SEMMELWEIS UNIVERSITY

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THERMODYNAMICS

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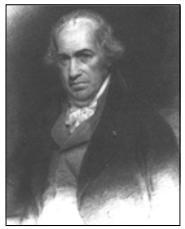
Thermodynamics

Early definition:

Thermodynamics is the study of thermal processes in macroscopic systems.



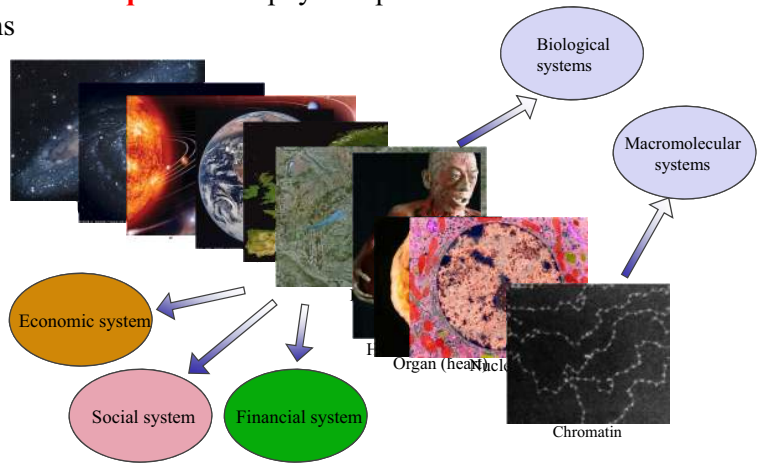
James Watt (1736-1819)

$$\Delta U = \Delta Q + \Delta W$$

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.

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



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

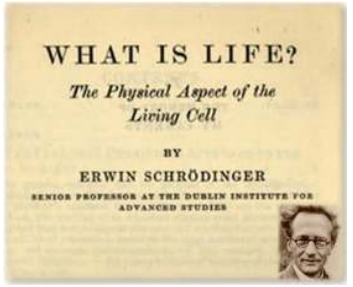
Some examples:

What reactions and/or physiological processes are possible?
What are the allowed mechanism in protein synthesis?
What are the necessary conditions required to cause 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,

Bio-thermodynamics (bioenergetics) dealts with how the energy is produced and transformed in living creatures.

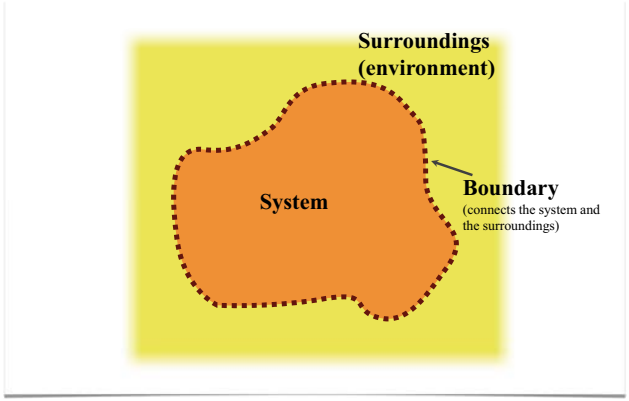
(***A.L. Lavoisier 1743-1794)***



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

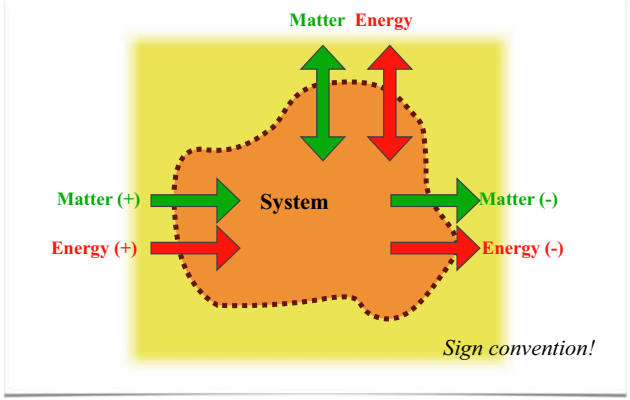
Abstraction of the thermodynamic system

Definition: the thermodynamic system is the part of nature under investigation.

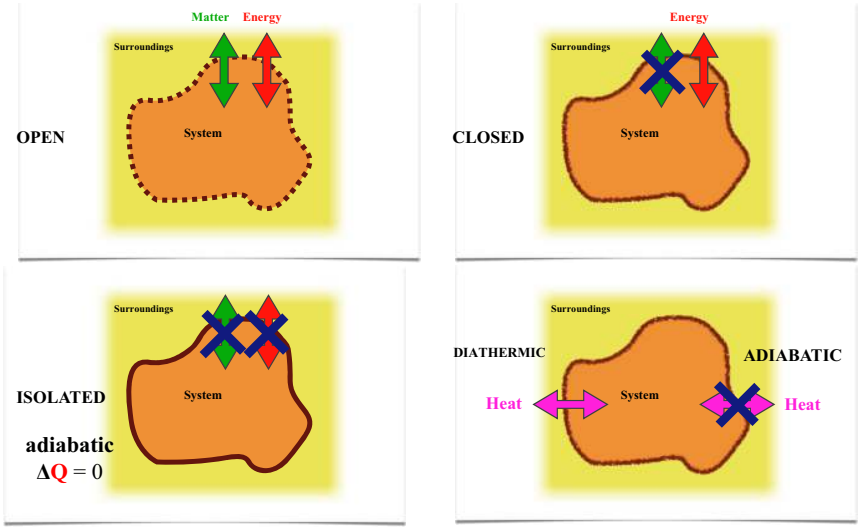


The thermodynamic system interacts with the surroundings

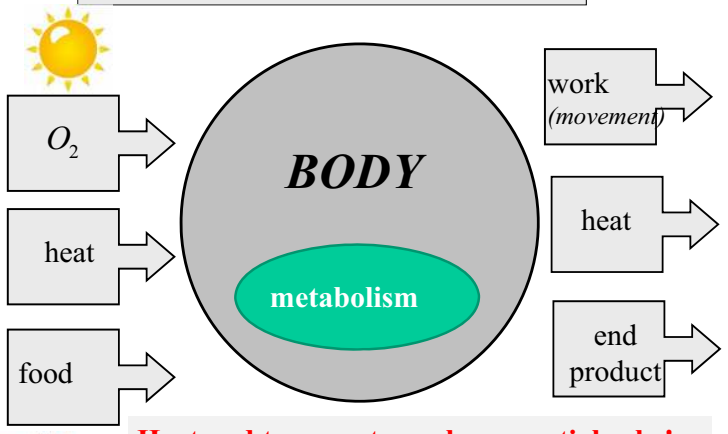
Exchange of matter and energy may occur across the boundary.



Types of thermodynamic systems

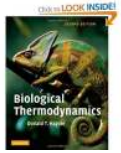


BIO-THERMODYNAMIC SYSTEM



Heat and temperature play essential role !

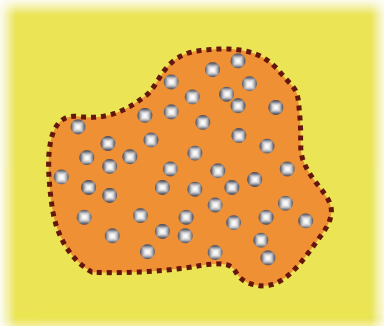
$0\ C^o \Rightarrow T \Rightarrow 42\ C^o$



Characterization of the thermodynamic system

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

Pressure: p
Volume: V
Temperature: T
Concentration: c

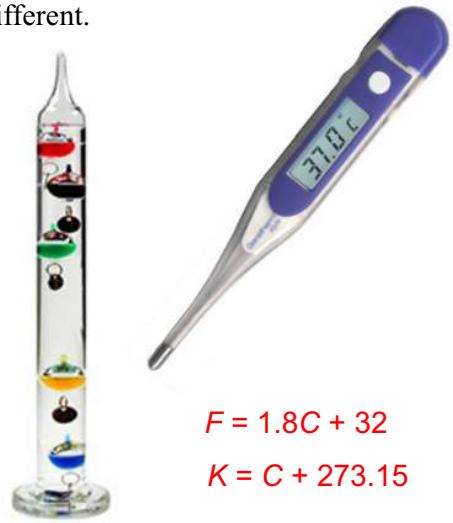


- ***Thermodynamic variables*** are the observable macroscopic variables of a system, such as P, V and T.
- If they are used to describe an equilibrium state of the system, they are known as ***state variables***.

- ***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…,

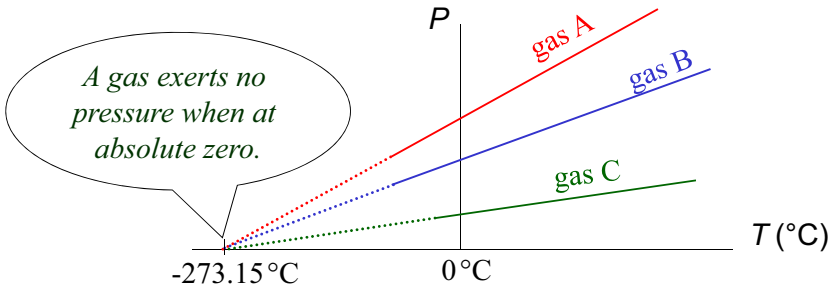
- Temperature and heat are different. (**Joseph Black**)
- First thermometer (**Galileo Galilei**)
- First clinical thermometer (**Jean Rey** 1631)
- Early temperature scale (**Anders Celsius** 1742).
- Temperature scale (**Carl von Linne**)



$F = 1.8C + 32$

$K = C + 273.15$

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.



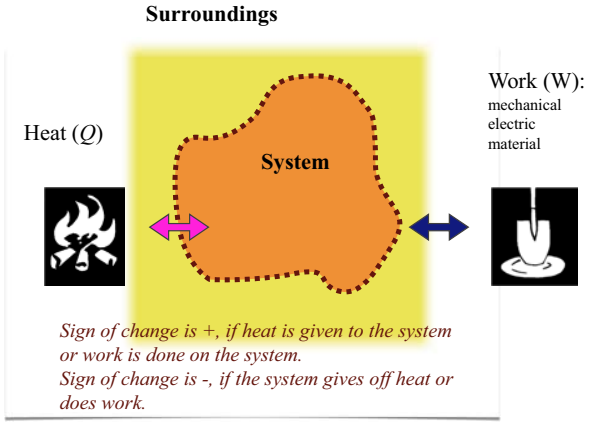
Spontaneous process ⟹ **equilibrium**

that can proceed without any outside intervention

- ***In equilibrium state*** the properties of the system do not change with time.
- In many cases, an **equilibrium state** has intensive variables which are uniform 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**.



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.

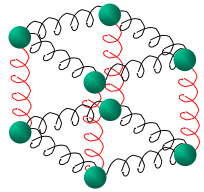
- An ***isobaric*** process is one in which the pressure is constant.
- An ***isochoric*** process is one in which the volume is constant.
- An ***isothermal*** process is one in which the temperature is constant.
- An ***adiabatic*** process is one in which no heat enters or leaves the system; i.e.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

change in the **internal energy**

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.

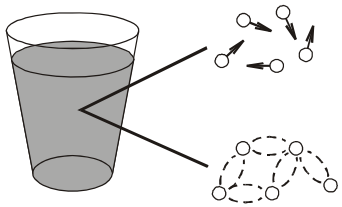
The kinetic energy is due to the motion of the particles. The potential energy is due to interactions between atoms, ions and molecules.



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

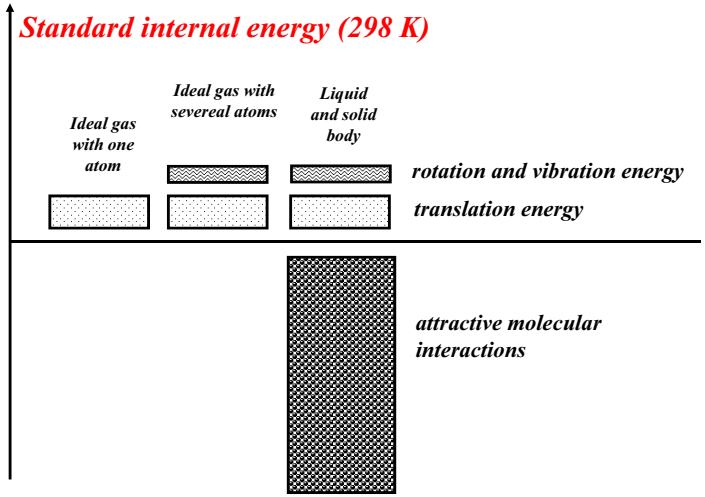
Microscopic characterization: **internal energy (*U*)**

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

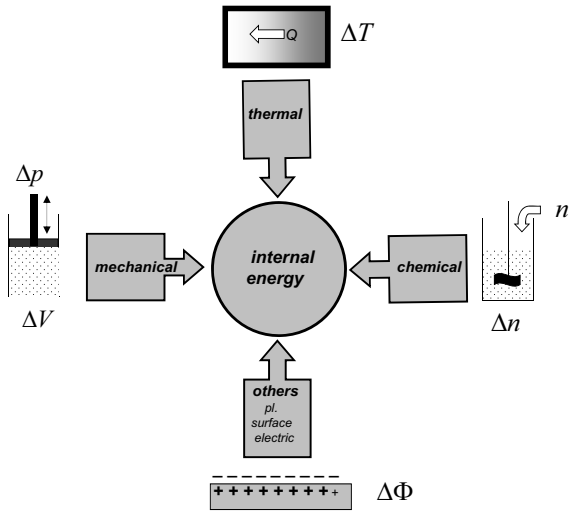


Molecular potential- and kinetic energies are in the internal energy.

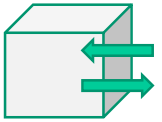
Internal energy does not contain the potential and kinetic energy of the macroscopic body.



Change of internal energy



Change in internal energy



ΔX>0

ΔX<0

Elementary energy exchanges

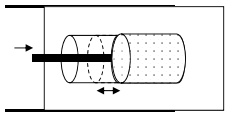
thermal | volume | surface | chemical | others

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: $W_i = y_i \cdot \Delta x_i$

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 (μΔ*n*) **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????

- Thermal interactions $\Delta Q = T\Delta S$ ⟸ **entropy**

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

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 $W_V = -p\Delta V$

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

Electric work: $W_Q = \varphi\Delta Q$

Material transport: $W_n = \mu\Delta n$

Generalized: $W^i = y^i_{\text{int}}\Delta x^i_{ext}$

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

chemistry

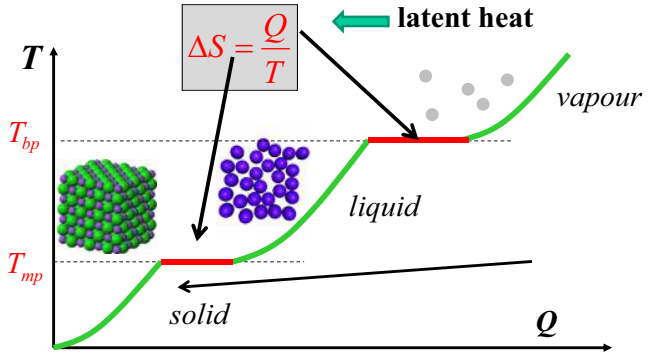
Izochoric process (ΔV=0): $\Delta E = Q_V$ Change in internal energy is caused only by the heat exchange.

Izobaric process (p=constant): $\Delta E = Q_p + W_V = Q_p - p\Delta V$

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

Thermal interactions ⟹ *temperature changes*

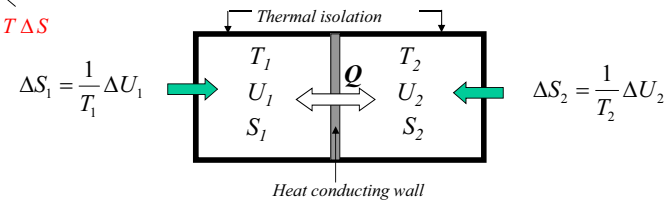
temperature does not change



Entropy change in isolated system when the temperature equalizes

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

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



$\Delta S_1 = \frac{1}{T_1}\Delta U_1$ $\qquad$ $\Delta S_2 = \frac{1}{T_2}\Delta U_2$

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

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

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

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

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

Due to temperature equalization the entropy increases!

Entropy change in isolated system when the pressure equalizes

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

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

Isotherm equalisation process :

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

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

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

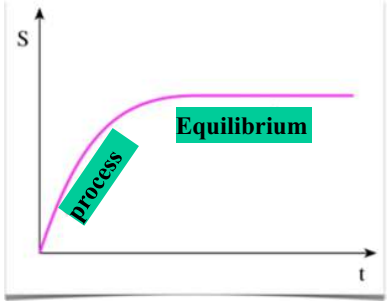
In isolated system during temperature and/or pressure equalization process the entropy increases!

Second Law of Thermodynamics

- The entropy of an isolated system never decreases; i.e.

$\Delta S \geq 0,$

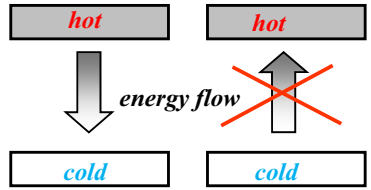
approaching equilibrium, $S \rightarrow S_{max}$.



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

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.



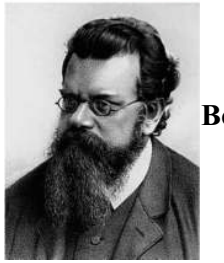
The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

entropy → ***arrow of time***

Entropy increases

Related to order – disorder transition?

YES!

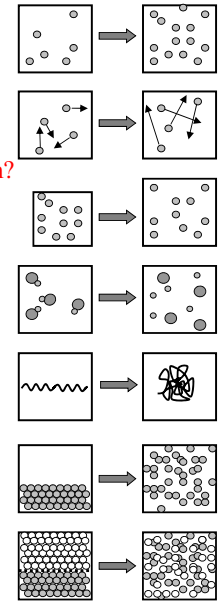


Boltzmann equation:

$$S = k_B \ln W$$

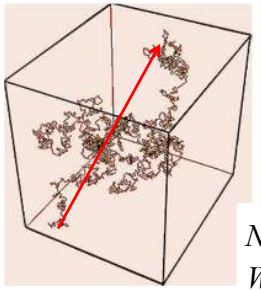
$k_B = 1.38 \cdot 10^{-23}$ J/K $\longrightarrow$ $k_B = \frac{R}{N_{Av}}$

W: thermodynamic probability

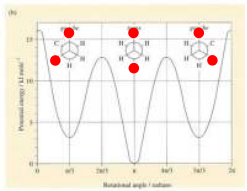


W thermodynamic probability gives the number of microstates for a given macrostate.

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



coiled, c



extended, e

$N_{C-C} = 10^4$
$W_c = 3^{10000}$
$S_g = k_B T \ln(3^{10000})$
$S_c = 10^4 k_B T \ln 3$

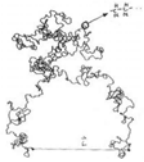
$N_{C-C} = 10^4$
$W_e = 1$
$S_{ny} = k_B T \ln 1$
$S_e = 0$

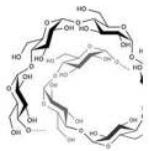
$\Delta S > 0$

$S = k_B \ln W$

Conformation and entropy

constitution - configuration - conformation



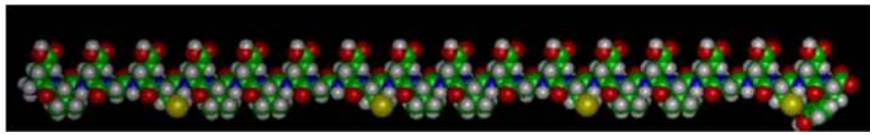


Random coil

Ordered conformations

Higher conformational entropy

Much smaller conformational entropy



W=1 $\longrightarrow$ $S_{konf} = 0$

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 → 0 as T → 0.

The unattainability of absolute zero

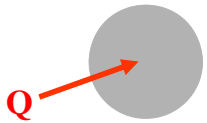
It is impossible to reach T = 0 in a finite number of steps.

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.

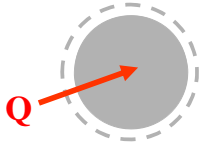
Usable energy $\neq$ Internal energy change



$V = konst.$

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

$C_V < C_p$



$p = konst.$

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.

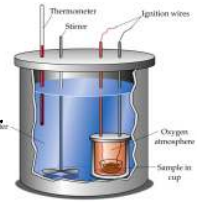
The remaining useable part of internal energy is called: **enthalpy.**

H enthalpy ➡ $H = U + pV$

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

$\Delta H = T\Delta S - p\Delta V + p\Delta V = T\Delta S = Q$ ⬅ ***Heat !***

calorymeter



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.

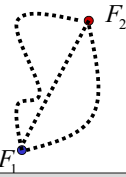
The remaining useable part of internal energy is called: **free energy**

free energy ➡ $F = U - TS$

extenzív mennyiség

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

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



$\Delta F = F_2 - F_1$

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.**

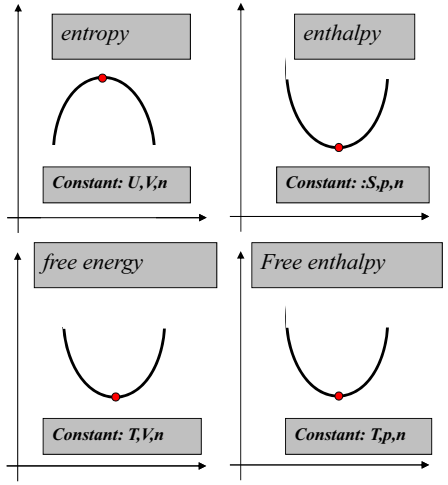
free enthalpy ➡ $G = H - TS$

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

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

chemical potential

Conditions of thermodynamic equilibrium



Thermodynamic equilibrium ⟺ Mathematical extremum problem

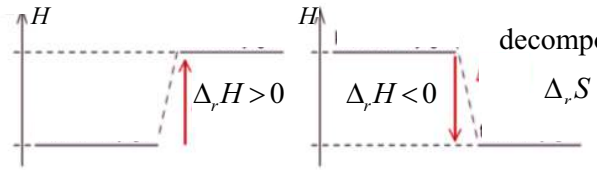
Driving force of chemical and biochemical reactions

$\Delta_r G < 0$

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

Heat of reaction

endotherm exotherm



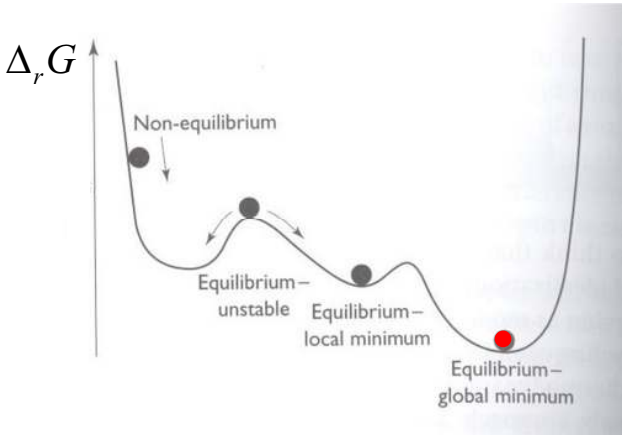
Entropy of reaction

Change in molecular order

decomposition ring formation

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

Stable and nonstable equilibrium condition



DRIVING FORCE OF MIXING

$\Delta_e G < 0$

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

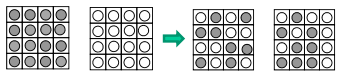
heat of mixing

endother athermic exotherm

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

entropy of mixing

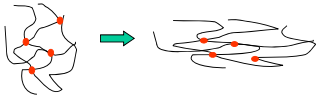
Change in molecular order



$\Delta_e S > 0$

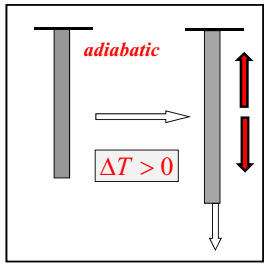
Flexibility of macromolecules

Entropic elasticity



$\Delta S_{konfig} < 0$

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

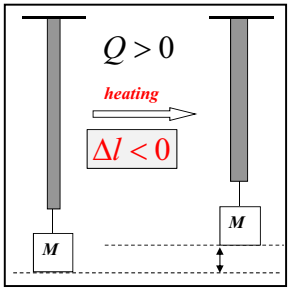


$\Delta S_{term} \Rightarrow \Delta S_{konfig}$

$\Delta S_{konfig} > 0$

streched ⇒ coiled

shrinking



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: $\Delta U = T\Delta S - p\Delta V + \sum_{i=1}^{K} \mu_i \Delta n_i + \ldots +$
(Conservation of energy)

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	$H=U+PV$	⇒	heat
free energy	$F=U-TS$	⇒	work
free enthalpy	$G=H-TS$	⇒	chemistry

(Gibbs free energy)