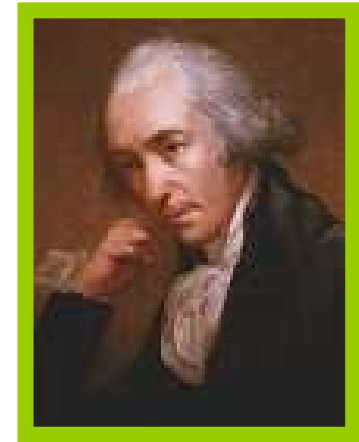


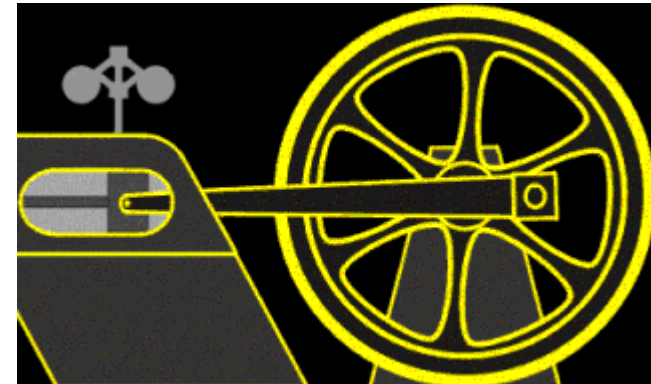
MUNI



JAMES WATT
19.1.1736 - 19.8.1819

Lectures on Medical Biophysics

Thermodynamic principles



Lecture outline

- understanding basic concepts of thermodynamics, work and heat, 1st and 2nd Law of thermodynamics
- explanation of the relationship between entropy and disorder of a thermodynamic system, the Boltzmann principle

Thermodynamics – physical discipline dealing with transformations of energy in macroscopic systems.

- Development: 18th to 19th century – steam engines, combustion engines, turbines.
- At the end of 19th century and the beginning of 20th century it became solid basis of physical chemistry.
- Key to understanding uniqueness of life today: non-equilibrium thermodynamics.

THERMODYNAMIC SYSTEM

□ Definitions:

- Thermodynamic system: A region of space bounded by arbitrary surfaces which delineate the portion of the universe we are interested in
 - **Isolated system**: one which cannot exchange particles or energy with its environment.
 - **Open system**: one which can exchange both particles and energy with its environment.
 - **Closed system**: can exchange energy but no particles.
-
- *An isolated system always reaches an **equilibrium state** in which it does not change macroscopically (~visibly). Open systems do not reach the equilibrium state in general.*
 - **LIVING SYSTEMS ARE OPEN SYSTEMS**

Basic terms

- Quantities describing a tmd. system in equilibrium are called **state parameters**.
- A defined set of state parameters is necessary for full description of a tmd system.
- These parameters are related to each other in the **equations of state**.
- The simplest tmd. System is **an ideal (perfect) gas**.
- Equation of state for the ideal gas (**universal gas law**):

$$p \cdot V = n \cdot R \cdot T$$

[Pa, m³, mol, J·K⁻¹·mol⁻¹, K]

Reversible process:

- is one in which a second process could be performed so that the *system and surroundings* can be restored to their initial states with no change in the system or surroundings.
- Irreversible process – in principle, any real process
- Cyclic process: the initial and final states of the system are identical (but not necessarily the surroundings)
- Sign convention: energy given to a system and work done by an external force on the system are positive, energy lost from the system to its surroundings and work done by the system on its surroundings are negative.

Work done by/on thermodynamic systems

Gas and piston system

$$W = p \cdot \Delta V$$

- *This work can be called mechanic or volumetric.*

electric system

$$W = Q \cdot U$$

- *This is the work necessary to transfer an electric charge Q between places with potential difference U .*

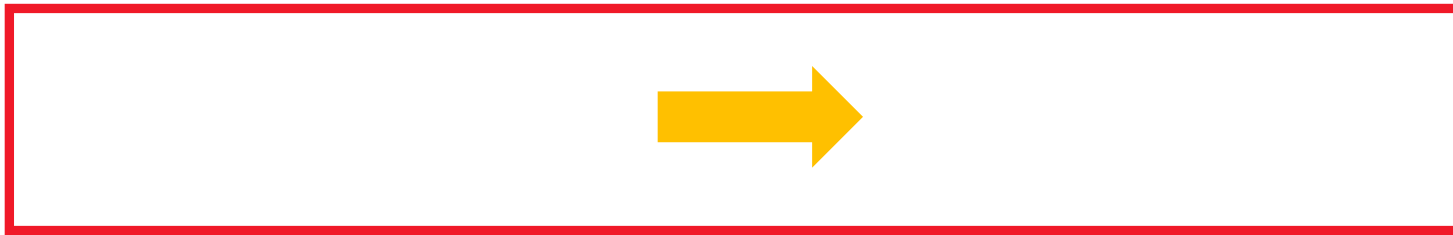
chemical system

$$W = \mu \cdot \Delta n$$

- This is the work necessary to increase or decrease amount of a chemical compound Δn in chemical reaction. μ is chemical potential.

Other important quantities:

Thermodynamic (Kelvin) temperature T is a quantity which indicates the average kinetic energy W_{KS} of the particles in a system e.g., for an ideal monatomic gas, k is the Boltzmann constant:



Internal energy of the system is the sum of all kinetic and potential energies of all particles forming the system.

Heat (thermal energy) is the part of internal energy of the system which can be exchanged between systems because of their different temperatures.

1st law of thermodynamics

(a formulation of the law of conservation of energy used in thermodynamics):

$$\Delta U = W + Q$$

We can read it, for example: Internal energy U of the system increases with the work W done on the system, and the heat Q transferred from the environment to the system.

Internal energy is a state parameter, heat and work are not.

2nd law of thermodynamics

2nd law of thermodynamics (and definition of entropy S):
It can be shown that, for a system with heat exchange with environment, it holds:

$$dS \geq dQ/T \quad (T \text{ is temperature})$$

*The total entropy of any **isolated** thermodynamic system ($dQ = 0$) tends to increase over time, approaching a maximum value i.e.,*

$$dS \geq 0.$$

This law determines the “direction” of natural processes, one of the most important natural principles.

$$dS = 0$$

for reversible processes only.

Entropy and disorder

Entropy S of a thermodynamic system depends on the number of different possible *microscopic* arrangements of particles (microstates) that result in the same observed *macroscopic* state of the thermodynamic system. The entropy of a system is higher when the microscopic arrangement of a system is more disordered and irregular.

Ludwig Boltzmann derived formula (principle) expressing this fact:

$$S = k \cdot \ln P$$

Where P is the number of microscopic arrangements (microstates) which can form the respective (the same) macrostate.

k is **Boltzmann constant** ($k = R/N_A = 1.38 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$, N_A is Avogadro constant)

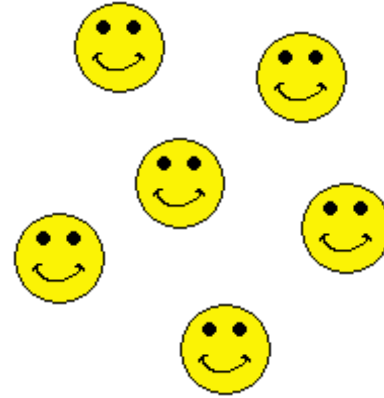
S is a state parameter.

Derivation of the above formula is lengthy and relatively difficult. Next slides show rather simplified qualitative explanation.

*In following considerations, we suppose that **the total energy of particles and their number do not change.***

Not comprehensible? It will be explained a little!

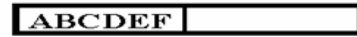
„An experiment with balls“



- The balls can be labelled by means of letters.
- We draw a line parting bottom of a shoe box into two equal halves.
- We shake the box and note positions (distribution) of balls.
- Simplification: we deal only with positions of the balls, their momentum or energy is ignored.*

Macrostate 1: 

Number of microstates: 1



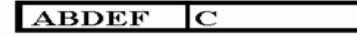
Macrostate 2: 

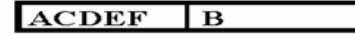
Number of microstates: 6









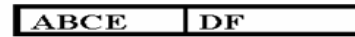





Macrostate 3: 

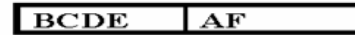
Number of microstates: 15




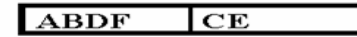


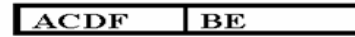


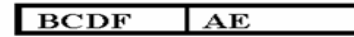








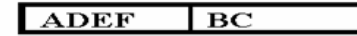


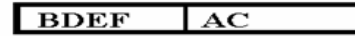















Macrostate 4: 

Number of microstates: 20










































Macrostate 5: 

Number of microstates: 15

Macrostate 6: 

Number of microstates: 6

Macrostate 7: 

Number of microstates: 1

A few terms of statistical physics:

- phase space** (the bottom of the box 😊)
- cell of phase space** (halves of the bottom 😊)
- “occupation number”** (number of balls in one of the halves 😊)
- distribution function**
- microstate and macrostate**

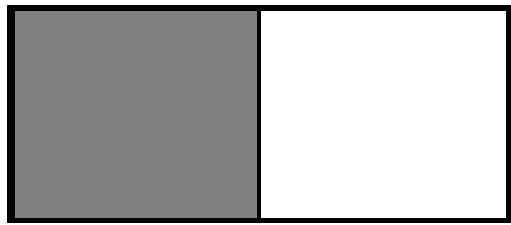
Supposed and verified in practice:

Probability of formation of an arbitrary possible microstate is the same.

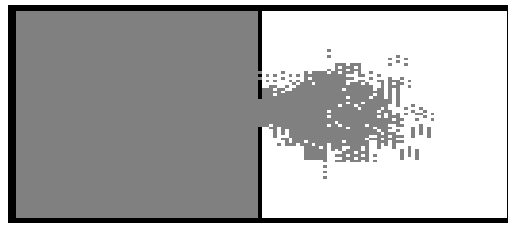
- In the isolated systems, the macrostates of highest probability are formed by largest number of microstates.
- The number of microstates forming the same macrostate, is called thermodynamic probability (P).**
- Macrostates differ one from another by their „occupation numbers“.

Free expansion of gas:

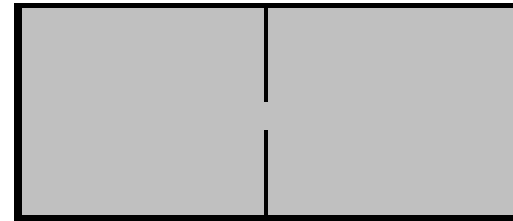
(time course of an irreversible process in the ideal gas)



A)



B)



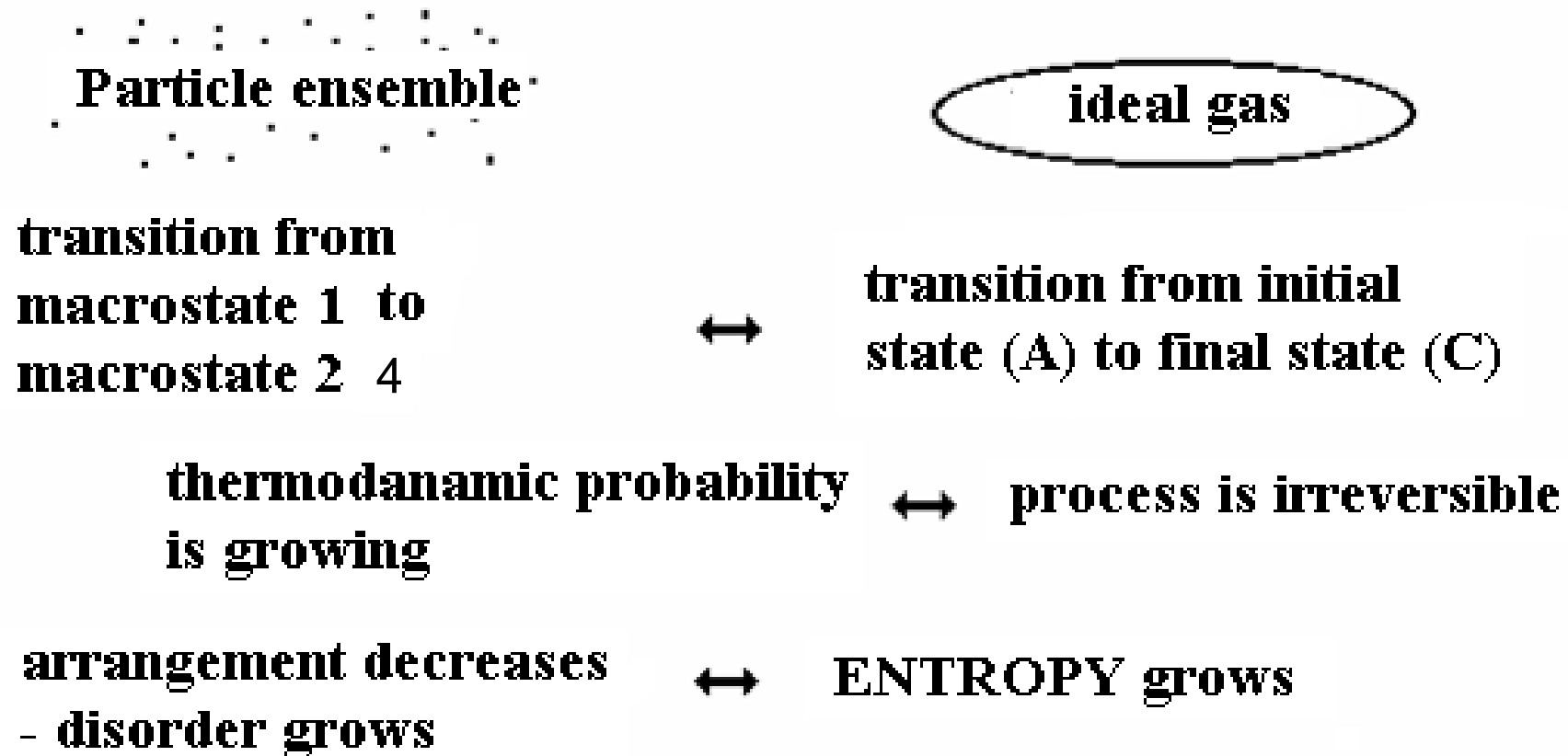
C)

A) A box is divided into two parts by a wall. In one of them, there is compressed ideal gas in equilibrium state.

B) We make an opening in the wall, and the gas expands in the second part of the box – an irreversible process is in progress.

C) After certain time, in both parts of the box tmd. equilibrium is reached.

Analogy between both experiments:



M U N I

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