

Chemistry course

ACME Faculty, EHVE course

B.Sc. Studies, I year, I semester

Leszek Niedzicki, PhD, DSc, Eng.

Organizational matters

- 30 hours lecture
- Two tests - in the eight and the last week (you can have one piece of paper with formulae)
- Make-up exam (if necessary) during exam session
- Lecturer:
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1

2

Plan of the lecture

- General chemistry:** atomic structure, atom bonds, elements classification, fundamental chemical definitions, concepts and laws; reactions types, red-ox and ac-bas reactions, chemistry of water solutions, inorganic compounds.
- Electrochemistry:** electrolytical dissociation, electrolysis, galvanic cells.
- Physical chemistry:** chemical reaction types in terms of kinetics - their equilibria, kinetics, rate of reaction, factors influencing chemical reaction rate, catalyst role; chemical thermodynamics basic concepts, state functions, three laws of thermodynamics, key concepts of thermochemistry.
- Organic chemistry:** classification of organic compounds, functional groups; most important organic compound types – basic information, synthesis methods and reactions: hydrocarbons and their halides, alcohols, ethers/epoxides, aldehydes, ketones, carboxylic acids, esters, amines, amino acids, carbohydrates and polymers.
- Industrial processes:** crude oil processing, polymerization, combustion (energetics), roasting processes; basics of the heat and material balance, other large-scale and/or specialistic processes.

3

Books

Books that are recommended, but not compulsory to have. They are recommended to complement knowledge from lectures, repeat topics, get another point of view on theories or calculations. To pass the final test, mastery of the lectures knowledge will be necessary and sufficient.

- D. Ebbing, S.D. Gammon – „General Chemistry”
- F.A. Cotton, G. Wilkinson – „Inorganic chemistry”
- G.M. Barrow – „Physical chemistry”
- J.E. McMurry – „Organic chemistry” and/or R.T. Morrison, R.N. Boyd – „Organic chemistry”
- D.C. Sikdar – „Chemical Process Calculations”

4

General chemistry

with elements of inorganic chemistry

What is chemistry?

- Chemistry is a science about atoms and their interactions;
- Those interactions can be weak or strong – weaker ones can be broken and atoms can bond again;
- Those interactions are called chemical bonds;
- To know which atoms can bond with other ones and what are the differences between atoms, we need to get to know atomic structure.

5

6

Atomic structure

- **Nucleus** consists of neutrons and protons
- Proton – nucleon with positive elementary charge
- Neutron – nucleon without electric charge
- Nucleus has to consist of both nucleons types. The charge per nucleon ratio is lower then and nucleons are not repelling each other with the electrostatic forces. Nuclear forces (strong interactions) are stronger then.
- Nucleus has positive charge (= proton number)
- Nucleus is not stable – it is only a matter of time...

7

Atomic structure

- Sum of masses of individual neutrons and protons forming nucleus is smaller than nucleus mass. The difference is nuclear binding energy.
- Nuclear binding energy per nucleon is the highest for average mass elements (50-90 nucleons) and lower for the heaviest and the lightest.
- The best stabilizer for nucleus is electron cloud around it.

8

Atomic structure

- Isotopes of element are nuclei of different mass and the same proton number. They differ by their neutron number. Different elements have different number of isotopes.
- Only about 220 isotopes are really stable - the rest is not (the heaviest stable isotope is Lead-208).
- Different isotopes are having mostly the same properties, but different abundance. Elements molecular masses are not integers because they are calculated as an weighted average of isotopes.

9

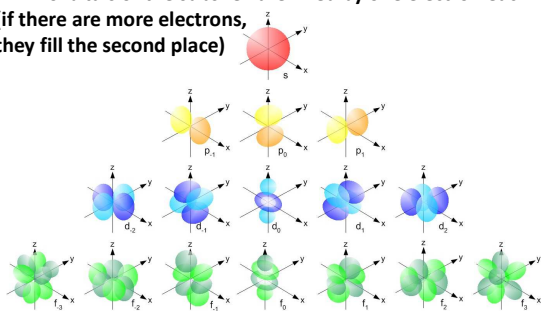
Atomic structure

- Atom diameter is of 10^{-10} m (1 Å) order
- Nucleus diameter is of 10^{-15} m (1 fm) order, but contains 99.9% atomic mass
- The rest of volume is electron cloud, which has 0.1% atomic mass
- **Electrons** possess elementary negative charge and their number is equal to proton number in nucleus
- Number of protons decide on which **element** is given atom
- Number of neutrons decide on nucleus stability (which **isotope** of given element it is)
- Electrons decide on **bonding ability** between atoms

10

Electron orbitals

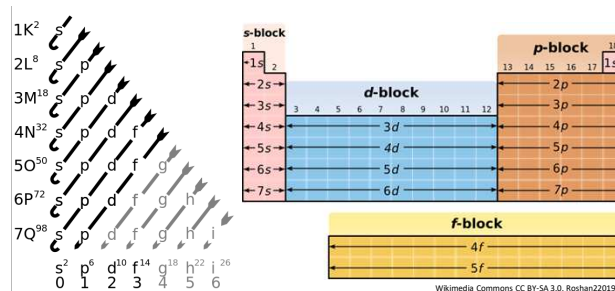
- Max 2 electrons per orbital
- All orbitals of the subshell are filled by one electron each (if there are more electrons, they fill the second place)



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11

Electron orbitals



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12

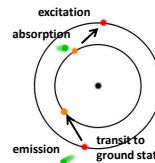
Electron energy

- Real-life order of filling subshells by electrons (...3s, 3p, 4s, 3d, 4p, 5s...) is different to theoretical one (...3s, 3p, 3d, 4s, 4p, 4d...), because for electrons it is most important to minimize their energy. Lower subshells of higher shells are sometimes more energetically favorable (electron on them has lower energy) than higher subshells of lower shells..
- Electron energy at the given subshell of given atom is strictly defined, electron cannot have energy 'in-between' – it has to have exact energy defined by the subshell and orbital. To shift to a higher or lower subshell it has to absorb or emit energy equal to the difference between energy levels of higher and lower state.

13

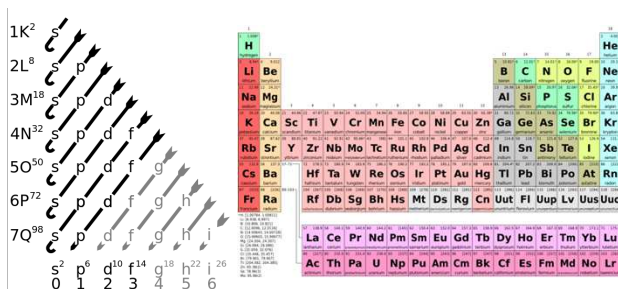
Electron energy

- There is also a possibility to 'kick' the electron out of the electron cloud, although that employs vast amount of energy.
- The above is applied to elements identification – absorption of specific energy value (e.g. as photons) is evidence of the given element presence (e.g. valence electron absorbs energy equal to its transit to a higher subshell). In the same way analytical methods use emission after excitation (when electron transits back to its ground state).



14

Valence electrons



Most electrons are critical to stabilize the nucleus - occupy whole orbitals and subshells and are uniformly distributed around nucleus. Electrons which are in the outermost subshell are not that critical and can be shared or outside electrons can access this subshell.

15

Valence electrons

- Depending on the last (outermost) occupied orbital, atoms have different bonding abilities (because they are trying to obtain fully occupied outermost electron subshell):
- In s-block they can be +1 or +2 cations
- In p-block they can possess charge between +1 and +7 or between -1 and -3
- In d block they can possess charge between +1 and +7
- In f-block atoms can possess +2/+3/+4 charge.

16

+ and -

- Most of the atomic and molecular phenomena can be explained through the attraction of + and -
- Bigger charges are attracting each other stronger: the more electrons in the shell, the smaller electron cloud is, so the atomic radius is smaller (lithium - 2s1 – is three times smaller than fluorine! - 2s2,2p5)
- Each subsequent shell (not subshell) is much bigger than its predecessor (electrons are repel each other having the same sign)

17

+ and -

- If positive charge is constant (nucleus) subtracting electrons (anion forming) decreases ionic radius (positive charge attraction is constant) – electrons number is decreasing – they repel each other less – so they can fit in a smaller volume. Adding electrons (cation forming) increases ionic radius – more electrons are not fitting in the same volume due to repulsion.
- + and – rule explains also why very big atoms (e.g. f-block elements) can form +2 to +4 cations without seeking full outer subshell. In case of lanthanides the order of filling subshells is disturbed and for cation forming 6s and 5d electrons are detached (to form 3+ cation). Thus, the f subshell is seeking 0, 7 (all orbitals with 1 electron) or 14 electrons. This way europium and ytterbium can form 2+ cations and cerium and terbium can form 4+ cations.

18

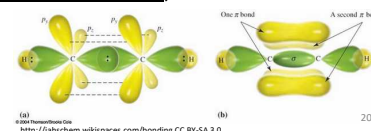
Atomic bonds

- Bonds between two (or more) atoms can be created when it is beneficial for all atoms - in terms of obtaining fully occupied outermost electron subshell. Depending on the starting point - in which direction the target is closer - they can 'accept' (acceptor) electrons from other atoms or 'donate' (donor) electrons to the bond (share them).
- Additionally, bonding is also beneficial energetically – the sum of solitary atoms energies is higher than energy of molecule made of them.
- So two **lithium** atoms (each 1 valence electron) will donate their electrons to **oxygen** atom (6 valence electrons $2s^2, 4p^4$), making it 8 valence electrons (full $2s$ and $2p$ subshells). Lithium atoms will have full $1s$ subshell after that.

19

Energy of bonds

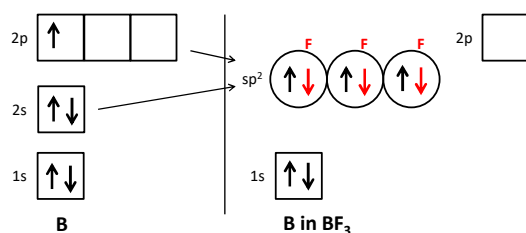
- Chemical bonds have different energies. Among most abundant ones we have: **ionic** (electrostatic interactions between two ions), **covalent** (bond is formed through equal electron input from both atoms which are of similar electronegativity) and **coordination** (all electrons in a bond come from only one atom) ones.
- Energy of chemical bond between given atoms in a given molecule will be always the same. It is used for analytical applications for compounds identification (through interactions with molecular orbitals).



20

Hybridization

- Hybridized orbitals have slightly lower energy than their components. That explains why not all molecules are not sticking to the full subshell rule (BF_3). It also explains the shape of many molecules (and their orbitals).



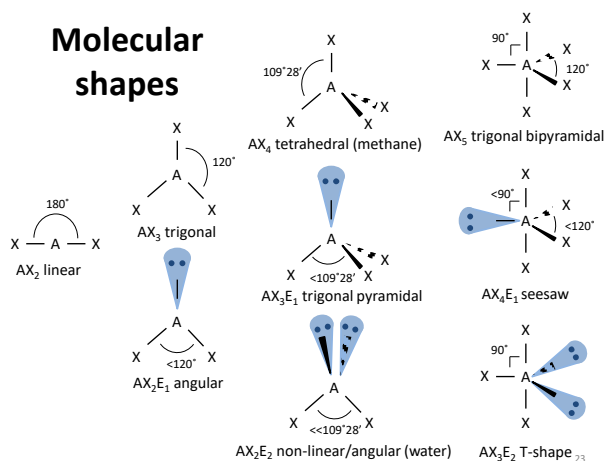
21

Molecular shapes

- They are effect of electron repelling each other – bonds 'coming out' of one atom 'want' to keep as far of each other as possible. Lone electron pairs are repelling even stronger than bonds (no positive charge weakening this force in this direction).

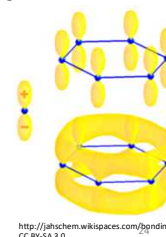
22

Molecular shapes



Chemical bonds

- Other type of chemical bond is sharing the electrons in a way of **metallic bonds**. All atoms in such a bond are cations (in a way – they give electron away) and within this group of atoms electrons are moving freely (conductivity of metals).
- Other type of bond is multielectron bond, of which most popular example is **delocalized** bond in aromatic (organic) compounds.



Hydrogen bond

- Small hydrogen without its electron has positive charge accumulated in a small volume (not distributed on any neutrons);
- In molecules in which hydrogen gives his electron away to atoms with strong affinity towards electrons (*e.g.* oxygen, nitrogen, fluorine) its electron (although formally shared) is 'closer' to the other atom;

25

Hydrogen bond

- Hydrogen is 'looking' for negative charges around it – from other sources than bonds. It is attracted by free electron pairs of other atoms (oxygen, nitrogen, fluorine, *etc.*) forming weak 'bonds' with other molecules or within the same molecule but different atom than bonded one.
- These bonds are very weak, but strong with their number. Because of that water is liquid and not gaseous (like it would seem from its analogs), ice is very hard and DNA, proteins and many polymers are working like they are thanks to this bond type.

26

Particles stability

- Ions, atoms or molecules are stable if all atoms in the given particle have filled outer subshells, *i.e.*:
- Atoms: He, Ne, Ar, Kr, Xe, Rn
- Homoatomic molecules: H₂, O₂, F₂, N₂...
- Single core anions: F⁻, S²⁻, Br⁻, Cl⁻...
- Single core cations: Li⁺, K⁺, Mg²⁺...
- Multicore ions/molecules: H₂O, CO₂, SO₄²⁻, PO₄³⁻, CN⁻, NH₄⁺... and of course all larger molecules as well.

27

Elements classification

- **metals / metalloids / nonmetals**
 - metals can form crystal structure with free electrons
- **metals: alkali, transition, rare earth, actinide**
 - according to valence orbital/occurrence/chemistry
- **gas / liquid / solid (at room temperature)**
 - phase, also derivative of valence electrons (different density of bonded atoms)

28

Allotropy

- When atoms of one element can form bonds between each other (like oxygen or carbon), sometimes they can form these bonds in few ways (and still fulfil need of full electron subshell for all atoms). Different structures lead to different properties of such substances.

Examples:

- oxygen: O₂, O₃ (ozone, unstable)
- carbon: graphite (bonded layers), diamond (spatial structure), fullerenes, graphene, nanotubes, *etc.*
- sulfur: rings – over eight-membered, S₈ (rhombic and monoclinic), S₇, S₆, S₄, S₂, chains/catena (amorphous sulfur), *etc.*
- phosphorus: white (P₄ tetrahedron), red (irregular chain), violet (chain of P₄), black (layers).

29

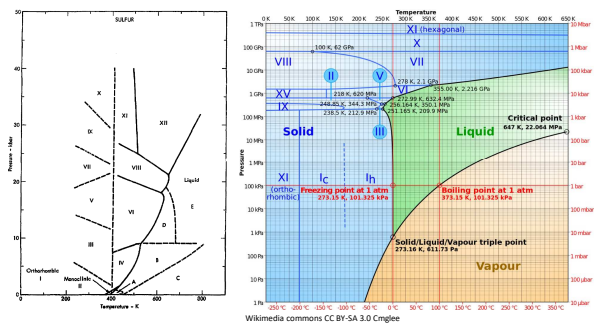
Different forms of substances

- All compounds (*e.g.* water), apart from phase changes due to temperature (ice-water-water vapor) can form different structures in one phase (*e.g.* multiple ice crystal structures). Different structures are result of different conditions of forming (*e.g.* freezing rate, pressure, possibly presence of other substances). Possibility of different structures forming for the same compound is also a result of electron shells structure of atoms making this compound up. These are long-range consequences (indirect), obviously.
- Glass is different from quartz and sand (meaning semi-amorphous silica) because of the freezing/cooling rate and starting temperature (all are the same compound – SiO₂).

30

Different forms of substances

Phase diagram of sulfur (left) and water (right)



31