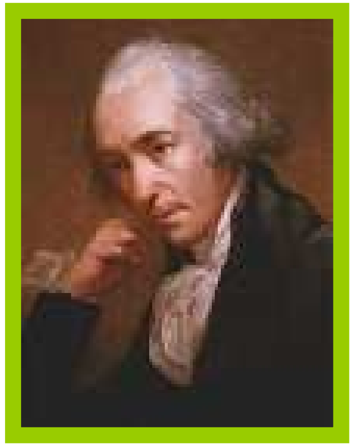
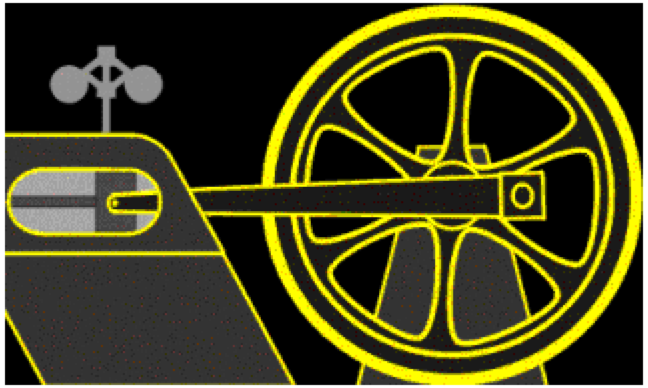


JAMES WATT
19.1.1736 - 19.8.1819

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** can be considered as any macroscopic body or a large set of interacting particles (an example of a thermodynamic system is the human body) bounded in some way.
  - **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 sufficient to fully describe the “thermodynamic” properties of the system at equilibrium are called **state quantities** (sometimes also mentioned to as state variables).
- A defined set of state parameters is necessary for full description of a thermodynamic system.
- These parameters are related to each other in the equations of state.

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)

Work done by/on thermodynamic systems

Gas and piston system $W = p \cdot \Delta V$

- This can be called mechanic or pressure-volume work.

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:

One of the most important state quantities is **temperature**. It is understood as a measure of the "thermal" state of matter and quantitatively expresses the degree of hotness or coldness. Temperature is related to the motion of matter and its parts down to the elementary level.

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.

0^{th} and 1^{st} law of thermodynamics

The zeroth law of thermodynamics states: If systems A and B are each in thermal equilibrium with a third system C, then A and B are also in thermal equilibrium with each other.

The first 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.

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.

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

2nd law of thermodynamics

2nd law of thermodynamics

It is impossible to construct a cyclically operating engine that would only take heat from a reservoir and convert it to equivalent work without transferring a certain amount of heat from a hotter to a colder body, so it is impossible to construct a so-called *perpetuum mobile* of the second kind. (Note: A *perpetuum mobile* of the first kind contradicts the law of conservation of energy.)

There is an additive state function *S*, entropy, defined by the relation:

$$\Delta S \geq \frac{Q}{T},$$

where ΔS is change in entropy and Q is the amount of heat added to the system at temperature T.

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

$$\Delta S \geq 0.$$

As a result, the second law of thermodynamics is sometimes referred to as **the law of entropy increase.** This law determines the “direction” of natural processes, one of the most important natural principles.

($\Delta S = 0$ for reversible processes only)

Entropy and disorder

Entropy is also related to statistical probability, that is, how many different ways a system can be arranged, and we also refer to it as the measure of disorder of the system.

Physics knows the exact relationship between statistical probability W (not to be confused with work) and entropy S. It is called **Boltzmann's principle**:

$$S - S_0 = k.\ln\frac{W}{W_0},$$

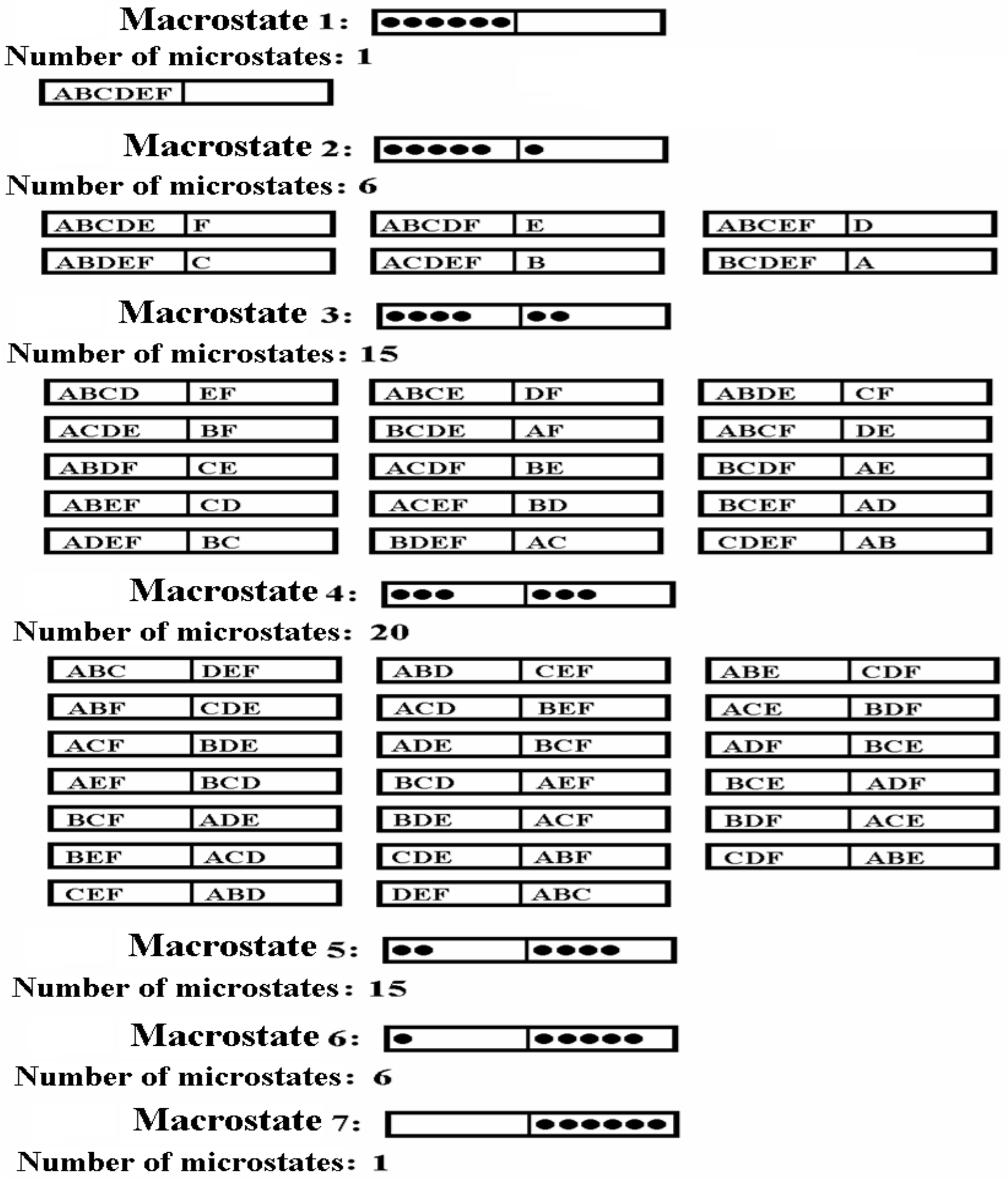
where *k* is **Boltzmann constant**, equal to the ratio of the universal gas constant R to the Avogadro constant N_A. The subscript “0” relates to the initial state.

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*****.**

„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

ABCDEF	

Macrostate 2: ●●●●● | ●

Number of microstates: 6

ABCDE	F	ABCDF	E	ABCEF	D
ABDEF	C	ACDEF	B	BCDEF	A

Macrostate 3: ●●●● | ●●

Number of microstates: 15

ABCD	EF	ABCE	DF	ABDE	CF
ACDE	BF	BCDE	AF	ABCF	DE
ABDF	CE	ACDF	BE	BCDF	AE
ABEF	CD	ACEF	BD	BCEF	AD
ADEF	BC	BDEF	AC	CDEF	AB

Macrostate 4: ●●● | ●●●

Number of microstates: 20

ABC	DEF	ABD	CEF	ABE	CDF
ABF	CDE	ACD	BEF	ACE	BDF
ACF	BDE	ADE	BCF	ADF	BCE
AEF	BCD	BCD	AEF	BCE	ADF
BCF	ADE	BDE	ACF	BDF	ACE
BEF	ACD	CDE	ABF	CDF	ABE
CEF	ABD	DEF	ABC		

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**

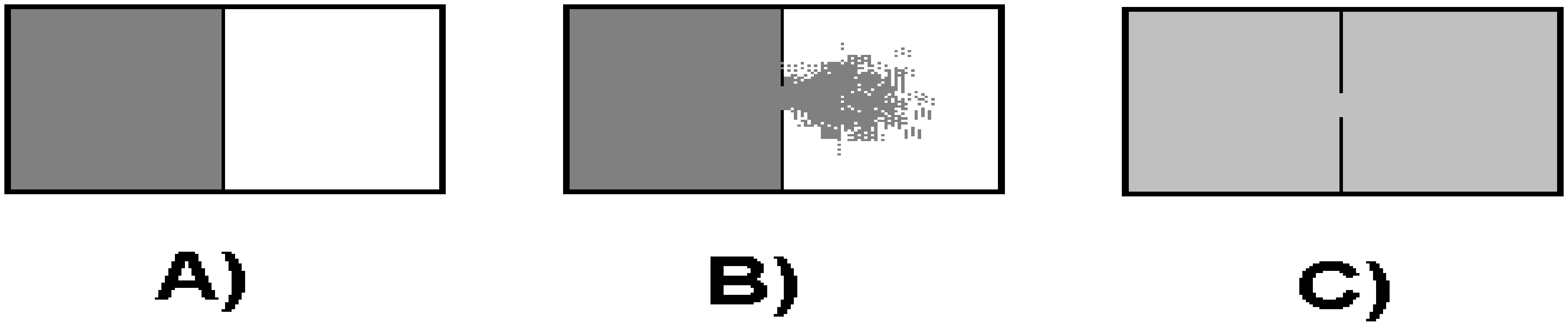
Supposed and verified in practice:

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“.

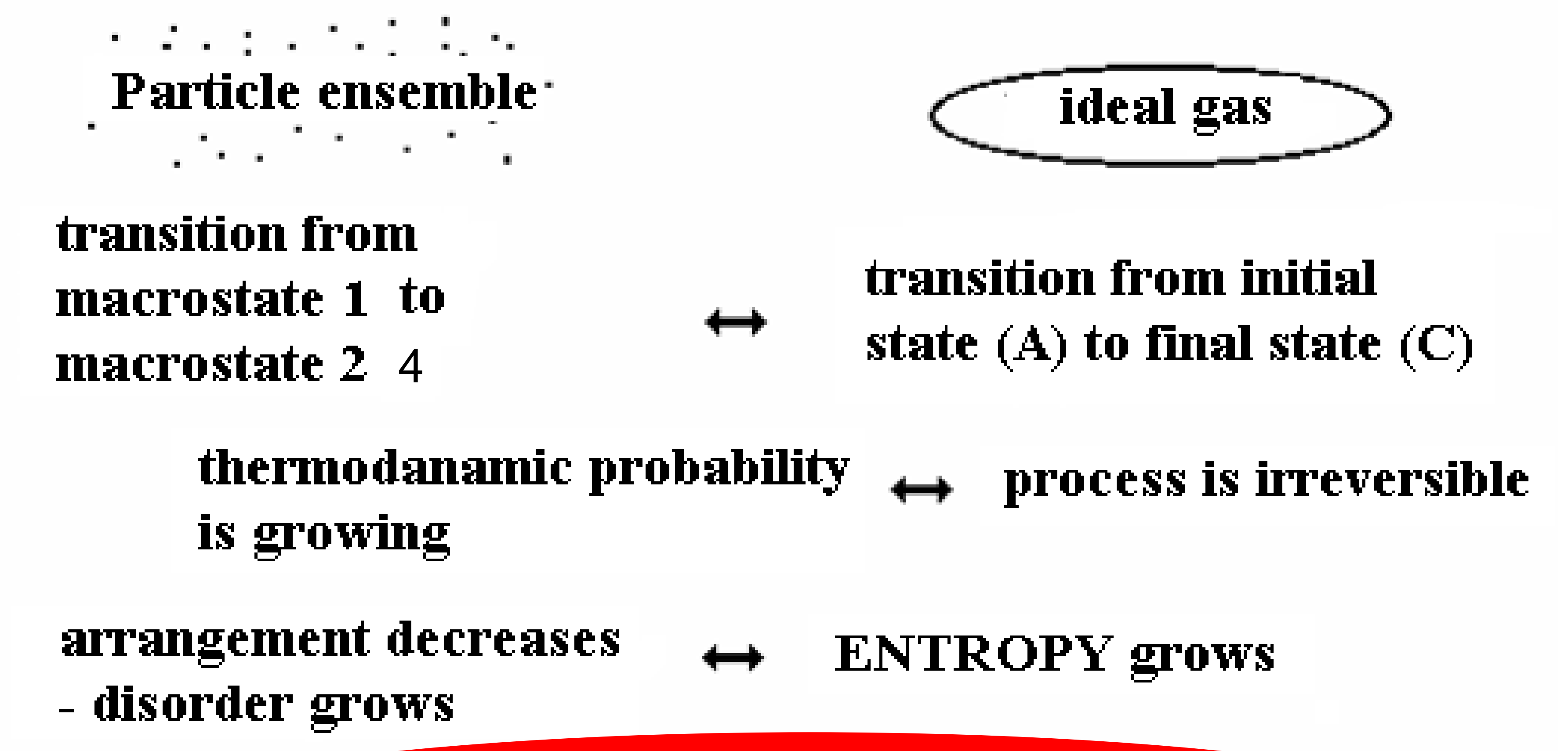
Free expansion of gas:

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



A) 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:



Particle ensemble ↔ **ideal gas**

transition from macrostate 1 to macrostate 2 4 ↔ transition from initial state (A) to final state (C)

thermodanamic probability is growing ↔ process is irreversible

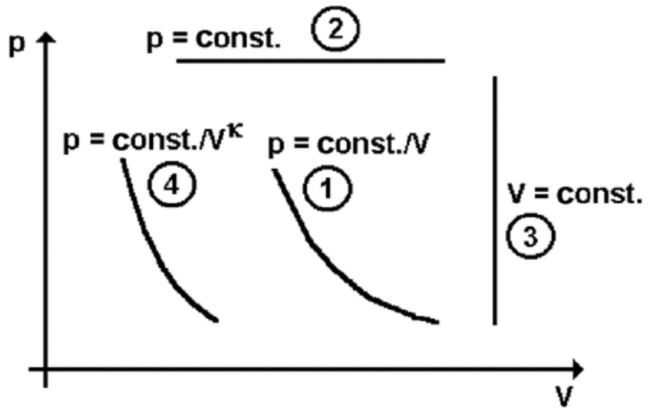
arrangement decreases - disorder grows ↔ ENTROPY grows

Basic processes in gases

- The simplest thermodynamic system is an ideal (perfect) gas.
- Equation of state for the ideal gas (universal gas law):

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

$$[\mathrm{Pa},\ \mathrm{m}^3,\ \mathrm{mol},\ \mathrm{J}\cdot\mathrm{K}^{-1}\cdot\mathrm{mol}^{-1},\ \mathrm{K}]$$



Four special thermodynamic processes can be distinguished:

isothermal
isobaric
isochoric
adiabatic

Authors:

Vojtěch Mornstein

Daniel Vlk

Language revision:

Carmel J. Caruana

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