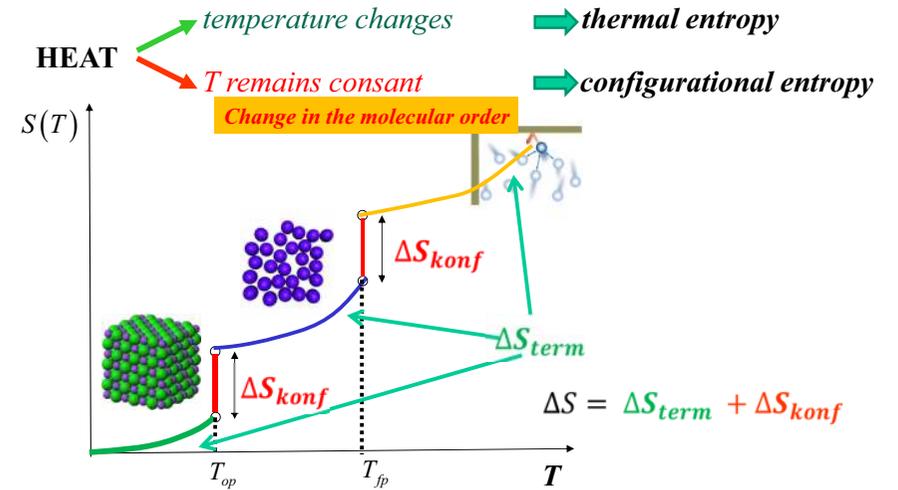
**entropy**
- thermal entropy *(temperature changes)*
- configurational entropy *(temperature does **not** change)*

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

Melting:

crystal ➡ melt

$\Delta Q_{op} > 0$, T_{op}

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

$\Delta Q = T \Delta S$

Boiling:

liquid ➡ vapour

$\Delta Q_{fp} > 0$, T_{fp}

$\Delta S_{konf}\left(T_{fp}\right) = \dfrac{\Delta Q_{fp}}{T_{fp}} > 0$
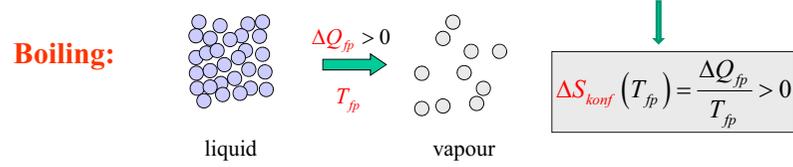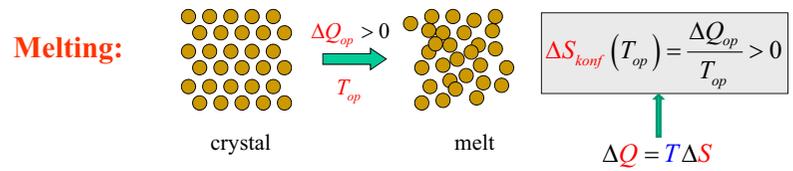
During phase transition at constant temperature the **entropy increases together with the increase of disorder.**

Entropy is a measure of molecular scale order or disorder

Bottom-right panel:

Entropy increases

Related to order – disorder transition?

**YES!**

Boltzmann equation:

$$S = k_B \ln W$$

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

W: thermodynamic probability

Increase of particle number

Increase of temperature

Increase of volume

Dissociation

Helix-coil transition

Melting

Mixing
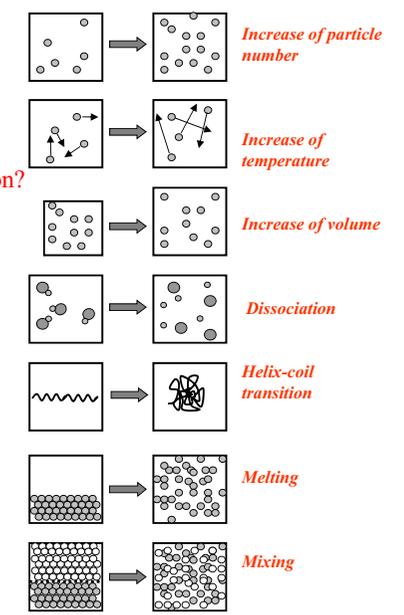
W **thermodynamic probability** defines the **number of microscopic states** belonging to **a macroscopic state**.

example: **makroscopic state**: distance of the extremities of a chain
**microscopic states**: all the possible conformations
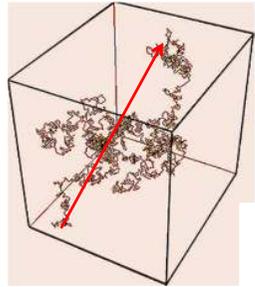
coil, g

All trans, ny

$$S = k_B \ln W$$
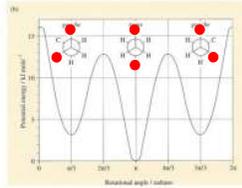
$$N_{C-C} = 10^4$$
$$W_g = 3^{10000}$$
$$S_g = k_B T \ln(3^{10000})$$
$$S_g = 10^4 k_B T \ln 3$$

$$N_{C-C} = 10^4$$
$$W_{ny} = 1$$
$$S_{ny} = k_B T \ln 1$$
$$S_{ny} = 0$$

Configuration and conformational entropy

*constitution - configuration - conformation*
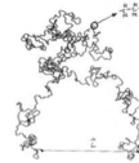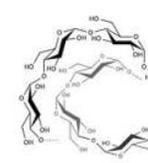
Random coil   Ordered structure
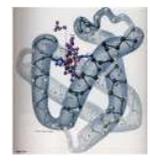
Large conformational entropy   **Much lower conformational entropy**
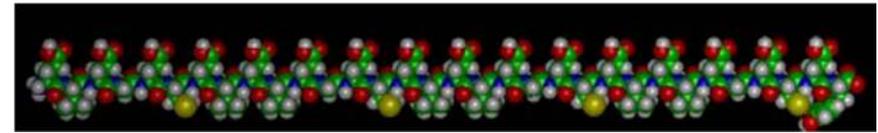
W=1 ⟹ $$S_{konf} = 0$$

Third law of thermodynamics

Entropy of pure crystalline materials at the absolute zero:

$$\lim_{T \to 0} S(T) = 0$$

*determined by Nernst experimentally and by Planck theoretically (based on the statistical approach)*

The third law enables the introduction of an **absolute scale of entropy**

A complex molecule has large standard entropy

Standard entropy at 298 K of selected materials
unit: J/molK

Methane, CH_4
$S° = 186.3$ J mol^{-1} K^{-1}
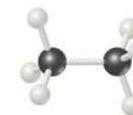
Ethane, C_2H_6
$S° = 229.6$ J mol^{-1} K^{-1}

Propane, C_3H_8
$S° = 270.3$ J mol^{-1} K^{-1}

solid		liquid		vapour	
C diamond	2,4	benzene	173,3	benzene	269,3
C graphite	5,7	water	69,9	water	188,8

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Environmetal effects

surroundings
- isotermal — $T = const.$
- isobaric — $p = const.$
- isochoric — $V = const.$
- adiabatic — $S = const.$
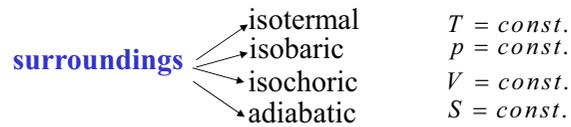
Part of the internal energy is devoted to maintain the constancy of environmental conditions!

Usable energy $\neq$ Change in the internal energy

The useful part of internal energy under given conditions:

Isobaric case: **H enthalpy**

Isothermal case: **F free energy**

Isothermal-isobaric case: **G free enthalpy**

### 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 $\Rightarrow$ $H = U + pV$

$$\Delta H = \Delta U + p\Delta V$$

calorymeter

$$\Delta H = T\Delta S - p\cancel{\Delta V} + p\cancel{\Delta V} = T\Delta S = Q \quad \Leftarrow \textbf{\textit{Heat !}}$$
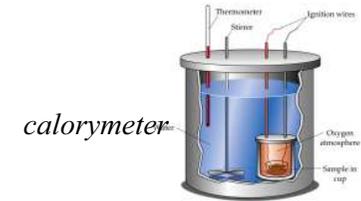
The enthalpy is the useable part of internal energy at constant pressure.

$$\Delta H = Q$$

Useable part of internal energy at constant temperature:

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** $\Rightarrow$ $F = U - TS$

extenzív mennyiség

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

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

$\Delta F = F_2 - F_1$
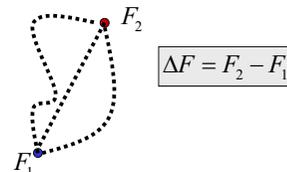
The fee energy is the useable part of internal energy at constant temperature.

$$\Delta F = W_{mech}$$

Useable part of internal energy at constant temperature and pressure:

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 $\Rightarrow$ $G = H - TS$

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

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

chemical potential

Slide 1

Direction and driving force of spontaneously occurring processes

The internal energy is not necessarily minimized during spontaneously ocurring thermodynamic processes!

Expamle: Melting of ice. The internal energy of water at nearly 0°C is larger than that of ice. However, ice at 1°C is spontaneously melting at atmospheric pressure. The energy change of the melting is +4,2 *kJ/mol*.

Thermodynamic functions

Isolated system $\Delta S > 0$

$\Delta F = \Delta U - T\Delta S$ ➡ *Isothermal system* $\Delta F < 0$

$\Delta G = \Delta H - T\Delta S$ ➡ *Isothermal - isobaric system* $\Delta G < 0$

Slide 2

Spontaneously occurring processes in isolated systems

$$\Delta U = 0$$

$T_1 > T_3$ T_1 T_3 → temperature equilibration → $T_1 > T_2 > T_3$ T_2

$p_1 > p_3$ p_1 p_3 → pressure equilibration → $p_1 > p_2 > p_3$ p_2

$c_1 > c_3$ c_1 c_3 → concentration equilibration → $c_1 > c_2 > c_3$ c_2

$$\Delta S > 0$$

Slide 3
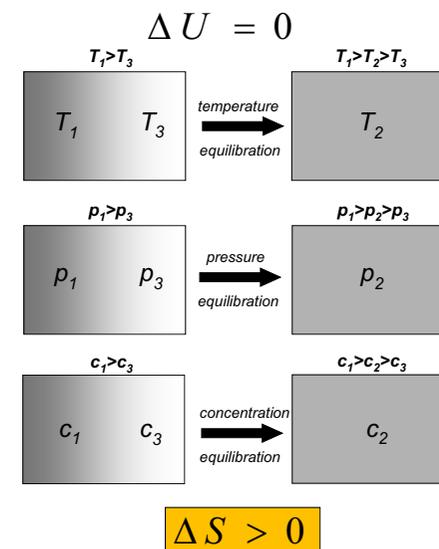
Condition of thermodynamic equilibrium

| characteristical function	interaction with surroundings	extremity of the equilibrium	spontaneously occurring process
$S(U, V, n)$	isolated	maximum	$\Delta S > 0$
$F(T, V, n)$	thermal	minimum	$\Delta F < 0$
$G(T, p, n)$	mechanical and thermal	minimum	$\Delta G < 0$

entropy

constant: U,V,n

Free energy

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

constant: T,V,n

Free enthalpy

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

constant: T,p,n

Slide 4
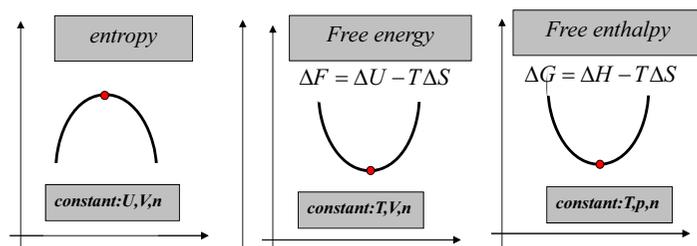
Driving force of chemical and biochemical reactions

$$\Delta_r G < 0$$

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

Heat of reaction

endotherm   exotherm

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

Entropy of reaction

Change in molecular order

decomposition   ring formation

$\Delta_r S > 0$ $\Delta_r S < 0$

Top-left panel
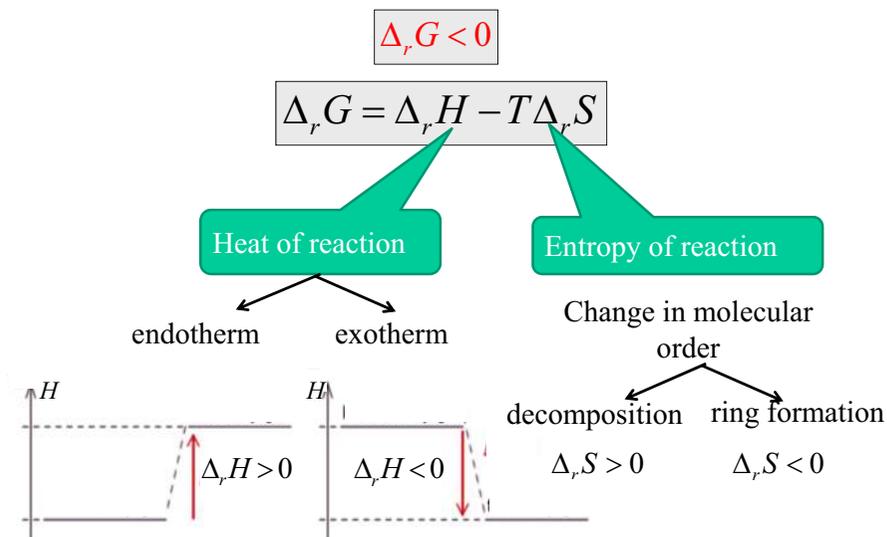
Stable and nonstable equilibrium condition

$\Delta_r G$

Non-equilibrium

Equilibrium – unstable

Equilibrium – local minimum

Equilibrium – global minimum

Top-right panel

DRIVING FORCE OF MIXING

$$\Delta_e G < 0$$

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

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

$$\Delta_e S > 0$$

Bottom-left panel
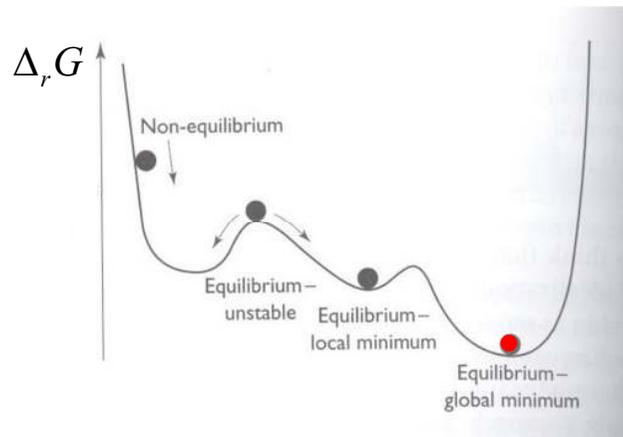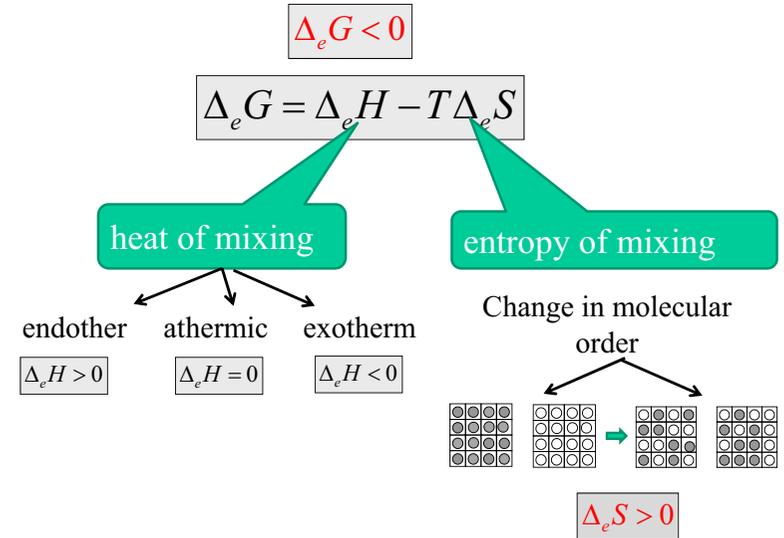
Flexibility of macromolecules

Entropic elasticity

$\Delta S_{konfig} < 0$

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

adiabatic

$\Delta T > 0$

$\Delta S_{term} \implies \Delta S_{konfig}$ $\Delta S_{konfig} > 0$

streched $\implies$ coiled

shrinking

$Q > 0$

heating

$\Delta l < 0$

M   M

Bottom-right panel
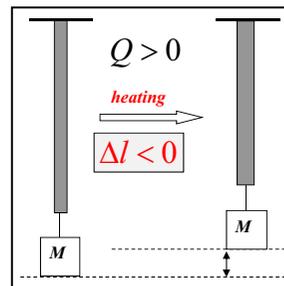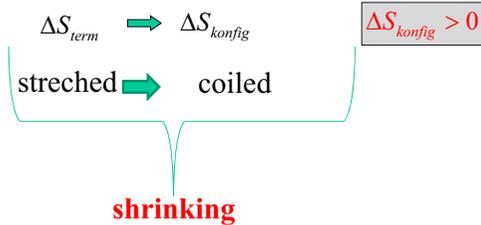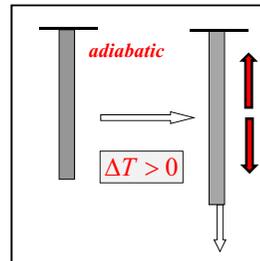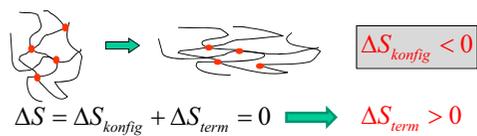
Looking back

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.

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

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

enthalpy	$H=U+PV$	$\implies$	heat
free energy	$F=U-TS$	$\implies$	work
free enthalpy	$G=H-TS$	$\implies$	chemistry
(Gibbs free energy)			