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Innovation and Development of Study Field Nanomaterials at the Technical University of Liberec

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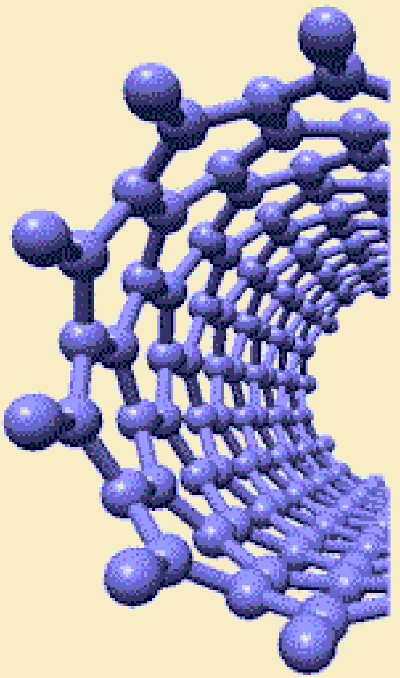

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THERMODYNAMICS

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POINTS OF VIEW

THERMAL PHYSICS -heat-related subject
macroscopic point of view
heat, temperature
THERMODYNAMICS – study of the conversion of energy into work and heat

MOLECULAR PHYSICS
microscopic point of view
work and heat; kinetic and bond energy

temperature of material associated with the random, and thermal properties	$\leftrightarrow$	disordered motion of particles of material (molecules, atoms)
increasing temperature	$\Leftrightarrow$	increasing kinetic energy of random motion

internal energy = sum of kinetic energies of the random thermal motion of all particles in a given body

in thermodynamics, only changes of internal energy are important (not absolute value)

THERMODYNAMIC SYSTEM

System with a real or imaginary **boundary** to separate it from the rest of the universe. The rest is referred to as the **environment** or **surroundings** (often called a **reservoir**)

Classification of thermodynamic systems is based on the boundary and exchange of matter, energy and entropy:

open systems (exchanging energy (heat and work) and matter with environment; example: ocean)

closed systems (exchanging energy (heat and work) but not matter with their environment, $dN = 0$) example: greenhouse

system can exchange *heat* and/or *work*:

adiabatic boundary: not allowing heat exchange, $TdS = 0$

rigid boundary: not allowing exchange of work, $pdV = 0$

isolated systems exchanging nothing:

$dN = 0$, $TdS = 0$, and $pdV = 0 \Rightarrow dE = 0$)

STATE OF THE SYSTEM

Described by state variables

Thermodynamic parameters

pressure p [Pa]
volume V [m^3]
temperature T [K] – „absolute temperature“: 0 = no thermal motion, absolute calm
entropy S [JK-1]

Thermodynamic potentials

internal energy E	$dU = T\mathrm{d}S - p\mathrm{d}V$	$U = H - pV = F + TS$
enthalpy H	$dH = T\mathrm{d}S + V\mathrm{d}p$	$H = G + TS = U + pV$
Gibbs free energy G	$dG = -S\mathrm{d}T + V\mathrm{d}p$	$G = F + pV = H - TS$
Helmholtz free energy F	$dF = -S\mathrm{d}T - p\mathrm{d}V$	$F = U - TS = G - pV$

$$\Delta Q = m \cdot c \cdot \Delta t$$

Q [J]	heat
t [K]	temperature
m [kg]	weight (mass)
c [J/kg K]	specific heat capacity

Gas: depends on the process resulting in temperature change
specific heat capacity for isochoric and isobaric system

FIRST LAW OF THERMODYNAMICS

Expression of the principle of conservation of energy.

The change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to or removed from the system and the work done.

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

U internal energy
Q heat
W work
(sign depends on convention
if work is done *on* or *by* the system)

First law of thermodynamics is a quantitative law, the individual forms of energy are quantitatively equivalent and can be reciprocally transformed. From the point of view of the thermal energy it can be transformed into another form.
Second law of thermodynamics is a qualitative law, describes the thermal process. Energy transformation can be done under some constraints.

Most processes can be run in both directions; some processes cannot be performed in opposite direction – they are irreversible.

↓

second law of thermodynamics

It is simple to change electric energy into heat;
it is not so simple to do the opposite;
(in fact, it is impossible; one should **use two** reservoirs of different temperatures).

SECOND LAW OF THERMODYNAMICS

Defines the direction of natural processes – general principle which places constraints upon the direction of heat transfer and the attainable efficiencies of heat engines

Efficiency of the heat engine (η) is give as ratio of the work done and the heat at the input.

$$\eta = \frac{W}{Q}$$

It is always lower than 1 and maximally is given as

$$\eta = \frac{T_2 - T_1}{T_2}$$

T_1 and T_2 – hot and cold reservoir thermodynamic temperatures

ENTROPY

Entropy – state quantity, tell us the level of disorder of the examined system or uncertainty of the process.

Entropy *S* („form change“),
state quantity, in the isolated system for reversible process constant, increasing for irreversible processes.

Change:

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

$[\Delta S]$ = J/K

Most general form of second law of thermodynamics.
In any cyclic process,
the entropy will either increase or remain the same.

ENTROPY
from the point of view of statistical physics

hot tea, cold spoon

MACROSTATES

tea and spoon have the same temperature

SOME CORRESPONDING MICROSTATES

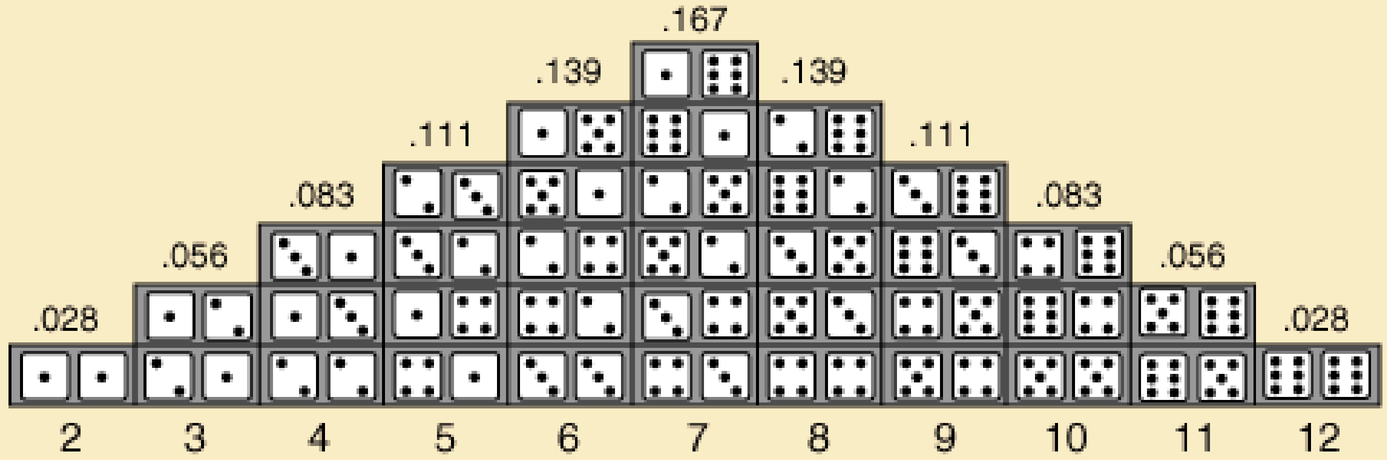
Macroscopic state of the system in equilibrium – described by properties (site, speed, momentum…) of elements (molecules, atoms …)

Submicroscopic point of view – more detailed, several **microstates** can correspond to one **macrostate**.

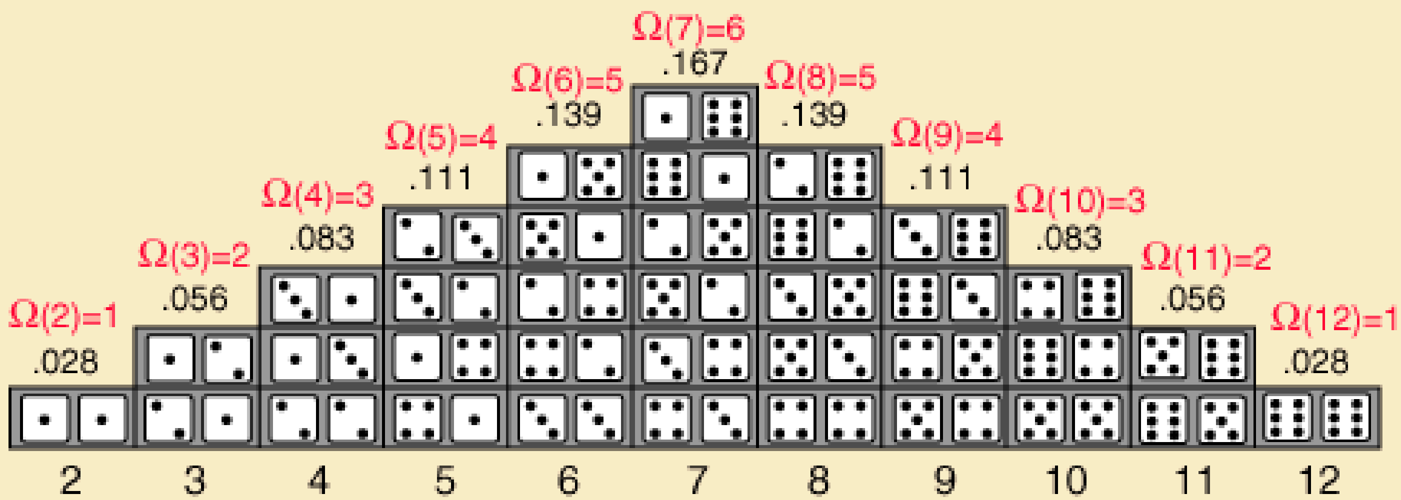
Number of microstates – **thermodynamic probability** *w*, used for definition of the entropy of the thermodynamic system.

$$S = k \ln w$$

$k = 1.3806505(24) \times 10^{-23}$ J/K is Boltzmann constant



Total number of states: 36



Total number of microstates: 36

Total number of macrostates: 11

THERMODYNAMIC EQUILIBRIUM

For any macroscopic system, some particular macroscopic state can be realized with much more microstates then any other macroscopic state.

Such most probable macroscopic state is denoted as state of thermodynamic equilibrium (shorter equilibrium state).

State functions do not change under thermodynamic equilibrium.

If the state quantities are stable for a certain period, we deal with metastable thermodynamic equilibrium. The metastable thermodynamic equilibrium converts to stable thermodynamic equilibrium

processes in isolated system → **entropy does not change** → **reversible process**

processes in isolated system → **entropy increases** → **irreversible process**

system is in thermodynamic equilibrium ↔ entropy is maximum for a given system

Non-isolated system: entropy can decrease
– of course, at the cost of increasing entropy in the surroundings of the system

LIVING ORGANISM
OPEN THERMODYNAMIC SYSTEM

The organism – open system - in continual interaction with the environment.

External sources of energy for an organism:

- food – nutrition (chemical energy)
- environmental energy (chemical, light, mechanical, thermal)
- stimuli for sense organs (source of information)
- radiation absorption (also photosynthesis for green organisms)

Source of energy in an organism:

- basal metabolism of all cells
- increased metabolism
  - muscular tension, muscular tremor-shivering
  - elevated temperature
  - some hormones (thyroxin, noradrenalin)

THERMAL ENERGY LOSS OF AN ORGANISM

- Direct
  radiation
  conduction
  convection (= heat transport)

- Indirect
  evaporation from lungs
  evaporation body surface (sweating)
    imperceptible
    perceptible

HEAT TRANSPORT

Conduction and convection supposes direct contact of materials.

Conduction

- heat transport in physical environment from the place of higher temperature to the place of lower temperature by the means of propagation of the kinetic energy of thermal vibrations of elements
- not associated with mass transfer, only thermal energy transfer
- transferred energy Q per time τ between two locations depends on temperature difference Δt, distance d and transfer area S and thermal conductivity coefficient λ

$$Q = \frac{\lambda \cdot S \cdot \Delta t \cdot \tau}{d}$$

By means of interactions among atoms/molecules, the kinetic energy of thermal vibrations propagates (it is transmitted from one atom to another) in a material

ability of the material to conduct heat = heat conductivity
thermal conductors (metals ..)
thermal insulators (dry air, polystyrene, adipose tissue ...)

HEAT TRANSPORT

Convection

- connected with conduction
- first, the heat transferred by conduction to a substance and consequently distributed by the means of convection of this substance
- transfer of both energy and substance
- the heat Q conducted per time τ from the surface area S, into the environment of lower temperature of temperature difference Δt (**α** thermal convectivity coefficient)

$$Q = \alpha \cdot S \cdot \Delta t \cdot \tau$$

gases and liquids: thermal energy transported by flowing substance

dry, non-flowing air insulates very well – opposite to wet circulating air

➔ influence of thermal properties of skin and wear

The most significant mechanism for heat transport in human body is blood circulation.

HEAT TRANSPORT

Radiation

- in our climate of high importance
- 60 % thermal wastage
- organism emits thermal electromagnetic radiation
  emitted wavelengths 5–20 μm (infrared radiation)
- amount of emitted energy proportional to T^4 – Stefan-Boltzmann law
  For „blackbody radiation“ (idealization)
  energy-flux density, emissive power $E = \sigma T^4$
  (Stefan-Boltzmann constant $\sigma = 5.670400 \cdot 10^{-8}$ $\mathrm{Wm^{-2}K^{-4}}$)
- by the same mechanism the environments reciprocally influence the organism –
  total emitted energy proportional to the fourth power of difference of body surface temperature and surrounding objects temperatures.

Thermal comfort of organism in residential areas: influenced by air temperature and wall surface temperature (sum should give about 37 ºC.

THERMAL COMFORT OF ORGANISM

↑ absorption of radiation from surrounding bodies
(depends on surface properties!!)

↓ radiative energy loss
(depends on surface properties!!)

↓/ ↓ convection/conduction heat exchange with surroundings

↓ energy loss by evaporation
(lungs, sweating)

EVAPORATION OF WATER, SWEATING

water has considerable heat of vaporization: 2260 kJ/kg
➔ energy loss by breathing, sweating

Breathing: expired air is almost saturated vapor

Imperceptible sweating

- spontaneous diffusion of water through skin without participation of sweat gland
- human organism is almost unable to control this process
- under normal conditions approximately 660 ml of water per day
- determined by properties of surroundings:
  - temperature
  - speed of air circulation
  - relative humidity of air

Perceptible sweating

- by means of sweat glands
- controlled by human organism
- under extreme conditions up to 1.5 l per hour
- it enables cooling of organism also if the temperature of environment is higher than body temperature
- depends on environment properties: temperature, humidity, air circulation

THERMOREGULATION OF ORGANISM

Thermoregulation mechanisms
preferably endeavour to keep constant temperature of deeply located internal organs

Centre for body temperature control is located in hypothalamus

Temperature of deeply located organs = temperature of blood flowing through hypothalamus – normally stabilized at 37°C

Sensors of cool and warm are located in various depths in the skin

Thermal insulator – skin, hypodermis, subcutaneous adipose tissue

Heat transfer depends on dermal blood circulation

Essential control mechanisms for organism temperature decrease

- vasodilatation
- perceptible sweating
- reduction of heat production

Essential control mechanisms for organism temperature increase

- vasoconstriction
- increased heat production – muscular shivering - tremor
- metabolism increase
- „goose skin“

- fever – higher temperature is set at thermoregulating centre (pyrogenous substances)