Physical bases of dental material science

Irén Bárdos-Nagy

Materials Science – Dentistry
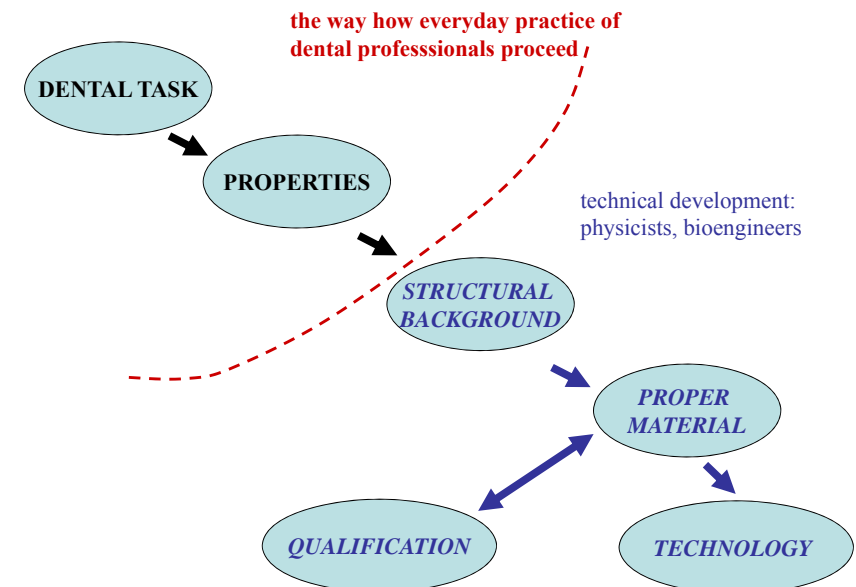
Physics ⟵ ⟶ Biophysics

Important informations

o **Tutor:** Károly Módos, PhD, Assistant Professor (karoly.modos@eok.sote.hu)

o Biofizikai és Sugárbiológiai Intézet – Department of Biophysics and Radiation Biology, EOK left, 2nd floor, Director: Prof. Miklós Kellermayer

o max 3 absencies

o http://biofiz.sote.hu

o www.tankonyvtar.hu

o W.D. Callister: *Materials Science and Engineering*. An Introduction (7th ed.), Wiley&Sons, 2007

o K.J. Anusavice: Phillips' *Science of Dental Materials* (11th ed.), Saunders, 2003

o Damjanovich, Fidy, Szöllősi: *Medical Biophysics*, Medicina, Budapest, 2009

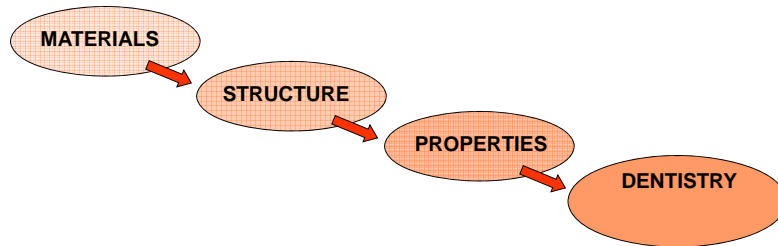o Exam: written test, completed by an oral exam for results higher then the passing mark

Good luck!

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the way how everyday practice of dental professsionals proceed

DENTAL TASK → PROPERTIES → STRUCTURAL BACKGROUND → PROPER MATERIAL

technical development: physicists, bioengineers

PROPER MATERIAL → QUALIFICATION

PROPER MATERIAL → TECHNOLOGY

How to start? – How to proceed?

?

The way how the lectures proceed

MATERIALS → STRUCTURE → PROPERTIES → DENTISTRY

Example for the importance of structure

All are Al_2O_3 !

A high degree of regularity... the principal feature that ... makes solids differ from ... liquids. A liquid has no struc-... long-range repetition of ... ture because the particles in a ... are jumbled and disor... they move about

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Classes of materials - structural basis

The structure of atoms

Demokritos (5th century BC): materials are constructed of an infinite number of indivisable units, **atoms**

Dalton (~ 1800): materials are constructed of **elements** characterized by **specific atoms**

J.J.Thomson (1897): discovery of the **electron** identical constituents in the specific atoms of each elements
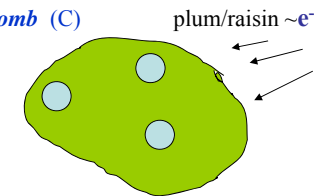
electron is a particle of
    mass << lightest atom, H $m_e=9.11*10^{-31} kg$
        ~ $2x10^3$-times smaller
    charge: *negative, $q_e= -1.6*10^{-19}$ Coulomb* (C)

    plum/raisin ~e^-

atom = plummy pudding
    structure of the atom
    was not known

Ernest Rutherford (1909-11) : scattering of He-ions (α particles) on a thin metal foil

He^{2+}
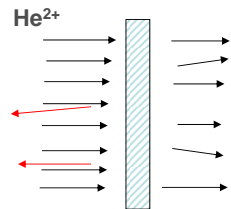
Only a few particles were influenced in their path, some slightly deviated, and very few got reflected/repelled

- the mass of the atoms is concentrated in very small regions
- these small regions carry positive charges
- Rutherford's model: atom is like Sun and its orbiting planets
- most part of the volume of materials is „empty"

Structure of atoms: **atomic nucleus** (small, carries the mass, positive charge)
                electron, with negative charge

Results and models concerning the electronic structure of atoms

Niels Bohr (1913) ⟶ **model**

James Franck, Gustav L. Hertz (1914) ⟶ **verification by experiment**

$$(hf = h\frac{c}{\lambda}$$
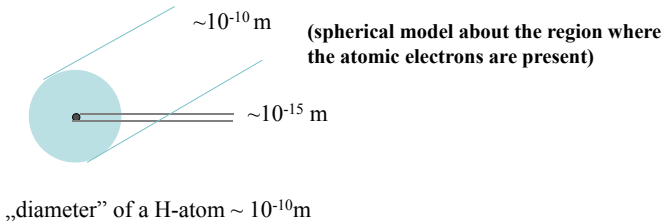$$h = 6.62*10^{-34} Js$$
$$c = 2.998*10^8 m/s)$$

Atomic electrons are bound on atomic orbitals of discrete energies

Results of quantum physics and supposting experimental results

Albert Einstein, Max Planck, Johannes de Haas, Otto Stern, Walther Gerlach

Present understanding of the atomic structure

Dimensions of the atomic structure

$\sim 10^{-10}$ m **(spherical model about the region where the atomic electrons are present)**

$\sim 10^{-15}$ m

„diameter" of a H-atom $\sim 10^{-10}$m

10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}
milli-	micro-	nano-	pico-	femto-

**The atoms interact with each other by their electronic „clouds"/orbitals.
The physical/chemical properties of materials derive from the properties of electronic orbitals.**

The atomic mass

It is based on the atomic nucleus composed of protons (p) and neutrons (n)

Proton (+)

Electric charge = (-1)* charge of the electron = $1.6*10^{-19}$ C
Mass $m_p \sim 1.66*10^{-27}$ kg, (~1840*m_e)
Number of protons in a nucleus: **Z**

Neutron

Electrically neutral
Mass $m_n \sim 1.67*10^{-27}$ kg, slightly larger than m_p
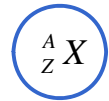Number of neutrons in a nucleus: **N**

} **nucleons**

The atoms are electrically neutral   **Atomic number**

Number of protons = number of bound electrons = **Z**

Mass number $A = N+Z$ (the total number of nucleons)

$$^A_Z X$$

**Symbol of an element X
„nuclide"**

The absolute value of the atomic mass is based on the „unified atomic mass unit" (u)
u = 1.660 538 782 × 10^{-27} kg (one-twelfth of the mass of the nucleus of a ^{12}C atom)
$1 \text{ u} \sim m_p \sim m_n$
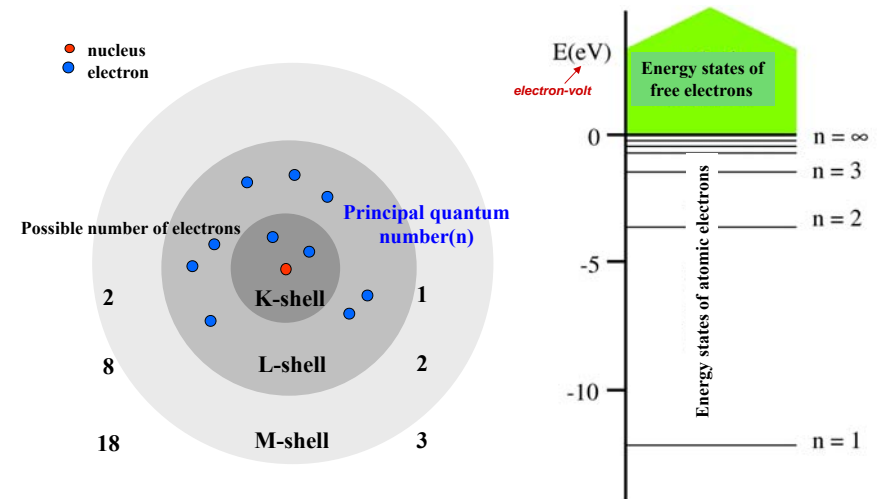

PERIODIC TABLE OF THE ELEMENTS

The structure and energetics of atomic electrons

- nucleus
- electron

Principal quantum number(n)

Possible number of electrons

2	K-shell	1
8	L-shell	2
18	M-shell	3

E(eV)   **electron-volt**

Energy states of free electrons

0 — $n = \infty$
— $n = 3$
-5 — $n = 2$
-10 — $n = 1$
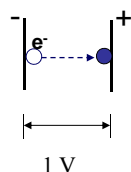
Energy states of atomic electrons

Electronic energy and momenta are quantized properties in the bound state.
Quantum numbers: principal-, angular momentum-, magnetic-, spin-

Pauli's principle: the bound electrons can not have identical quantum numbers

The „electron-volt" as an energy unit

1 eV energy = the kinetic energy of one electron after it got accelerated by a voltage of 1 V
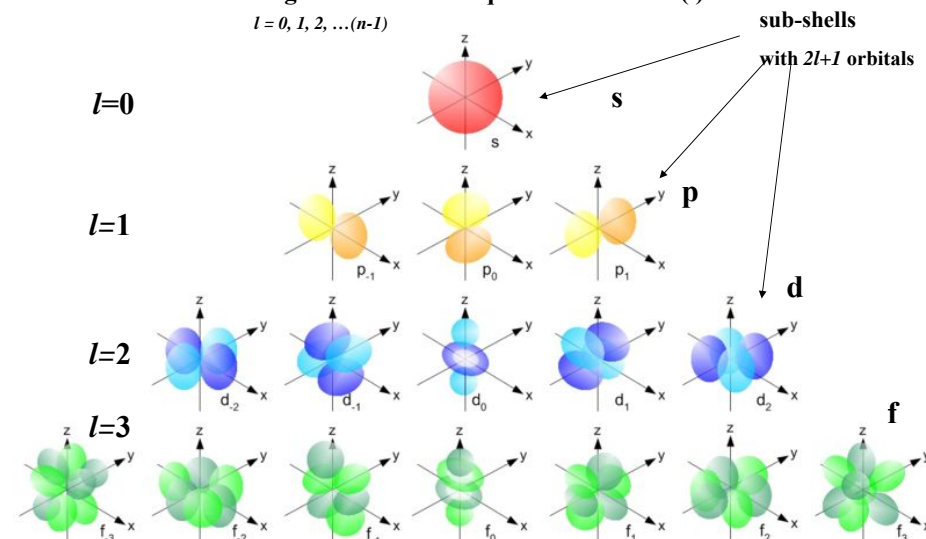
1 V

$$1 eV = q * U = 1.6 * 10^{-19} C * 1V = 1.6 * 10^{-19} Joule$$

charge

voltage

The electron-volt unit is widely used in the field of spectroscopy, and radiations like light and ionizing radiations (X-rays, γ, β, α, etc.)

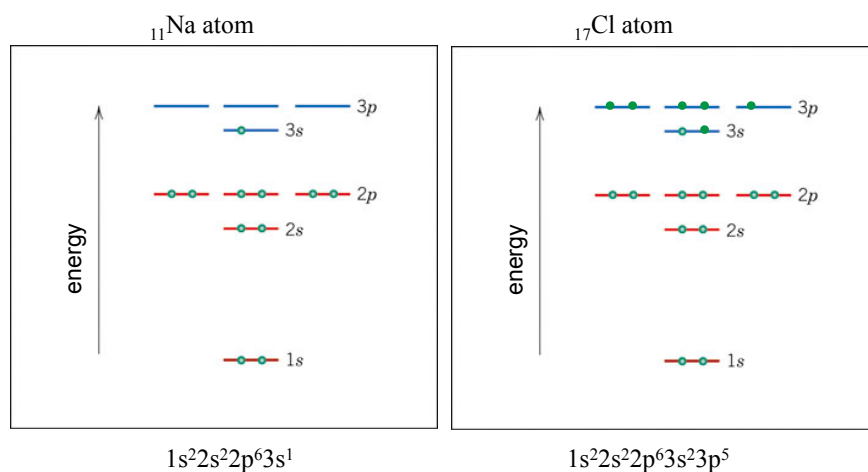## Role of the orbital angular momentum quantum number (*l*)

$l = 0, 1, 2, …(n-1)$

sub-shells

with *2l+1* orbitals

l=0   s

l=1   p

l=2   d

l=3   f

Examples for the population of electronic orbitals
subshells may lead to a fine structure of the energy levels

$_{11}$Na atom

$_{17}$Cl atom

energy

3p
3s
2p
2s
1s

$1s^22s^22p^63s^1$

energy

3p
3s
2p
2s
1s

$1s^22s^22p^63s^23p^5$

Population of electronic orbitals – relation to the state of free electrons

Symplified sketch of the electronic energy levels in an atom   (subshells are not shown separately)

free electron states

0

orbital energy

ΔE

ΔE

n=3

n=2

n=1

$_{10}$Ne

$1s^22s^22p^6$
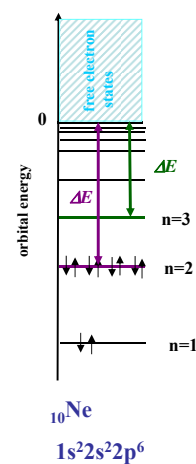
the energy states affected the most in chemical reactions, atomic bond formation, etc.

LUMO Lowest Unoccupied Molecular Orbital

HOMO Highest Occupied Molecular Orbital

ΔE ~ Ionization energy – I (eV/atom or kJ/mol)
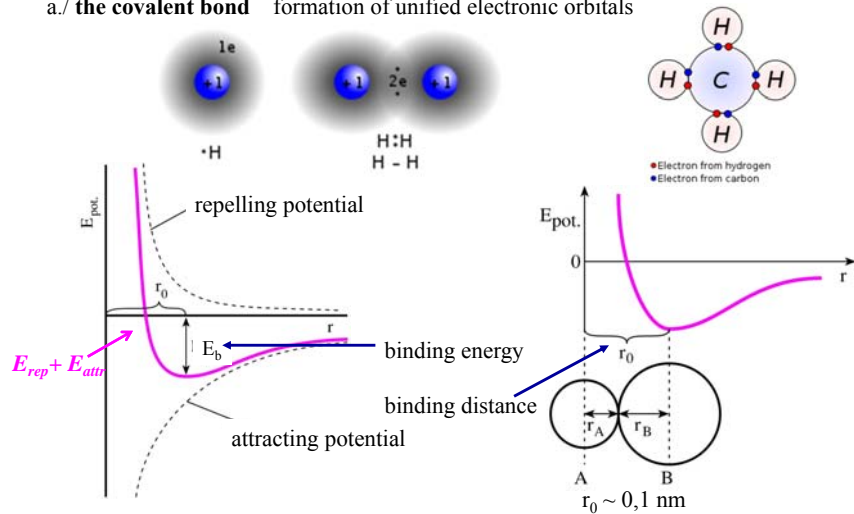
ΔE ~ Electron affinity - E_{ea} (eV/atom or kJ/mol)

Interaction between the atoms ⟶ chemical binding

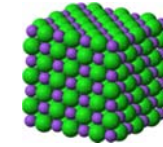**General concept of the formation of atomic bonds: minimizing the potential energy**

Primer (strong) chemical bonds (binding energy 100 – 500 kJ/mol few eV/bond)

(1eV/bond ~ 100 kJ/mol)

a./ **the covalent bond** formation of unified electronic orbitals

H:H
H – H

- Electron from hydrogen
- Electron from carbon

$E_{pot.}$

repelling potential

$E_{rep}+ E_{attr}$

E_b

binding energy

binding distance

attracting potential

$r_0 \sim 0{,}1$ nm

b./ **the ionic bond**

sodium contributes electron, leaving it with a closed shell

chlorine gains electron, leaving it with a closed shell
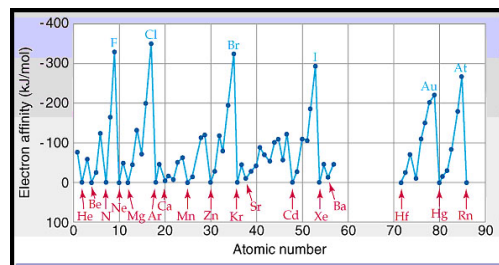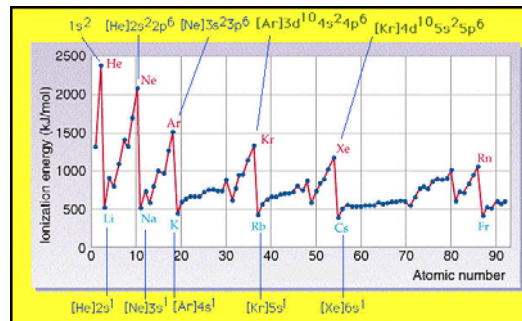
forming ionic bond

forming ionic bond

c./ **the metallic bond**

Zn 2+   Zn 2+
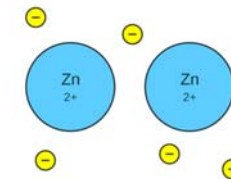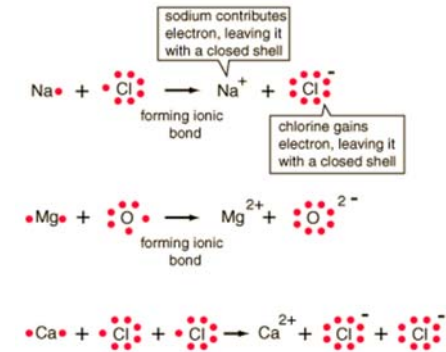
Ionization energy (I):

The minimum energy required to remove an electron bound in an atom in the gas phase (eV/atom; kJ/mol)

Electronaffinity (E_{ea}):

The energy released when an electron attaches to an atom in the gas phase (eV/atom; kJ/mol)

Exothermic electron attachment: $E_{ea}>0$
-- incoming electron interacts strongly with the nucleus on its orbital
Endothermic electron attachment: $E_{ea}<0$
-- A⁻ has higher energy than A and e⁻

Electronegativity χ

is the measure of the power of an atom of an element to attract electrons when it is part of a compound

Mulliken's absolute definition: $\chi_M = \frac{1}{2}(I + E_{ea})$

arithmetical average of the ionization energy and electron affinity
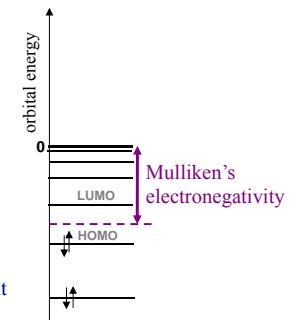
Pauling's relative scale:
characterizes the polar character of bonds

$\Delta = E_{bond,AB}(\exp.) - E_{bond,AB}(theor., non-polar)$

$E_{bond,AB}^{non-polar} = \dfrac{E_{bond}^{A-A} + E_{bond}^{B-B}}{2}$ ← if the bonds were purely covalent

$0.104*\sqrt{\Delta} = |\chi_A - \chi_B|$

one of the electronegativities is empirically fixed – relative scale

orbital energy

Mulliken's electronegativity

LUMO

HOMO

Pauling-scale (relative):

eV/atom

Practical use of electronegativity
(e.g. for molecule AB)

$$\left|\chi_A - \chi_B\right|$$

is related to the - electric dipole moment
   - ionic character of the bond, given in %
   - ionic-covalent resonance energy

When a molecule is formed, the electrons flow towards the atoms of high electronegativity,
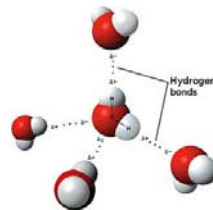the electronegativities of the atoms tend to equalize and acquire the same, uniform value

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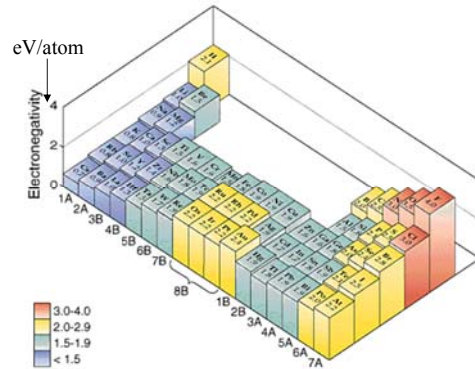
$$\left|\chi_A + \chi_B\right|$$

is related to the type of primary
bond formed between A and B

$\left|\chi_A - \chi_B\right|$

ionic

metallic

covalent

$$\left|\chi_A + \chi_B\right|$$
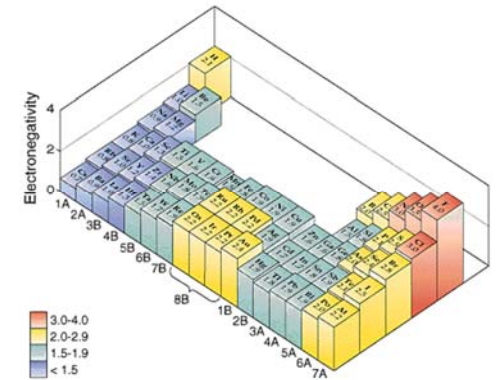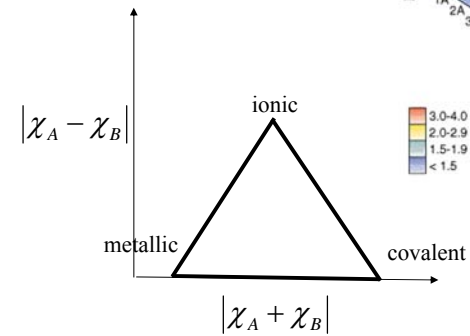
Secondary (week) chemical bonds (binding energy less than 50 kJ/mol   few 0.1 eV/bond)

a./ **the H – bond**   (~20 kJ/mol, 0.3 eV/bond)   (water, HF)
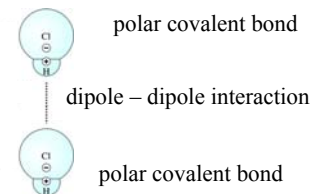

Hydrogen bonds

b./ **electrostatic interaction**

ion – dipole (few kJ/mol, 0.05 eV/bond)
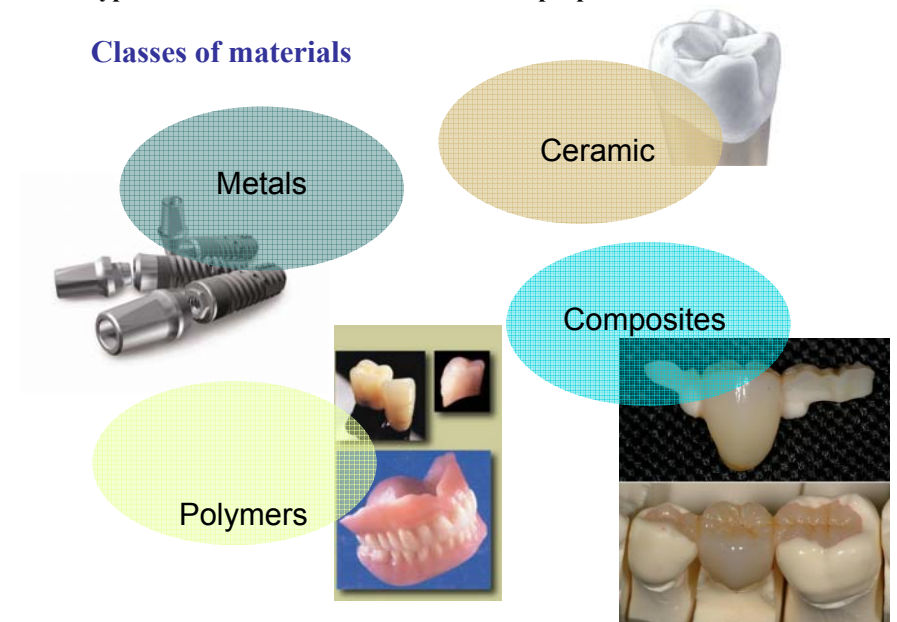
dipole – dipole (~ 2 kJ/mol, 0.02 eV/bond)

hydrophobic (~2 kJ/mol, 0,02 eV/bond)

van der Waals (dispersion) (~ 0.1 kJ/mol, 0. 001 eV/bond)
(Noble gases, F_2, H_2, Cl_2 molecules)

polar covalent bond

dipole – dipole interaction

polar covalent bond

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type of bonds ⟶ structure ⟶ properties

Classes of materials

Ceramic

Metals

Composites
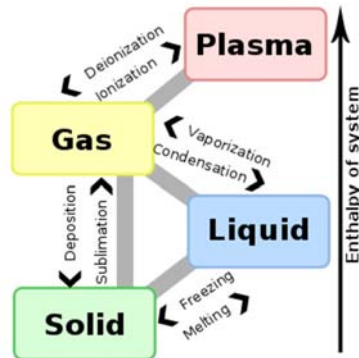
Polymers

The broad states of matter: gas
liquid
(liquid – crystal)
solid

General phase transitions

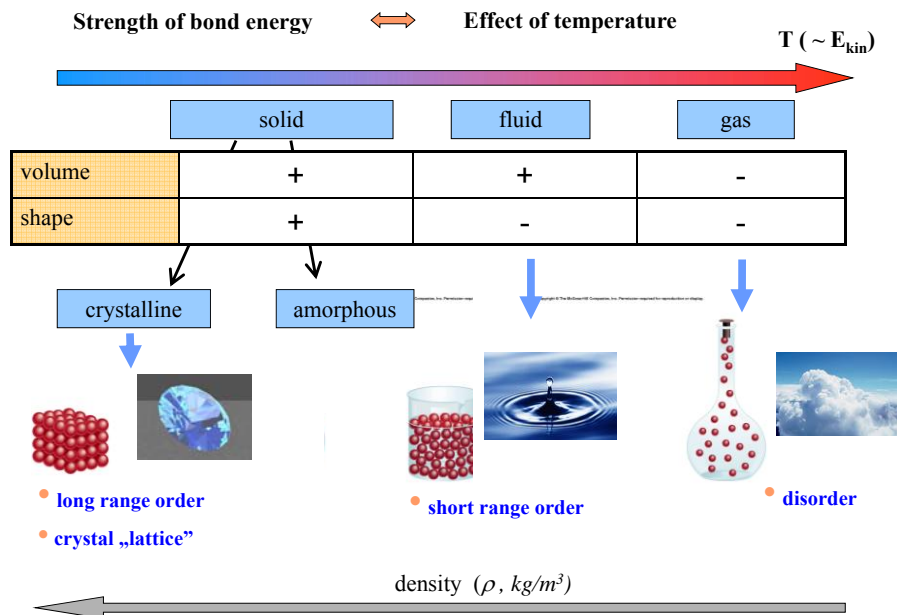phase: physically and chemically homogeneuos part of the material

General properties of different phases:

gas: no definite volume and shape (there is no (or very week) interaction between the particles), isotropic

liquid: the volume is definite, the shape is changing, short range order (secondary interactions between the molecules), isotropic

liquid – crystal: special shape of individual molecules, relatively long range of order, anisotropy (intermediate phase between liquids and crystals)

solid: definite shape and volume (strong (primer) bonds between the particles)
macroscopic range order (crystals)
periodic crystal structure, symmetry, frequent anisotropy
low degree of translational motion

Strength of bond energy ⟷ **Effect of temperature**

$T (\sim E_{kin})$

	solid	fluid	gas
volume	+	+	-
shape	+	-	-

crystalline   amorphous

• **long range order**

• **crystal „lattice"**

• **short range order**

• **disorder**

density $(\rho, kg/m^3)$

Density of materials used in Dentistry

$$1\frac{kg}{m^3} = \frac{10^3\,g}{\left(10^2\right)^3\,cm^3} = \frac{10^3\,g}{10^6\,cm^3} = 10^{-3}\,\frac{g}{cm^3}$$

Broad scale of materials – broad scale of structures and properties

material	ρ (g/cm³)
dental enamel	2,2
dentine	1,9
water	1
amalgam	≈ 12
gold	19,3
gold-alloys	12-17
Pd-Ag alloys	10-12
Co-Cr alloys	8-9
Ni-Cr alloys	≈ 8
glass	2,2-2,7
ceramic	1,6-3,9
porcelain	2,2-2,4
gypsum ($CaSO_4 \times 2H_2O$)	2,31-2,76
PMMA poly(methylmethacrylate)	≈ 1,2
silicon poly(dimethylsiloxane)	≈ 1,4

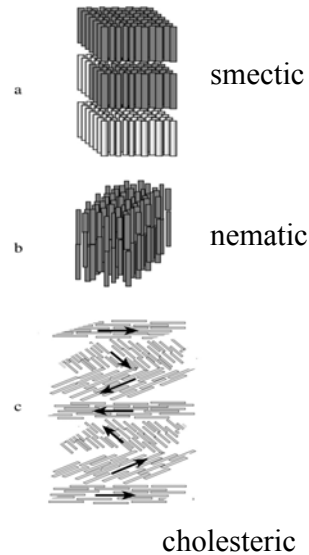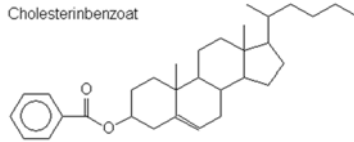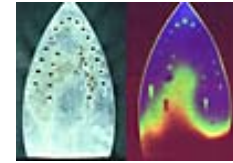## Liquid crystals: a mesomorphous state of matter

Thermotropic - liotropic

General properties
- elongated shape of molecules
- relativly long range order stabilized by secondary bonds
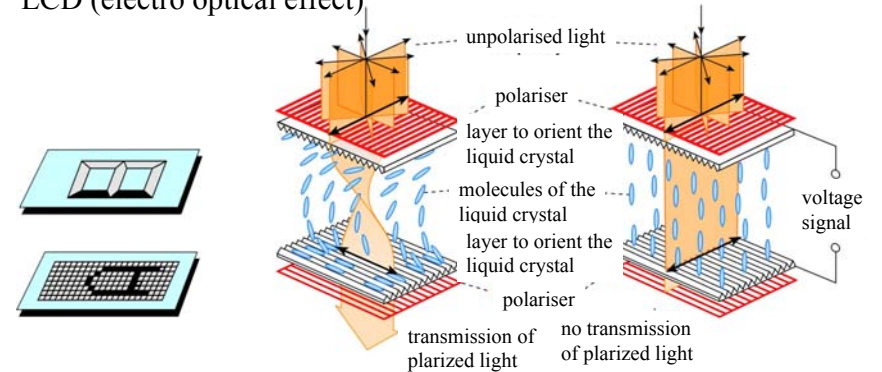- fluidity, deformability
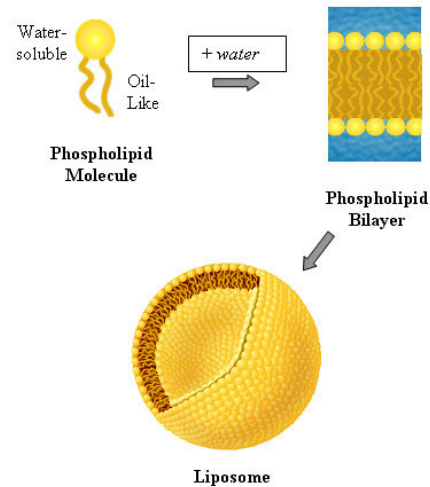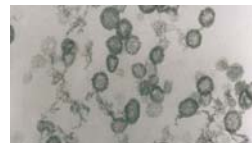- anisotropy in fluid state

Cholesterinbenzoat

a — smectic

b — nematic

c — cholesteric

Use of thermotropic liquid crystals

LCD (electro optical effect)

unpolarised light

polariser

layer to orient the liquid crystal

molecules of the liquid crystal

layer to orient the liquid crystal

polariser

voltage signal

transmission of plarized light

no transmission of plarized light

Liotropic liquid crystals

Water-soluble

Oil-Like

+ water

Phospholipid Molecule

Phospholipid Bilayer

Liposome

Cellular bi-layer membranes

proteins

lipids
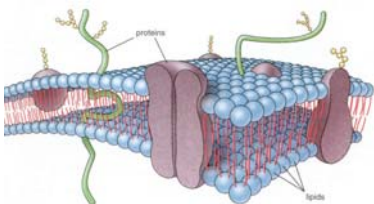
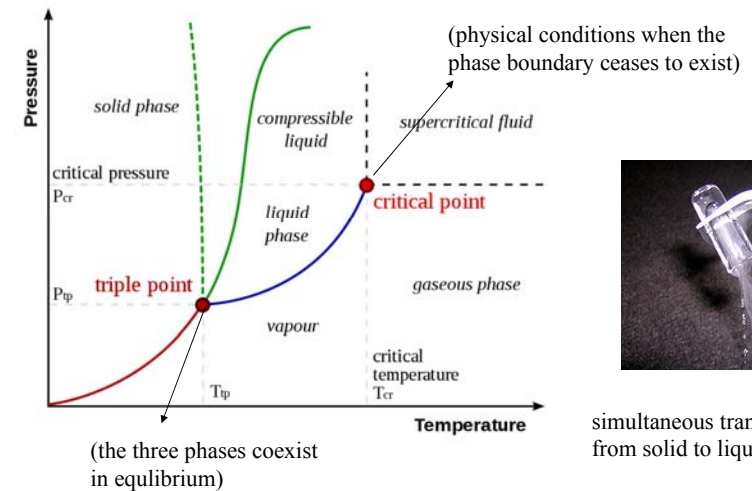
A typical phase diagram

phase diagram: graphical presentation of stable phases as a function of different parameters

Pressure

solid phase

compressible liquid

supercritical fluid

(physical conditions when the phase boundary ceases to exist)

critical pressure P_{cr}

P_{tp}

triple point

liquid phase

critical point

gaseous phase

vapour

critical temperature T_{cr}

T_{tp}

Temperature

(the three phases coexist in equlibrium)

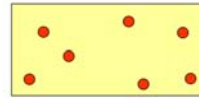simultaneous transition of Ar from solid to liquid and to gas

Classes of materials

Gas phase (ideal gas)

characteristics

- filling the container – no volume in itself
- disorder
- composed of independent particles
- isotropy

Macroscopic properties/parameters

p, V, ν, T

R – universal gas constant
R= 8.314 J/mol*K

$$pV = \nu\,RT$$

Equation of state

mole number

Gas phase (ideal gas)
without force field

Macroscopic description

Uniform density

Macroscopic
properties/parameters

$$pV = \nu\,RT$$

Microscopic description

Maxwell-Boltzmann distribution

0°C

300°C

frequency of occurrance
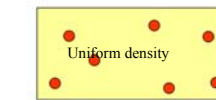
$$\frac{1}{2}m\overline{v}^2 = \frac{3}{2}kT$$

average kinetic energy

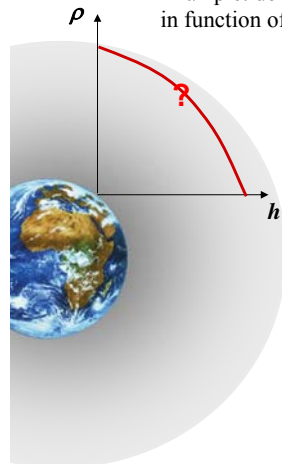$$k = \frac{R}{N_A} = 1.38*10^{-23}\,\frac{J}{K}$$

Boltzmann constant
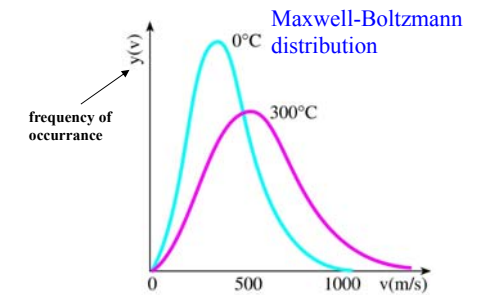
individual velocities of O_2 molecules are distributed in a broad range

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Gas phase (ideal gas)
in a force field – gravitation

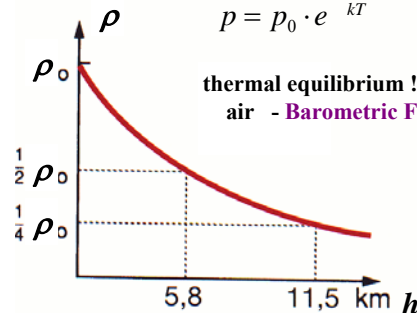Example: density (ρ) of air *changes* in function of the potential energy

$$\rho = \rho_0 . e^{-\frac{mgh}{kT}}$$

$$p = const * \rho$$

$$p = p_0 \cdot e^{-\frac{mgh}{kT}}$$

thermal equilibrium !
air - Barometric Formula

ρ_0

$\frac{1}{2}\rho_0$

$\frac{1}{4}\rho_0$

5,8   11,5 km h

less and less particles are found (in the same volume) at the levels of higher potential energy (at higher altitudes)

The Barometric formula is a special case of a general law

Boltzmann distribution

Distribution of particles on the levels of potential energy ε_i

n_i —— ε_i

n_0 —— ε_0 $\Big\}\Delta\varepsilon$

$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i - \varepsilon_0}{kT}}$$

$$n_i = n_0 \cdot e^{-\frac{\varepsilon_i}{kT}} = n_0 \cdot e^{-\frac{\Delta\varepsilon}{kT}} = n_0 \cdot e^{-\frac{\Delta E}{RT}}$$

$$\begin{pmatrix} \Delta E = \Delta\varepsilon \cdot N_A \\ R = k \cdot N_A \end{pmatrix}$$
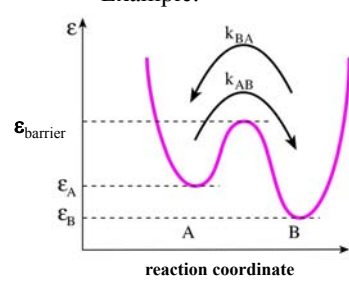
- the number of particles is smaller at the levels of higher energy
- on the same level, the number is smaller at higher temperatures
- the lowest energy level has the highest number of population

Wide range of applications

- **barometric formula**
- **thermal emission of metals**
- **Nernst equation**
- **equilibrium and rate of chemical reactions**
- **concentration of thermal defects in ordered, structured systems**
- **conductivity of semiconductors**...

Example:

$$k_{AB} = const. \cdot e^{-\frac{\varepsilon_{barrier} - \varepsilon_A}{kT}}$$

$$K = \frac{n_A}{n_B} = e^{-\frac{\varepsilon_A - \varepsilon_B}{kT}}$$

Arrhenius plot

energy of activation