Materials Science – Dentistry

Physics

Materials Science – Dentistry

Biophysics – 2nd Semester

Physics

About the Semester

- ***Tutor:*** Károly Módos, PhD, Assistant Professor (karoly.modos@eok.sote.hu)
- Biofizikai és Sugárbiológiai Intézet – Department of Biophysics and Radiation Biology, EOK left, 2nd floor, Director: Prof. Kellermayer
- max 3 absencies
- W.D. Callister: *Materials Science and Engineering*. An Introduction (7th ed.), Wiley&Sons, 2007
- K.J. Anusavice: Phillips' *Science of Dental Materials* (11th ed.), Saunders, 2003
- Damjanovich, Fidy, Szöllősi: *Medical Biophysics*, Medicina, Budapest, 2009
- Exam: written test, completed by an oral exam for results higher then the passing mark

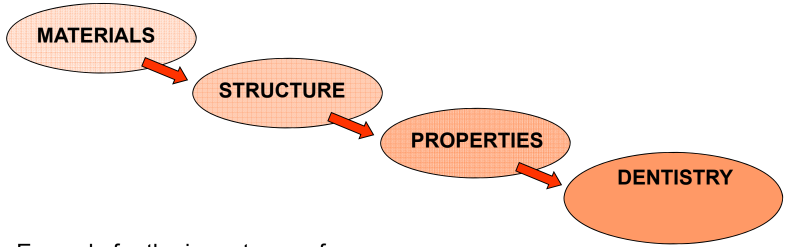
Good luck!

Irén Bárdos-Nagy
Department of Biophysics and Radiation Biology

How to start?
How to proceed?

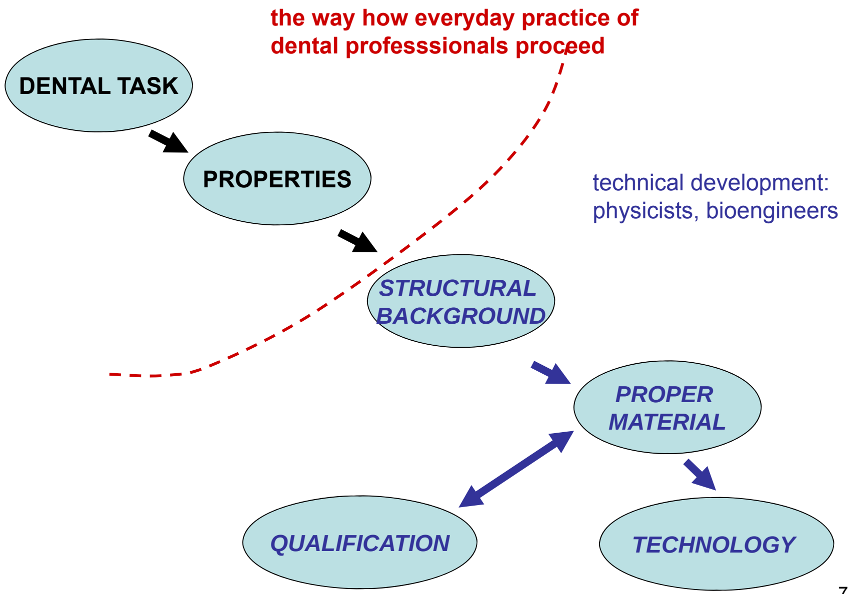
How to start? – How to proceed?

The way how the lectures proceed



Example for the importance of structure

All are Al_2O_3 !



The most exciting phrase to hear in science, the one that heralds new discoveries, is not 'Eureka!' (I found it!), but 'That's funny…'
Isaac Asimov (1920 - 1992)

Classes of materials - structural basis

1. History

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

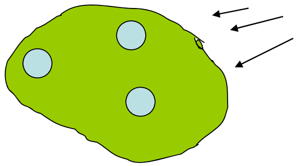
Dalton (~ 1800): materials are constructed of **elements** characterized by **specific atoms**

J.J.Thomson (1897): discovery of the **electron**
identical constituents in the specific atoms of each elements

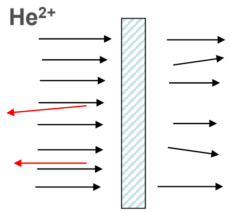
electron is a particle of
mass << lightest atom, H ***m_e=9.11*10^{-31} kg***
~ $2x10^3$-times smaller
charge: ***negative, q_e= -1.6*10^{-19} Coulomb*** (C)

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



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
- most part of the volume of materials is „empty"
-Rutherford's model: atom is like Sun and its orbiting planets

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

+ spectral measurements

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

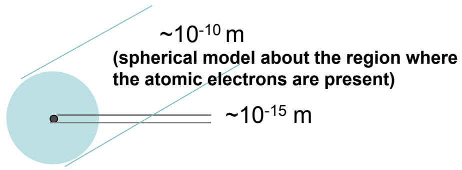
Atomic electrons are bound on atomic orbitals of descrete energies

Results of quantum physics and suppposting experimental results
– Albert Einstein, Max Planck, Johannes de Haas, Otto Stern, Walther Gerlach

Present understanding of the atomic structure

2. The structure of atoms

Dimensions of the atomic structure



„diameter" of a H-atom ~ 10^{-10}m

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

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

Neutron

- **Electrically neutral**
- **Mass m_n~$1.66 \cdot 10^{-27}$ kg, slightly larger than m_p**
- **Number of neutrons in a nucleus: *N***

} **nucleons**

The atoms are electrically neutral

Number of protons = number of bound electrons = Z

Atomic number

Mass number $A = N+Z$ = total number of nucleons

$^{A}_{Z}X$

Symbol of an element X „nuclide"

Isotopes of an element

A is different, but *Z* is identical (N is different)

=> identical electron-structure

identical chemical properties

„isotopos"
Two objects that are able to replace each other

e.g. ^{12}C and ^{11}C

	^{12}C	^{11}C
A	12	11
Z	6	6
N	6	5

The atomic mass

The absolute value of the atomic mass is based on the

„ unified atomic mass unit" (Symbol u)

***u* = 1.660 538 782 × 10^{-27} kilogram,**

with a one-standard deviation uncertainty of ± 0.000 000 083 × 10−27 kilogram.

one-twelfth of the mass of the nucleus of a ^{12}C atom

The above definition was agreed upon by the International Union of Pure and Applied Physics in 1960 and the International Union of Pure and Applied Chemistry (in 1961), resolving a longstanding difference between chemists and physicists. The unified atomic mass unit replaced the atomic mass unit (chemical scale) and the atomic mass unit (physical scale), both having the symbol ***amu***. The amu (physical scale) was one-sixteenth of the mass of an atom of ^{16}O. The amu (chemical scale) was one-sixteenth of the ***average mass*** of oxygen atoms ***as found in nature.***

1 ***u*** = 1.000 317 9 ***amu*** (physical scale) = 1.000 043 ***amu*** (chemical scale)

1 $u \sim m_p \sim m_n$

Periodic Table of elements

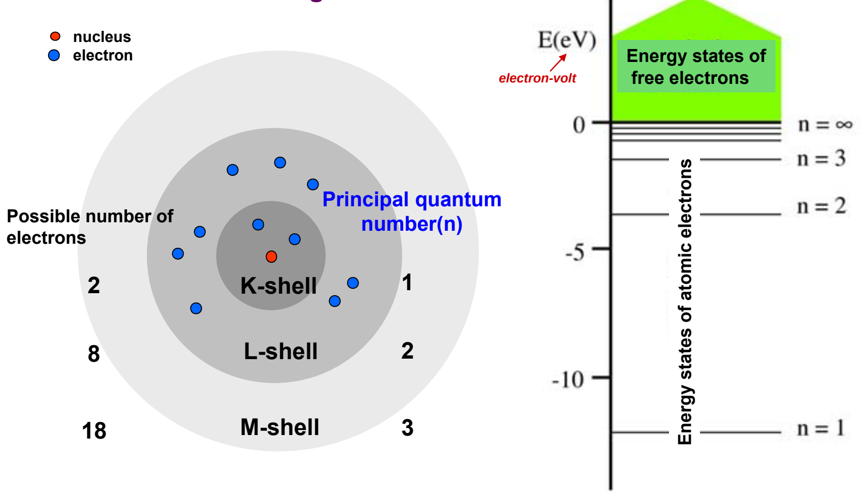
Key: 29 – Atomic number; Cu – Symbol; 63.54 – Atomic weight

Metal / Nonmetal / Intermediate

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.87	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.69	29 Cu 63.54	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.2	76 Os 190.23	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (281)								

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

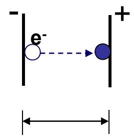
The structure and energetics of atomic electrons



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

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

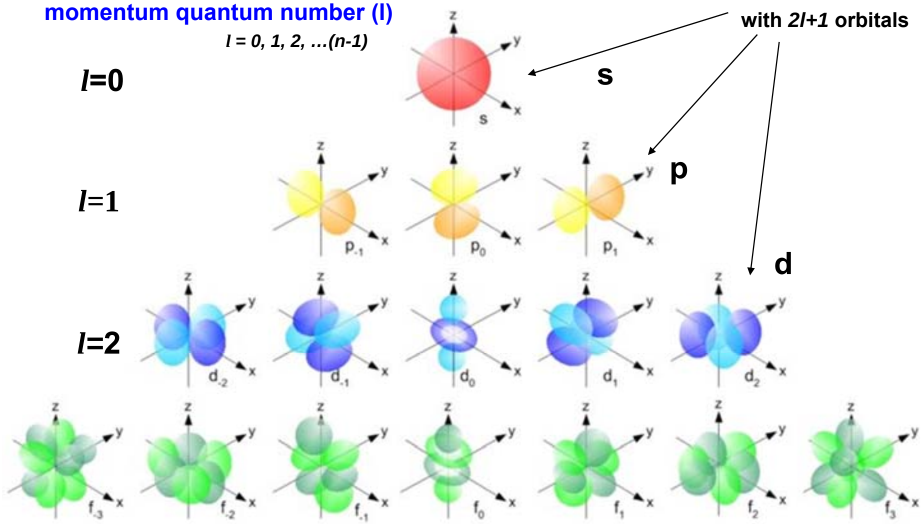
charge voltage

*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)

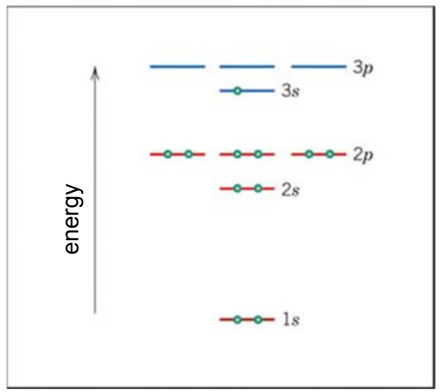
l = 0, 1, 2, …(n-1)

sub-shells
with *2l+1* orbitals



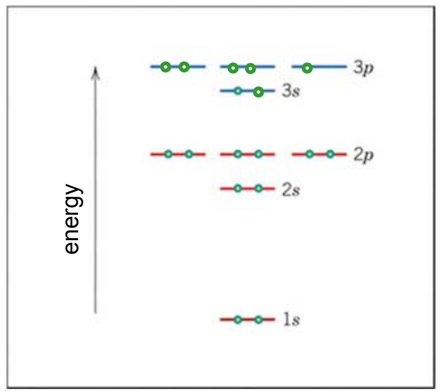
Examples for the population of electronic orbitals – subshells may lead to a fine structure of the energy levels

$_{11}$Na atom



$1s^2 2s^2 2p^6 3s^1$

$_{17}$Cl atom

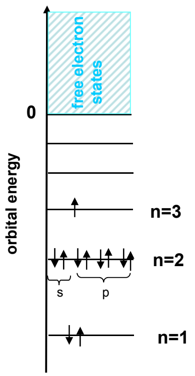


$1s^2 2s^2 2p^6 3s^2 3p^5$

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



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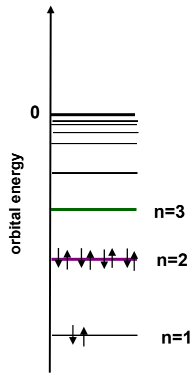

the states affected the most in chemical reactions, atomic bond formation, etc.

LUMO Lowest Unoccupied Molecular Orbital

HOMO Highest Occupied Molecular Orbital

$_{10}$Ne

$1s^2 2s^2 2p^6$

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

Symplified sketch of the electronic energy levels in an atom

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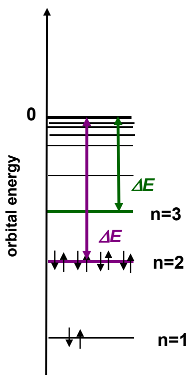


the states affected the most in chemical reactions, atomic bond formation, etc.

LUMO Lowest Unoccupied Molecular Orbital

HOMO Highest Occupied Molecular Orbital

ΔE ~ Ionization energy – I (eV/atom or kJ/mol)

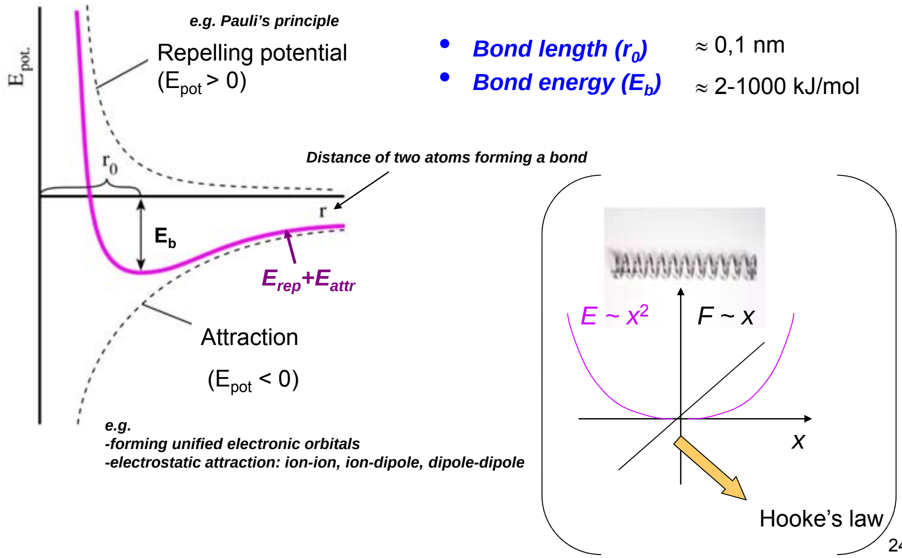
ΔE ~ Electron affinity - E_{ea} (eV/atom or kJ/mol)

$_{10}$Ne

$1s^2 2s^2 2p^6$

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

- ***Bond length (r_0)*** ≈ 0,1 nm
- ***Bond energy (E_b)*** ≈ 2-1000 kJ/mol



Atomic/molecular bonds

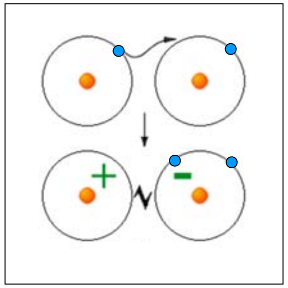
- ***Primary bonds - atomic***

E_{bond}**≈500 kJ/mol**

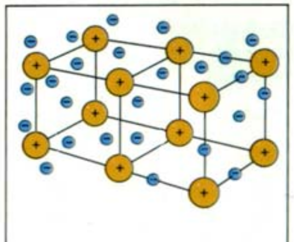
- covalent
- metallic
- ionic

ionic bond

e.g. NaCl

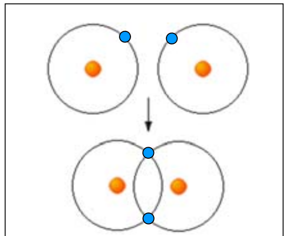


$$1(eV/atom) = 96.485(kJ/mol) \cong 100(kJ/mol)$$



metallic bond

e.g. Na-metal



covalent bond

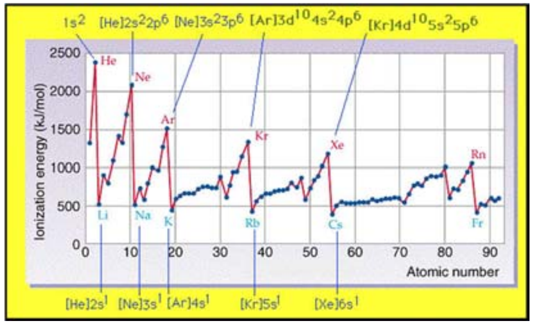
e.g. H_2 gas

Electronegativity

in relation to the polarity of primary bonds

Ionization energy (*I*):

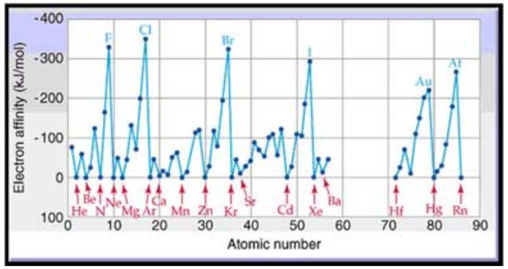
The minimum energy required to remove an electron bound in an atom in the gas phase (eV/atom; kJ/mol)



$$1(eV/atom) = 96.485(kJ/mol) \cong 100(kJ/mol)$$

Electronaffinity (E_{ea}):

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



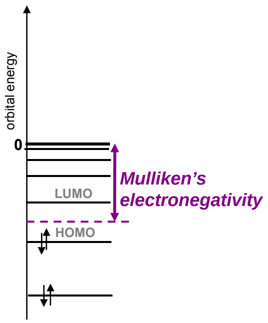
Exothermic electron attachment: E_{ea}>0
-- incoming electron interacts strongly with the nucleus on its orbital
Endothermic electron attachment: E_{ea}<0
-- A^- has higher energy than A and e-

Electronegativity - χ

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

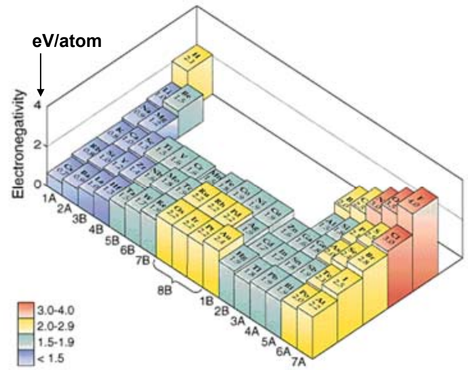
$$\Delta = E_{bond,AB}(\exp.) - E_{bond,AB}(theor., non-polar)$$

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

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

one of the electronegativities is empirically fixed – relative scale

Pauling-scale (relative):



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

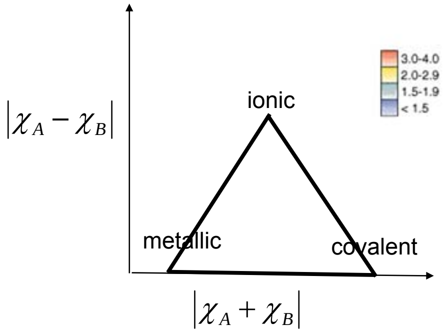
$$\underbrace{|\chi_A - \chi_B|}$$

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

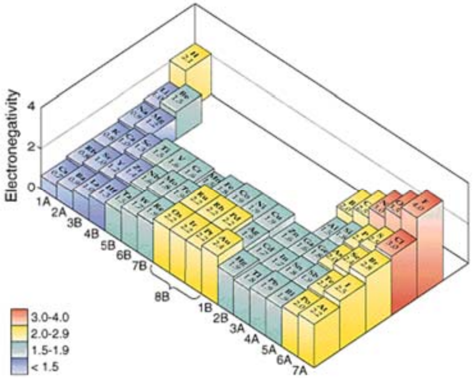
When a molecule is formed, the electrons flow towards the atoms of high electronegativity, the electronegativities of the atoms tend to equalize and acquire the same, uniform value

$$|\chi_A + \chi_B|$$

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



$|\chi_A - \chi_B|$ (vertical axis), $|\chi_A + \chi_B|$ (horizontal axis)

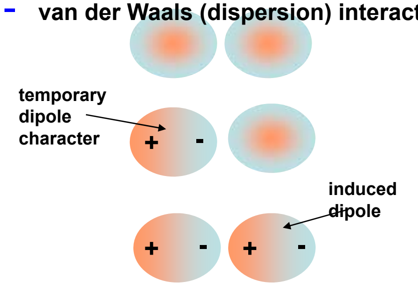


- ***Secondary/molecular bonds***

$E_{bond} \approx$ 0.5 - 100 kJ/mol (⟷ primary:~500 kJ/mol)

broad range of bonds of *dipole character*

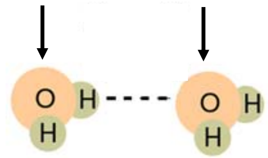
- **H-bond**
- **hydrophobic interaction**
- **ion-dipole, dipole-dipole interactions**
- **van der Waals (dispersion) interaction**



dispersion interaction

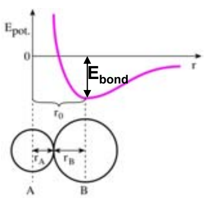
e.g. molecules of noble gas

H-bond



between two atoms (of two molecules) of high electronegativity (e.g. O, N, F...)

Bond energy and bond length depends on the type of interaction



class of secondary bonds

Type of attraction	Bond energy (kJ/mol)
Ion-dipole	10-20
Dipole-dipole (fixed)	2
Dipole-dipole (+thermal motion)	0.3
Dispersion	2
H-bonds	5 -150

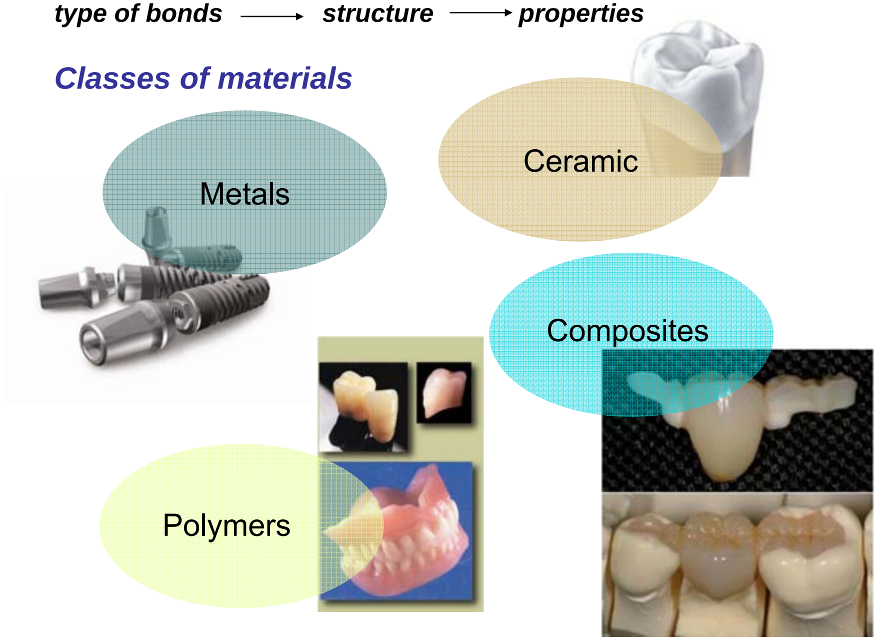
Bond length and the atomic radii – dependence on the interaction

$$r_0 = r_{bond} = r_A + r_B$$

Element	r_A(van der Waals) nm	r_A(covalent) nm	r_A(ionic) nm	ion
H	0,120	0.037		
C	0.170	0.077	0.029	C^+
N	0.155	0.075	0.025	N^+
O	0.152	0.073	0.140	O^{2-}
F	0.147	0.071	0.117	F^-
P	0.180	0.106	0.058	P^{3+}
S	0.180	0.102	0.184	S^{2-}

type of bonds* ⟶ *structure* ⟶ *properties

Classes of materials

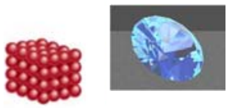


State of matter

Strength of bond energy ⟺ **Effect of temperature** — ***T* (~ E_{kin})**

	solid	fluid	gas
volume	+	+	-
shape	+	-	-

solid → crystalline, amorphous



- **long range order**
- **crystal „lattice"**
- **short range order**
- **disorder**

density (ρ, *kg/m³*)

Density of materials used in Dentistry

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

Broad scale of materials – - broad scale of structures and properties

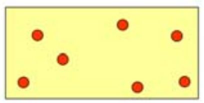
material	ρ (g/cm³)
dental enamel	2,2
dentine	1,9
water	1
amalgam	≈ 12
gold	19,3
gold-alloys	12-17
Pd-Ag alloys	10-12
Co-Cr alloys	8-9
Ni-Cr alloys	≈ 8
glass	2,2-2,7
ceramic	1,6-3,9
porcelain	2,2-2,4
gypsum ($CaSO_4 x 2H_2O$)	2,31-2,76
PMMA poly(methylmethacrylate)	≈ 1,2
silicon poly(dimethylsiloxane)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

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

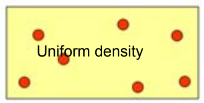
$$pV = \nu RT$$

Equation of state

mole number

Gas phase (ideal gas)

without force field



Macroscopic properties/parameters

$$pV = \nu RT$$

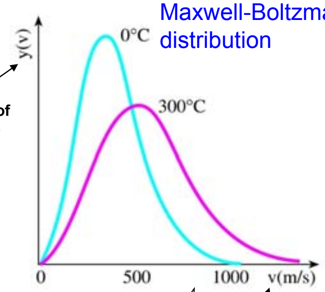
$$k = \frac{R}{N_A} = 1.38*10^{-23}\frac{J}{K}$$

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$$

average kinetic energy

Microscopic description

Maxwell-Boltzmann distribution



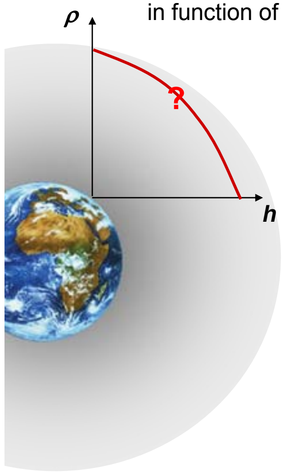
frequency of occurrence

individual velocities of O_2 molecules are distributed in a broad range

Gas phase (ideal gas)

in a force field – gravitation

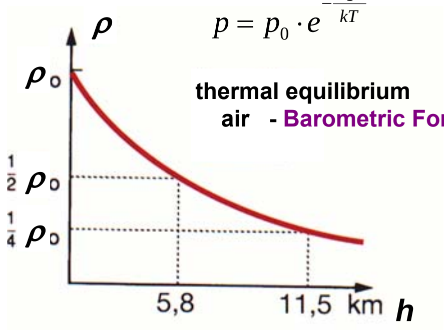
Example: density (ρ) of air ***changes*** in function of the potential energy



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

$$p = const * \rho$$

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



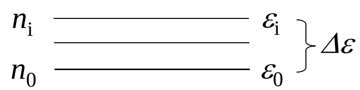
thermal equilibrium
air - Barometric Formula

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



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

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

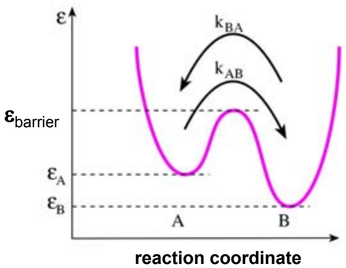
$$\Delta E = \Delta\varepsilon \cdot N_A \qquad R = k \cdot N_A$$

- 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