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FOR PHARMACY STUDENTS

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This work is addressed to first-year students at the Faculty of Pharmacy and aims to familiarize them with the basic notions of general chemistry: the structure of the atom, the chemical bond, electronic configurations.

The first part of the book summarizes essential notions regarding the understanding of the structure of the atom: the atomic nucleus, the structure of the electron shell, notions of radioactivity.

The second part presents the structure of the periodic table, the periodic properties of the elements. The third part includes notions regarding the theoretical notions regarding the formation of chemical bonds. The fourth part introduces general concepts of chemical thermodynamics and the structure of the crystalline solid.

 I believe that this work can be of real use to pharmacy students, familiarizing them with the essential notions of general chemistry.

Scientific Reference,

Prof. univ. dr. Codruţa Şoica

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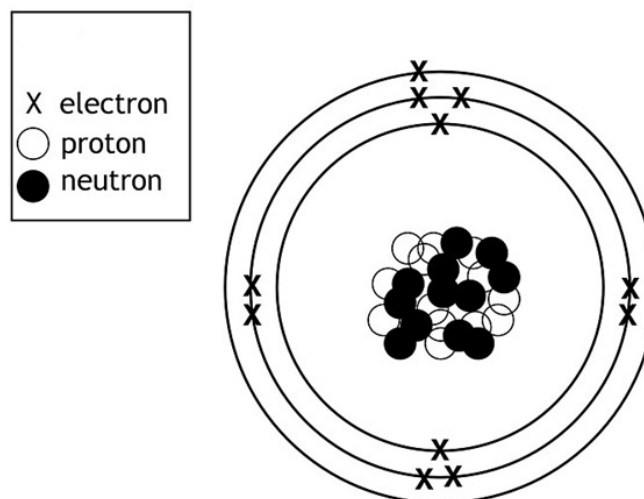
BASIC CONCEPTS
- elementary particles
- atomic number and mass number
- radioactivity

LEARNING OBJECTIVES
- determining the composition of the nuclei based on the atomic number and   mass number
- identification of isotopes, isotones, and isobars
- calculation of the relative atomic mass
- predicting the stability of nuclides
- identification of the main types of nuclear disintegration

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I.1.1. ATOMIC NUCLEUS STRUCTURE

The atom is the smallest constituent unit of matter that has the properties of a chemical element. The atom consists of the nucleus (the central part, which contains protons and neutrons) and the electronic shell, made up of electrons.

The main characteristics of the atomic nucleus are the following:
- the nucleus is placed in the center of the atom and has a spherical shape;
- represents ≈99.9% of the mass of the atom;
- it is characterized by the following parameters: Z (atomic number, represents the number of protons in the nucleus); N (number of neutrons) and A (mass number, represents the number of protons and neutrons in the nucleus); A = Z + N;
- a fully characterized nucleus has a specific number of protons and neutrons; it is called a nuclide;
- the particles that compose the nucleus, the protons and the neutrons, are called nucleons;
- the atomic nucleus determines the identity of the atom to which it corresponds.

! In a neutral atom, the number of protons (positive charges) always equals the number of electrons (negative charges).

The particles that compose the atom are characterized by their mass number and charge. These are:

- the proton, particle with positive charge (+1) and mass number A=1. It is symbolized as $_1^1p$ or $_1^1H$; - the neutron, neutral particle and mass number A=1. It is symbolized as $_0^1n$; - the electron, particle with negative charge (-1) and A=0. It is symbolized as $_{-1}^0e^-$.	Elementary particles n^0 e^- p^+

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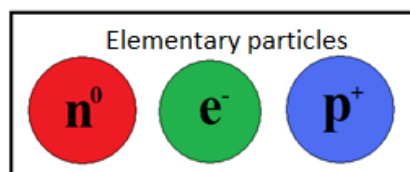
An atomic nucleus can be symbolized as follows: $^{A}_{Z}E$

Examples: $^{12}_{6}C$; $^{42}_{20}Ca$; $^{80}_{35}Br$.

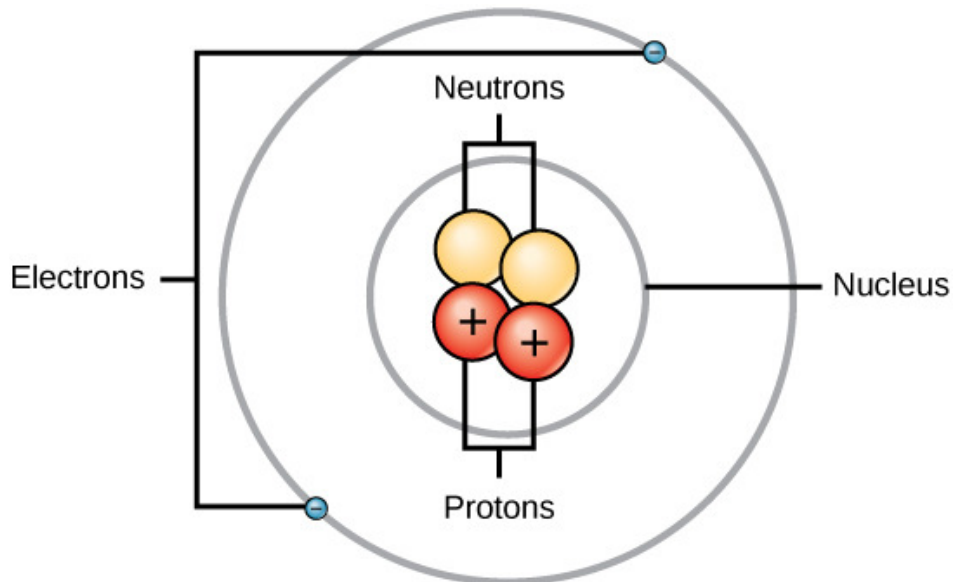The atom structure is shown in the figure below:

Figure 1. *Atom structure* [2]

Consider the helium atom, whose nuclide can be symbolized $^{4}_{2}He$. Its nucleus contains two protons and two neutrons, and the electron shell is populated with two electrons. The graphic representation is shown in Figure 2:
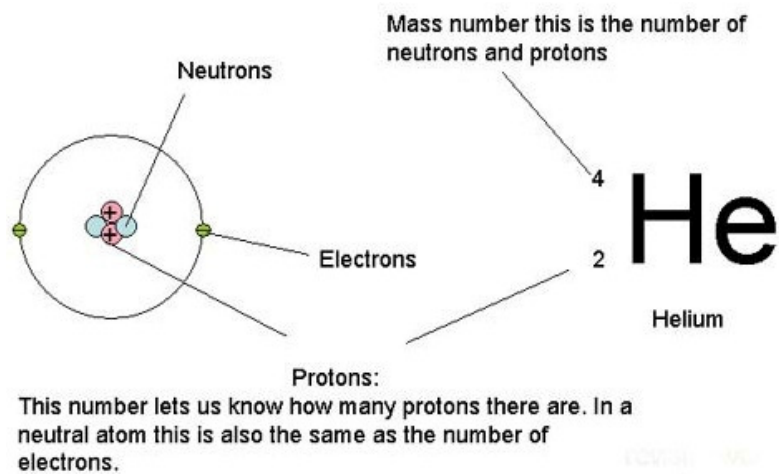

Figure 2. *The structure of the helium atom* [3]

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According to the atomic number Z value, nuclei can be divided into:

- light: Z ≤ 20

- medium: 20 < Z ≤ 82

- heavy: Z > 82

I.1.2. ISOTOPES, ISOTONES, ISOBARS

Considering the possible relationships between the atomic number Z, the number of neutrons N and the mass number A we encounter the following species: isotopes, isotones and isobars.

Species of atoms that have the same number of protons, but a different number of neutrons, are called isotopes (same Z, different N and A).

Example: oxygen isotopes

$$^A_Z X \qquad ^{16}_8 O \qquad ^{17}_8 O \qquad ^{18}_8 O$$
$$^A X \qquad ^{16} O \qquad ^{17} O \qquad ^{18} O$$

Element A	^{16}O	^{17}O	^{18}O
protons	8	8	8
neutrons	8	9	10

The chemical element is defined as the species of identical atoms -with the same number of protons, therefore the same atomic number Z-, respectively with the same number of electrons in the electron shell. A chemical element can have several isotopes, depending on the number of neutrons in the nucleus. In this case, its relative atomic mass is calculated with the relation:

$$\text{Relative atomic mass} = \Sigma \frac{a_i}{100} \cdot A_i$$

where: a_i – relative abundance of isotope i (%); A_i – mass number of isotope i.

Example: chlorine has two isotopes, ^{35}Cl and ^{37}Cl, which are found in the following relative abundances: a ^{35}Cl = 75%; a ^{37}Cl = 25%

$$A_{Cl} = \frac{75}{100} \cdot 35 + \frac{25}{100} \cdot 37 = 35,5$$

! The values of the relative abundances of the various isotopes are determined experimentally and can be found tabulated in specialized literature.

Species of atoms that have the same number of neutrons, but a different number of protons, are called isotones (same N, different Z and A).
Example: $_1^3H$ and $_2^4He$.

Species of atoms that have the same mass number, but a different number of protons and neutrons, are called isobars (same A, different Z and N).
Example: $_1^3H$ and $_2^3He$; the hydrogen nucleus has 1 proton and 2 neutrons, while the helium nucleus has 2 protons and 1 neutron. The mass number is identical for the two species, each having 3 nucleons.

I.1.3. NUCLEI STABILITY

A stable nuclide is one that cannot be transformed in the absence of a supplementary quantity of energy (from external sources).

The graphic representation of the number of neutrons against the number of protons (for stable nuclei) outlines that the stable isotopes are found within a narrow band called the stability band [c]. In general, light stable nuclei have approximately an equal number of protons and neutrons. A higher number of neutrons than protons is encountered for the stable nuclei with higher atomic mass, as a result of proton-proton repulsions, which require a greater number of neutrons to compensate for these repulsive forces [4].
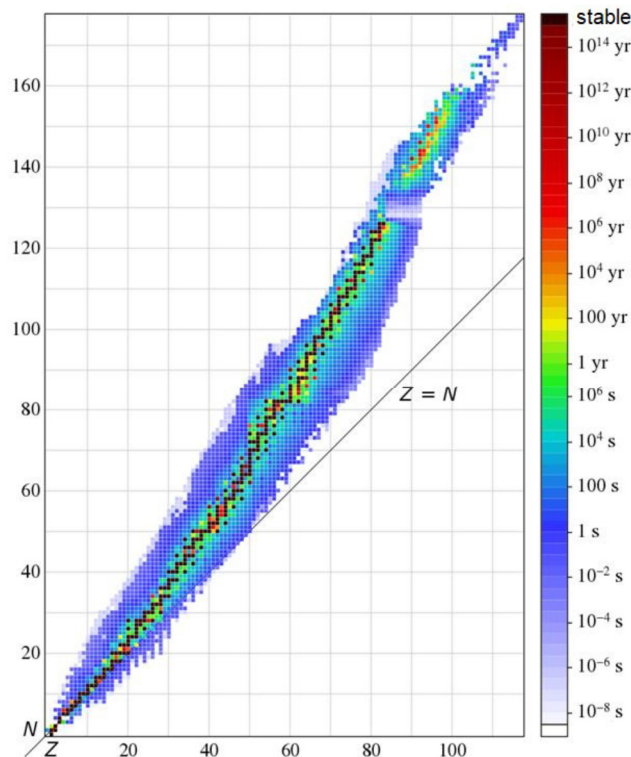
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Figure 3. *Graphic representation N=f(Z); stability band of nuclei* [5]

Radioactive disintegration

Radioactivity consists in the spontaneous disintegration of atoms of radioactive substances. During this disintegration, the atoms emit alpha, beta or gamma radiation, resulting in atoms of a new element, different from the initial one. The initial nuclide is called the parent nuclide; the nuclide that results from the disintegration is the daughter nuclide. Also, the daughter nuclides can disintegrate into other atoms; thus, the radioactive disintegration can continue until a stable atom is obtained as a final product. Function of the produced radiation type (alpha, beta or gamma) the daughter nucleus is closer to the stability band than the parent nuclide. This way, the location of a nuclide relative to the stability band is a good indicator of the radioactive decay [6,7].

I.1.4. RADIOACTIVITY

The chemical reaction involves changes in the electronic structure of the atoms participating in the reaction. The structure of the nucleus, the number of protons and neutrons

of the atoms involved in the reaction remains unchanged. In contrast, nuclear chemistry deals with the **study of reactions involving changes in the structure of nuclei.**

Types of particles found in nuclear reactions:
- **protons** and **neutrons**, the components of the atomic nucleus
- **alpha particles**: helium nuclei ($_2^4He$)
- **_β particles**: electrons ($_{-1}^0e-$)
- **+β particles**: positrons ($_{+1}^0e+$)
- **gamma radiation**: ($_0^0\gamma$)

! The fact that gamma radiation is not deflected in the electric field proves that they have no electric charge. They are electromagnetic waves with shorter wavelengths. The ionizing power of gamma radiation is reduced. Gamma rays are produced when a nucleus undergoes a transition from a higher energy state to a lower energy state. Gamma radiation emission occurs consecutively to alpha and beta emissions. Once the alpha and beta particles are emitted, there is a redistribution of the particles in the atom, a process that occurs with the emission of gamma radiation. [8]

Thus, we can encounter the following types of nuclear disintegration reactions:

α emission: the emission of an alpha (α) particle from the nucleus.

$$_Z^AE \rightarrow _{Z-2}^{A-4}E' + _2^4He$$
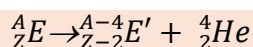
It occurs mainly in heavy nuclei with Z > 82. The result is a daughter nuclide with lower mass number and lower atomic number than those of the parent nuclide. As a result, the neutrons:protons ratio of the daughter nuclide will be higher compared to the parent nucleus.

Emission _β: emission of an electron.

$$_Z^AE \rightarrow _{Z+1}^AE'' + _{-1}^0e^-$$
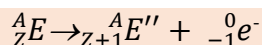
Beta disintegration mainly occurs in nuclides with a higher neutrons:protons ratio, nuclei that lie above the stability band. The mass number of the nuclide remains unchanged after the electron emission, but increases the number of protons and decreases the number of neutrons. As a

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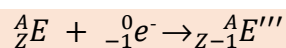results, the neutrons:protons ratio is lower and the daughter nuclide is closer to the stability band than the parent nuclide [9].

Emission₊β: emission of a positron from the nucleus.

$$^{A}_{Z}E \rightarrow ^{A}_{Z-1}E''' + ^{0}_{+1}e^{+}$$
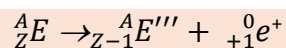
Positron emission is observed for nuclides where the neutrons:protons ratio is low. These nuclides are below the stability band. Positron disintegration is the conversion of a proton into a neutron with the emission of a positron. The neutrons:protons ratio increases and the daughter nuclide is closer to the stability band than the parent nuclide.

Electron capture (K capture): the stabilization of the nuclide can also be achieved by capturing an own electron of the atom.

$$^{A}_{Z}E + ^{0}_{-1}e^{-} \rightarrow ^{A}_{Z-1}E'''$$

Unstable radioactive elements that have in their nucleus a large excess of protons compared to neutrons can capture (their nucleus) an electron from their own electronic shell. An electron will be taken from the K shell, closest to the nucleus. The captured electron from the K shell forms a neutron with a proton from the nucleus. Thus, the daughter nuclide formed will have an atomic number lower by one unit. This increases the n:p ratio and the daughter nuclide is closer to the stability band than the parent nuclide.

γ-Emission: Occurs when a nuclide goes from an excited state and then decays to its ground state with the emission of a γ-ray, a quantum of high-energy electromagnetic radiation. Gamma emissions occur with no change in mass number or atomic number of the nuclide [10].
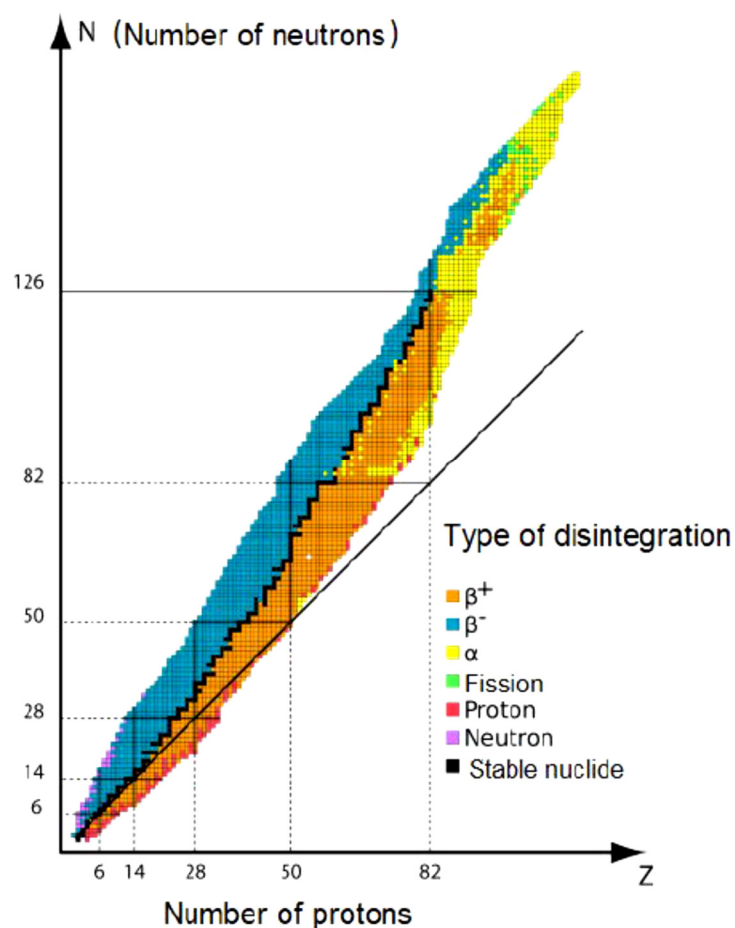
Figure 4. *The main types of radioactive disintegration depending on the stability of nuclei* [11]

Balancing nuclear reactions [4]

A balanced nuclear reaction equation indicates that there is a rearrangement of subatomic particles during such a reaction. Nuclear reactions obey the laws of conservation of matter and are balanced in two ways:

1. The sum of the mass numbers of the reactants is equal to the sum of the mass numbers of the reaction products;

2. The sum of the atomic numbers of the reactants is equal to the sum of the atomic numbers of the reaction products.

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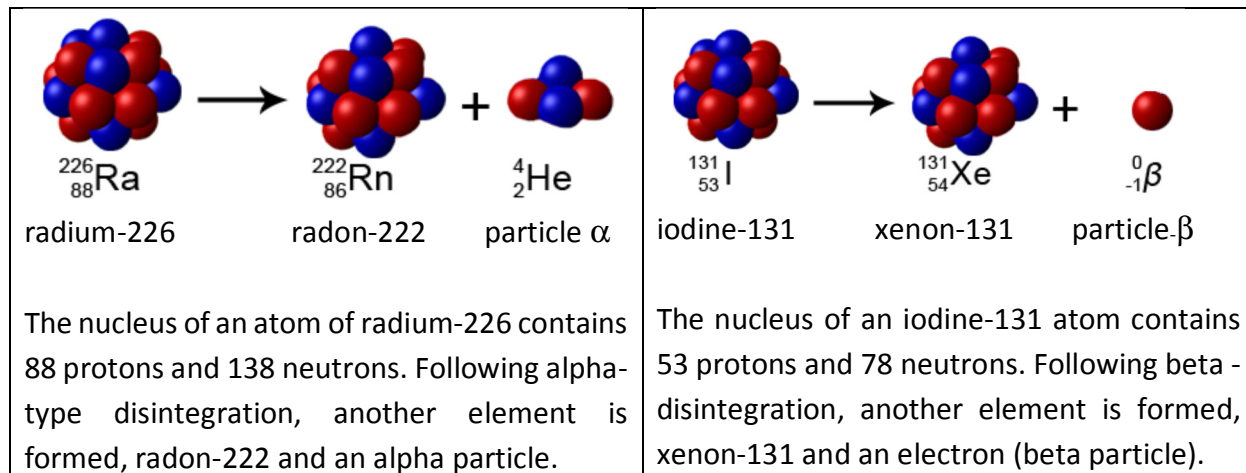|	
radium-226 radon-222 particle α	iodine-131 xenon-131 particle-β
The nucleus of an atom of radium-226 contains 88 protons and 138 neutrons. Following alpha-type disintegration, another element is formed, radon-222 and an alpha particle.	The nucleus of an iodine-131 atom contains 53 protons and 78 neutrons. Following beta - disintegration, another element is formed, xenon-131 and an electron (beta particle).

Figure 5. *α and _β radioactive disintegration* [12,13]

α-Type emission is specific to heavy nuclei, while β-emission is found in both heavy and light nuclei.

Stabilization of light nuclei

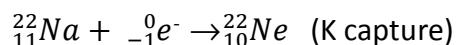In the case of light nuclei, their stability is determined as follows:

• If Z is **even number**, the isotope with **A = 2·Z** is stable
• If Z is **odd number**, the isotope with **A = 2·Z + 1** is stable

Light nuclei can be neutron-excess (have more neutrons than the stable isotope) or neutron-deficient (have fewer neutrons than the stable isotope).

Neutron-excess nuclei: $_0^1n \rightarrow _1^1p + _{-1}^0e^-$ (-β emission)

Neutron-deficient nuclei: $_1^1p \rightarrow _0^1n + _{+1}^0e^+$ (+β emission)

$_1^1p + _{-1}^0e^- \rightarrow _0^1n$ (K capture)

Examples:

$_6^{14}C \rightarrow _7^{14}N + _{-1}^0e^-$ (-β emission)

$_{11}^{22}Na \rightarrow _{10}^{22}Ne + _{+1}^0e^+$ (+β emission)

$_{11}^{22}Na + _{-1}^0e^- \rightarrow _{10}^{22}Ne$ (K capture)
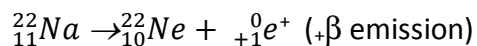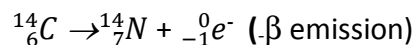
Stabilization of heavy nuclei

Nuclei with atomic number Z > 82 are unstable. These nuclei decay to form new nuclei (via α and β emissions) → natural radioactivity.

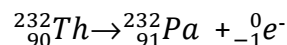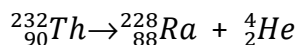$$^{232}_{90}Th \rightarrow {}^{228}_{88}Ra + {}^{4}_{2}He$$

$$^{232}_{90}Th \rightarrow {}^{232}_{91}Pa + {}^{0}_{-1}e^{-}$$

Radioactive series (families)

The radioactive disintegration of an element into another radioactive element, from which a third radioactive element can be obtained, etc., leads to obtaining a series of radioactive decay products. The total number of decay products resulting from a radioactive element forms the decay series of that element.

Three radioactive elements are known from which a series of disintegrations is derived: actinium, thorium and uranium. A fourth series is an artificial one, and starts from neptunium.

A radioactive series consists of successive α and _β emissions of an unstable nuclide; all the elements that are formed by the successive disintegration of the first term of the series form a radioactive family, the last term of the series always being a stable nuclide.

The four radioactive series are: (4n+0), (4n+1), (4n+2), (4n+3).

Series	Series parent (first term)	Last term
4n	^{232}Th	^{208}Pb
*4n+1	^{237}Np	^{209}Bi
4n+2	^{238}U	^{206}Pb
4n+3	^{235}U	^{207}Pb

*artificial series

! Nuclei within a series are characterized by the same value of the mass number A compared to the number 4: A = 4n + a, where a is the remainder of dividing A by 4.

I.2. ATOMIC MODELS
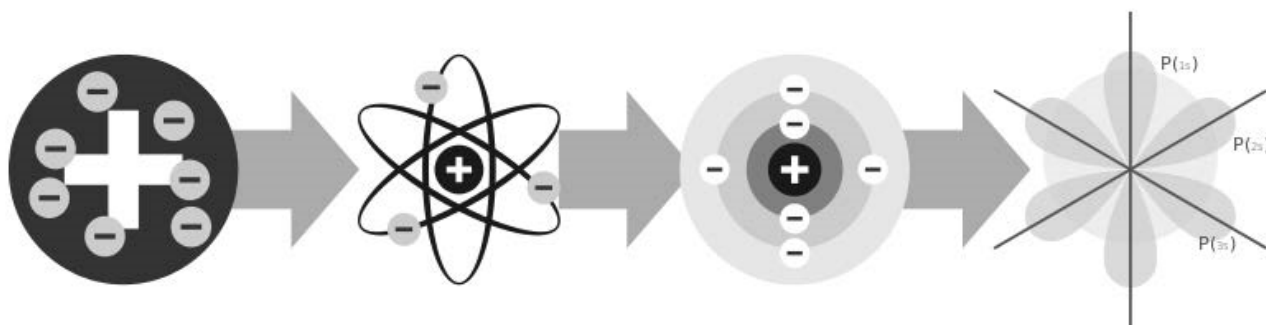
Evolution of atomic models [14]

BASIC CONCEPTS
- the nature of the electron; wave-particle duality
- quantum numbers
- atomic orbitals

LEARNING OBJECTIVES
- knowledge of the characteristics of various atomic models
- knowing the meaning of quantum numbers and their use for the characterization of atomic orbitals
- knowledge of the main characteristics of atomic orbitals

I.2.1. ATOMIC SPECTRA. BOHR'S ATOMIC MODEL

When it is possible to absorb energy, the electrons of an atom will receive energy and move from lower orbits to higher orbits. The return of these electrons from the higher levels to the lower ones will take place with the emission of the received energy. Each energy transition will correspond to a line of a certain frequency in the emission spectrum.

If a beam of white light (containing a continuous distribution of wavelengths) is passed through a gas it will be possible to analyze the resulting beam. It is found that only certain wavelengths were absorbed [15]. Each atom is characterized by a possible number of different energy levels, so a number of electronic transitions are also possible, which will correspond to the lines recorded in the spectra. These spectra can serve as "digital fingerprints" that allow identification of the various elements present in a sample, even in small amounts [15].

The emission spectrum of hydrogen was obtained by passing electric current through hydrogen gas at very low pressures. At the end of the 19th century, J. Balmer and J. Rydberg showed that the wavelengths of the different lines in the hydrogen spectrum can be correlated by a mathematical equation:

$$\bar{\nu} = \frac{1}{\lambda} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where n are positive integers, and n_1 is smaller than n_2.

The Balmer-Rydberg equation is an empirical equation. In 1913, Niels Bohr formulated the equations that describe the electron of a hydrogen atom rotating in circular orbits around the nucleus. Also, he formulated the hypothesis that electronic energy is quantified; that is, only certain energy values are possible [15].

Absorption and emission of energy are not continuous phenomena, but occur discontinuously. When an atom absorbs energy, it goes from an energy state E1 to an energy state E2 (E2>E1). When emitting the absorbed energy, the atom passes from the energy state E2 to the energy state E1. The energy difference E2-E1 represents the energy emitted or absorbed by the atom, E=E2-E1.

Each orbit thus corresponds to a defined energy level for the electron. When an electron moves from a lower energy level to a higher one, it absorbs a certain amount of energy. When the electron returns to its original energy level, it emits exactly the same amount of energy that it absorbed in the transition from the lower to the higher level. The values n_1 and n_2 in the Balmer-

Rydberg equation correspond to the lower and upper levels of these electronic transitions, respectively.

Summarizing, we can say that the Bohr atomic model, proposed for the **hydrogen atom**, is based on the following assumptions:

• **The electron rotates around the nucleus in circular orbits;**

• **The energy of an electron in an orbit is directly proportional to its distance from the nucleus. The further the electron is from the nucleus, the more energy will have;**

• **There is a limited number of allowed orbits, of a certain energy (multiple of Planck's constant);**

• **The movement of the electron from a lower orbit to a higher one is done with energy absorption; the movement of the electron from a higher orbit to a lower one takes place with energy emission;**

• **The energy emitted or absorbed will be exactly equal to the difference between the energies of the orbits.**
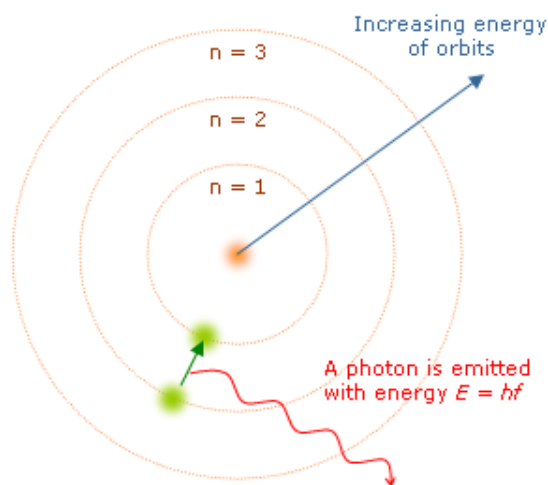

Figure 6. *Graphical illustration of the Bohr's atomic model* [16]

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Thus, the following two postulates were formulated:

Postulate 1

The electron rotates around the nucleus only in certain allowed circular orbits, without emitting or absorbing energy.

Postulate 2

An atom emits or absorbs electromagnetic radiation only when passing from one stationary state to another. The energy it absorbs or emits is equal to the energy difference between the two levels between the transition occured.

The emitted or absorbed radiation has the frequency given by the relation:

$$h\nu = E_{n2} - E_{n1}$$

h – Planck's constant; h = 6.626 x 10^{-34} J·s
ν = frequency of emitted/absorbed radiation;
E_{n1}, E_{n2} = the energies of the stationary states between which the transition takes place

The radius of an electron orbit is given by:

$$r_n = \frac{n^2}{Z} \cdot r_1$$

n – the number of the electronic layer
Z – atomic number
r_1 – radius of the first allowed orbit (r_1 = 0.53Å)

The speed of the electron in an orbit:

$$\nu_n = \frac{Z}{n} \cdot \nu_1$$

v_1 = speed of the electron in the first Bohr orbit in the hydrogen atom (v_1 = 2,2 · 10^6 m/s)

The energy of the electron in an orbit n:

$$E_n = -\frac{Z^2}{n^2} \cdot E_1$$

E_1 – the energy of the electron in the first orbit in the hydrogen atom (E_1 = -13,6 eV)

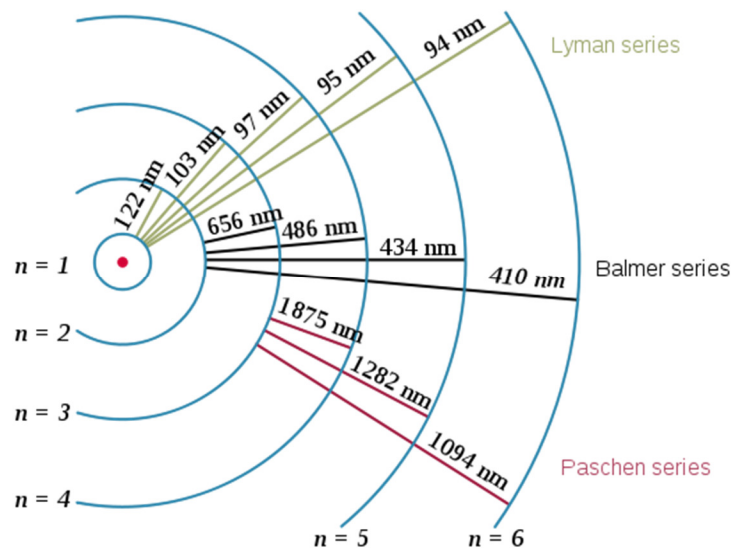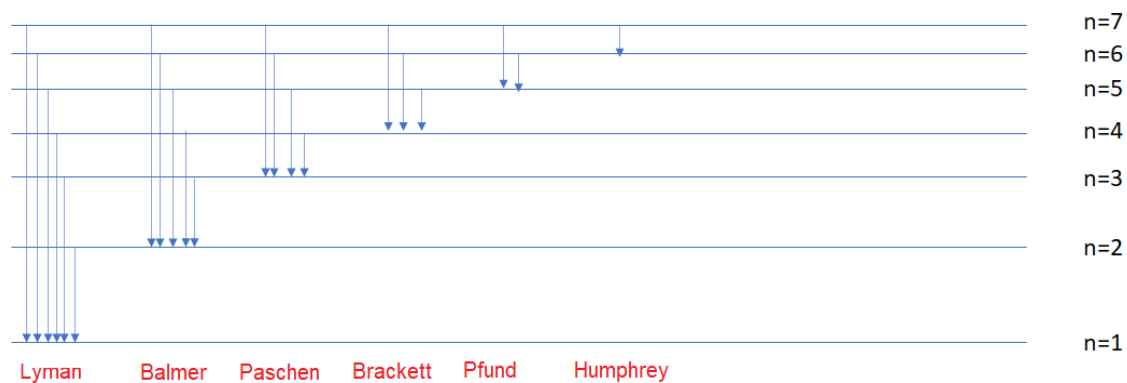**Figure 7**. *Spectral series* [17]

The emission spectrum of the hydrogen atom is divided into a number of spectral series, with wavenumber given by the previous formula (Rydberg). They are due to the movement of electrons between two energy levels in the atom (n_f → n_i).

Electronic transitions were divided into several **spectral series**: Lyman, Balmer, Paschen, Brackett, Pfund, Humphrey.

Each spectral series consists of several lines, called spectral lines:

$$\Delta n = n_f - n_i = 1 \rightarrow \text{line } \alpha$$

$$\Delta n = n_f - n_i = 2 \rightarrow \text{line } \beta$$

$$\Delta n = n_f - n_i = 3 \rightarrow \text{line } \gamma$$

$$\Delta n = n_f - n_i = 4 \rightarrow \text{line } \delta$$

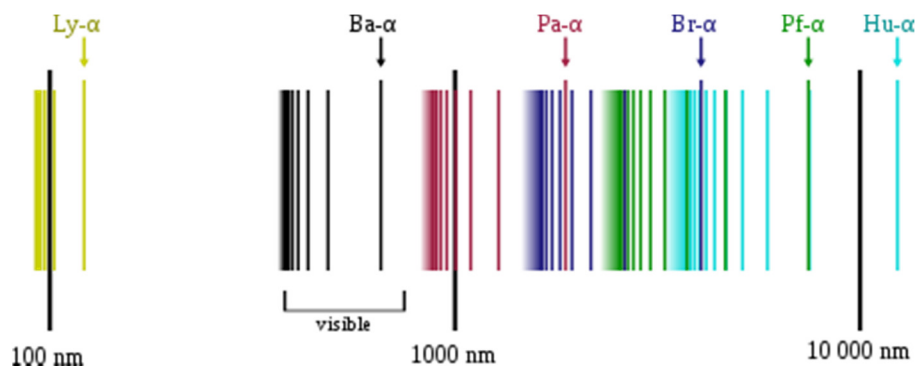$$\Delta n = n_f - n_i = 5 \rightarrow \text{line } \varepsilon$$

Figure 8. *Spectrum of the hydrogen atom* [18]

BOHR-SOMMERFELD ATOMIC MODEL

Sommerfeld's modification of Bohr's atomic model can be summarized as follows: **electrons are found in elliptical orbits around the nucleus (not in circular orbits).**
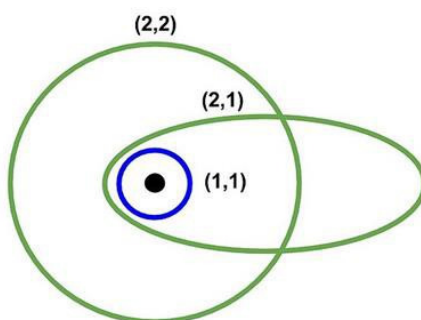

Figure 9. *Graphic representation of the Bohr-Sommerfeld atomic model* [19]

I.2.2. THE SCHRÖDINGER ATOMIC MODEL. QUANTUM NUMBERS

Models showing the movement of electrons around the nucleus (based on the principles of classical mechanics) allow the explanation of a limited number of properties of elements.

Quantum mechanics - developed on the basis of the works of E. Schrödinger and W. Heisenberg - shows that the various atomic phenomena are also determined by the existence of quanta.

Principle of quantum mechanics: In 1924, L. de Broglie states the concept that **the electron has both wave and particle properties**. The dual wave-particle character is expressed by the relation in which the wavelength λ depends on the mechanical momentum m·v:

$$\lambda = \frac{h}{m \cdot v}$$

When an electron moves in a circular orbit around the nucleus, the wave associated with it expands around the orbit.

The length of the orbit's circumference (2πr) must be an integer multiple of the electron's wavelength, the relation below representing the stability condition of electron orbits:

$$2 \cdot \pi \cdot r = n \cdot \lambda = n \cdot \frac{h}{m \cdot v}$$

This condition for quantization of electron orbits is identical to Bohr's postulate.

Schrödinger's equation: **H·Ψ = E·Ψ**, where:

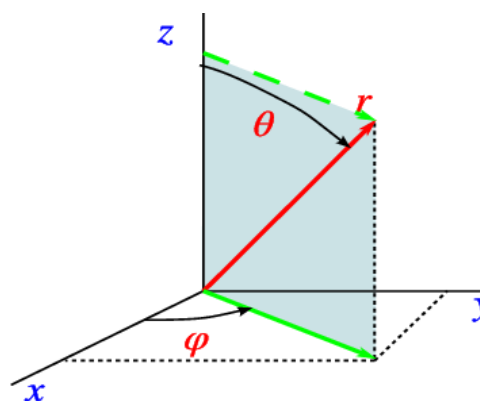H – Hamiltonian operator; E – total energy; Ψ (psi) – wave function.

The solution of the Schrödinger equation for atomic orbitals can be expressed in the form of spherical coordinates: r, θ and ϕ.

For a point (r, θ, ϕ),

r – distance to the center of the nucleus,

θ – the angle formed with the z axis,

ϕ - the angle formed with the x axis in the O_{xy} plane.

The general solution of the Schrödinger equation has the form:

Ψ$_{n,l,m}$ = R$_{n,l}$(r) · Y$_{l,m}$(θ,φ), where

Ψ$_{n,l,m}$ = solution of Schrödinger's equation; represents the surface where the electron is most likely to be found (in other words, it represents an **atomic orbital**)

R$_{n,l}$(r) = radial component

Y$_{l,m}$(θ,φ) = angular component

The expression for the radial component of the Schrödinger equation is:

$$R_{n,l}(r) = ct \cdot r^l \cdot \left[P(r)^\beta \right] \cdot e^{-\frac{r}{n}}$$

l = secondary quantum number

P(r) = polynomial

β = number of internal nodal surfaces

β = n - *l* − 1

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> **Definition**: Nodal plane (**nodal surface**) – the region where the electron density is ≈ 0 (the lowest probability of finding an electron)

Nodal surfaces can be:
- Internal: their number is calculated with the formula $\beta = n - l - 1$
- External: depending on the secondary orbital quantum number l

The solution of the Schrödinger equation for the hydrogen atom leads to obtaining the wave functions, which describe the different states of the electron in the hydrogen atom. Each of these possible states is described by **four quantum numbers**. These quantum numbers can be used to denote the arrangement of electrons in atoms, the so-called electronic configurations. These quantum numbers play an important role in describing the energy levels of electrons and the shape of the orbitals that describe the distribution of electrons in space.

> ! An atomic orbital can be defined as the region in space where an electron is most likely to be found.

The state of the electron in the atom is determined by the following **four quantum numbers**:

n = principal quantum number, determines the energy and the location of the electronic shells.
$$n = 1, 2, 3, 4, 5, 6, 7$$

l = secondary (orbital) quantum number. The secondary quantum number shows the shape of the space region occupied by an electron. Within an electronic shell (defined by the value of n, the principal quantum number), different secondary levels or subshells are possible, each with a specific geometry. A level is split into l sublevels denoted by *s, p, d, f*, corresponding to the values of l.

l = 0   s
l = 1   p
l = 2   d
l = 3   f
$$l = 0, 1, 2, \ldots \quad , (n-1)$$

_____

Thus, the n=1 electron shell will contain only one s-type orbital, the 2nd shell will contain s and p orbitals, and the 3rd shell will contain s, p, and d orbitals.

m = magnetic quantum number; the magnetic quantum number m designates a particular orbital in a substrate. Orbitals in a substrate differ in their orientations in space but have the same energy. Within each substrate, m takes values from -l, …, 0, …, +l.

$$m = [-l,..., 0,. , +l]$$

s = spin quantum number, characterizes the rotational movement of the electron around its own axis and the orientation of the magnetic field produced by this rotation.

$$s = \pm 1/2$$

A set of values of the quantum numbers **n**, **l**, and **m** describe a particular **atomic orbital**. Each atomic orbital **can be occupied by a maximum of two electrons**, one of positive spin and the other of negative spin.

Atomic orbitals

Each electron of an atom occupies an atomic orbital defined by a set of quantum numbers *n*, *l*, and *m*. In any atom, each orbital can contain a maximum of two electrons of opposite spin. Within each atom, these atomic orbitals can be represented as a diffuse cloud of electrons.

The shell that each atomic orbital belongs to is indicated by the principal quantum number *n*. The principal quantum number takes values from 1 to 7. The value n=1 describes the first electronic shell, the closest one to the nucleus, with the lowest energy. Successive electronic shells are at increasingly greater distances from the nucleus and are characterized by higher energies. For example, the third shell with n=3 is found at a greater distance from the nucleus compared to the second electronic shell and its energy is higher than the one of the second electronic shell.

s-type atomic orbitals

Each electronic shell contains an s-type substrate (characterized by l=0) which consists of a single s-type atomic orbital (characterized by m=0). The differentiation between the atomic orbitals s in the different electronic shells is done by means of the principal quantum number n; thus, 1s designates the orbital in the 1st electronic shell, 3s indicates the s orbital in the third electronic shell [15].

In any principal shell there is one *s* orbital; all *s* orbitals have spherical symmetry.
   ✓ Secondary quantum number l = 0 (n = 1, 2, 3, ..., 7)
   ✓ m can take (2l + 1) values → when l is 0, m has one value (there is only one s orbital)
   ✓ They do not have an external nodal plane
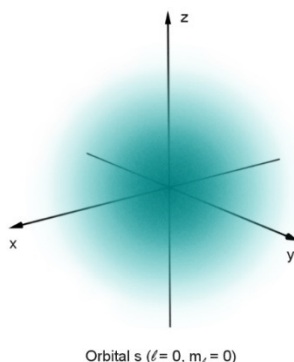
! An s-type atomic orbital is spherically symmetric:

Orbital s (ℓ = 0, m$_\ell$ = 0)

Figure 10. *s-type atomic orbital* [20]

Taking into account the spherical shape of the s-type atomic orbitals it can be said that they have no external nodal surfaces (where the possibility of finding an electron is zero); instead, depending on the electronic shell in which the orbital is found, internal nodal surfaces appear.
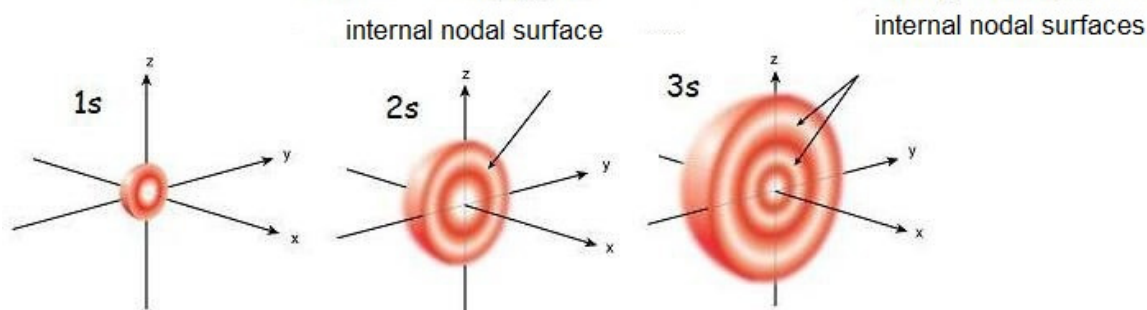

Figure 11. *Internal nodal surfaces (examples)* [21]

---

p-type atomic orbitals

Starting with the second electronic shell, each of the six electronic shells (n=2 to n=7) will contain a substrate defined by $l=1$. Each of these p subshells consists of a set of three p atomic orbitals, which correspond to the three allowed values of magnetic number m (-1, 0, and 1). Subshells are named 2p, 3p, 4p ... to indicate the main electronic shells in which they are found. A p-type orbital is represented by two lobes of equal size, placed perpendicularly. The p_x, p_y, and p_z notations refer to the axis on which the two lobes are placed.

The electron density of these orbitals is maximum at two opposite points, located on either side of the nucleus. For this reason, the shape of the p orbitals is bilobar.

✓ Secondary quantum number $l = 1$ (n = 2, 3, ..., 7)
✓ m has $(2l + 1)$ values → m has 3 values (there are 3 p orbitals: p_x, p_y, p_z)
✓ 1 external nodal plane (directed, two lobes symmetrical to the nucleus)
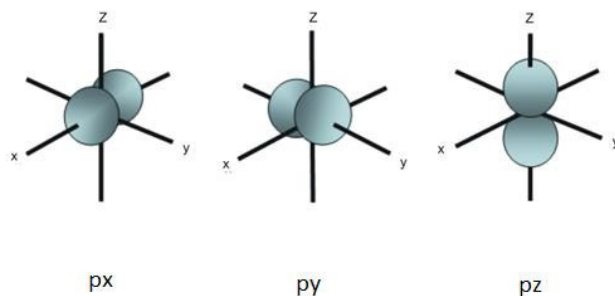

Figure 12. *p-type atomic orbitals* [22]

A p-type atomic orbital has only one external nodal surface (located at the intersection of the two lobes).
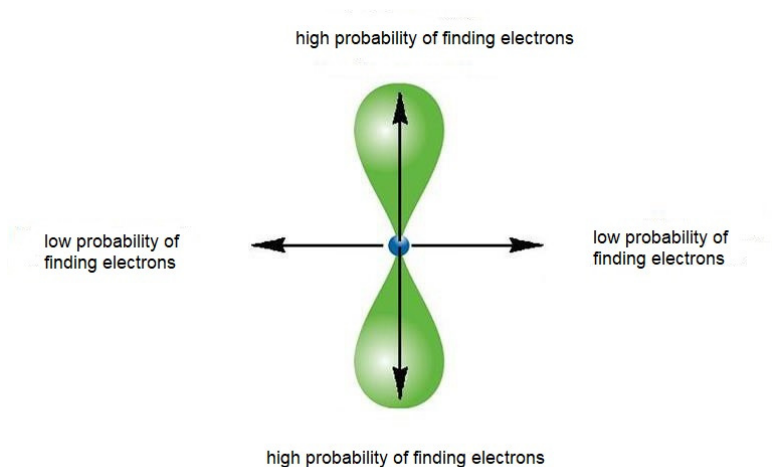
_____

high probability of finding electrons

low probability of finding electrons

low probability of finding electrons

high probability of finding electrons

Figure 13. *The external nodal surface of the p-type atomic orbital* [23]

d-type atomic orbitals

Starting with the 3rd electronic shell (n=3), each shell has five d-type orbitals. The d_z^2 orbital is symmetric with respect to the z axis; the $d_{x^2-y^2}$ orbital has lobes directed along the x and y axes; d_{xy}, d_{yz}, and d_{xz} orbitals have lobes represented between the O_{xy}, O_{yz}, and O_{xz} axes.

- ✓ Secondary quantum number *l* = 2 (n = 3, ..., 7)
- ✓ m has (2*l* + 1) values → m has 5 values (there are 5 d orbitals: d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_z^2)
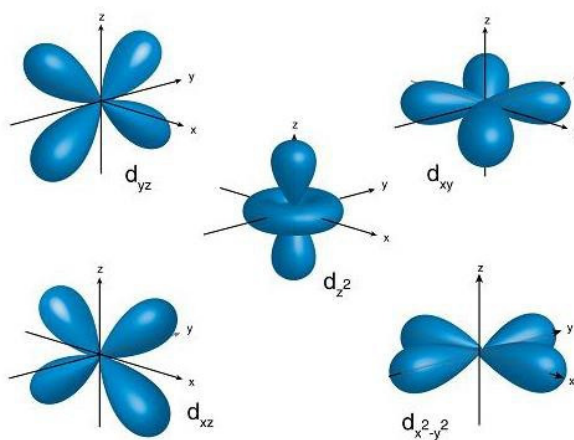- ✓ 2 external nodal planes (directed, four lobes symmetrical to the nucleus)

Figure 14. *d-type atomic orbitals* [24]

f-type atomic orbitals

Starting with n=4, each principal shell contains seven *f* orbitals (of complex shape and orientation).

- ✓ Secondary quantum number *l* = 3 (n = 4, ..., 7)
- ✓ m has (2*l* + 1) values → m has 7 values (there are 7 f atomic orbitals)
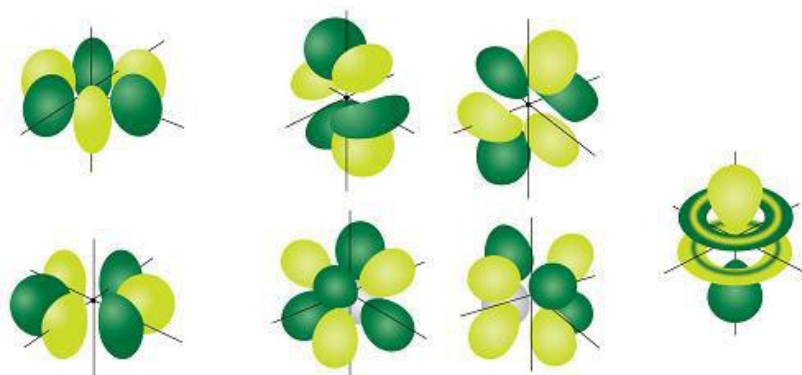

Figure 15. *f-type atomic orbitals* [25]

Summarizing the information from the presented atomic models, we can say that:

- ➢ The electron shell of the atom is a layered structure.
- ➢ Electrons that have the same principal quantum number **n** form an **electronic shell.**
- ➢ Each electronic shell contains **n²** orbitals.
- ➢ Each electronic shell contains **2n²** electrons.
- ➢ Orbitals that have a certain value of n and a certain value of *l* form **electronic substrates.**
- ➢ Each substrate consists of (2*l*+1) orbitals.
- ➢ Each orbital contains a **maximum of 2 electrons**.
- ➢ Orbitals are characterized by **3 quantum numbers: n, *l*, m**.
- ➢ Electrons are characterized by **4 quantum numbers: n, *l*, m, s.**

For example, for the electronic shell n=4 we will have the following situation:

n=4	l	m	s	Number of electrons
	0 (s)	0	+1/2; -1/2	2
	1 (p)	-1	+1/2; -1/2	6
		0	+1/2; -1/2	
		+1	+1/2; -1/2	
	2 (d)	-2	+1/2; -1/2	10
		-1	+1/2; -1/2	
		0	+1/2; -1/2	
		+1	+1/2; -1/2	
		+2	+1/2; -1/2	
	3 (f)	-3	+1/2; -1/2	14
		-2	+1/2; -1/2	
		-1	+1/2; -1/2	
		0	+1/2; -1/2	
		+1	+1/2; -1/2	
		+2	+1/2; -1/2	
		+3	+1/2; -1/2	
				32 electrons
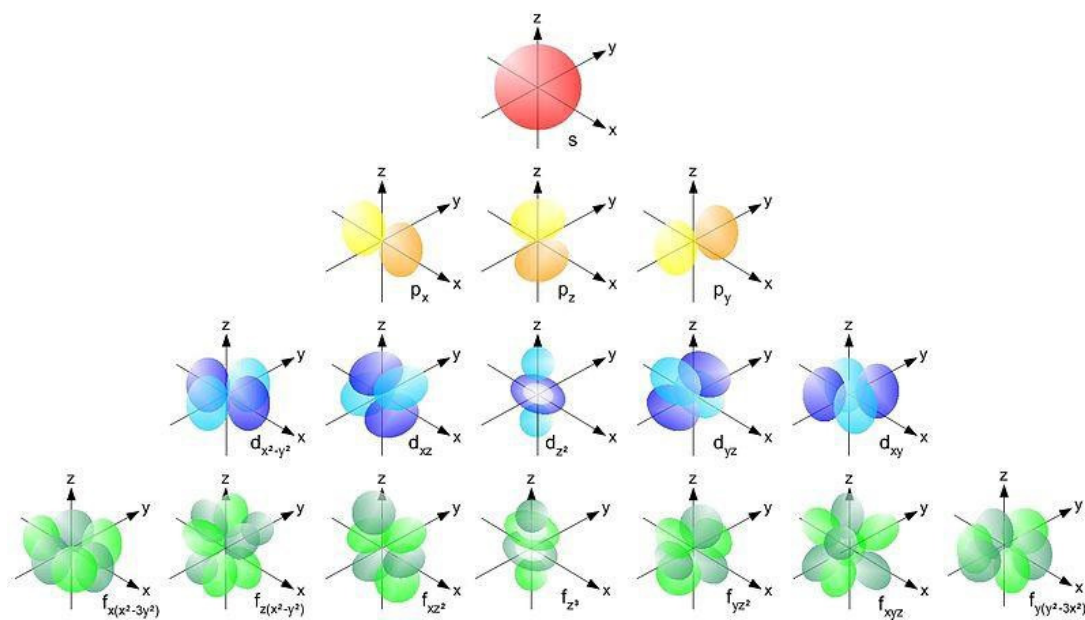
Figure 16. *Graphic representation of atomic orbitals s, p, d, f* [26]

I.3. ELECTRON CONFIGURATION

(total: 1 electron) $1s^1$

principal quantum
number: n = 1

1 valence electron
in an s orbital

1s

2s   2p

3s   3p   3d

4s   4p   4d   4f

5s   5p   5d   5f

6s   6p   6d

7s   7p
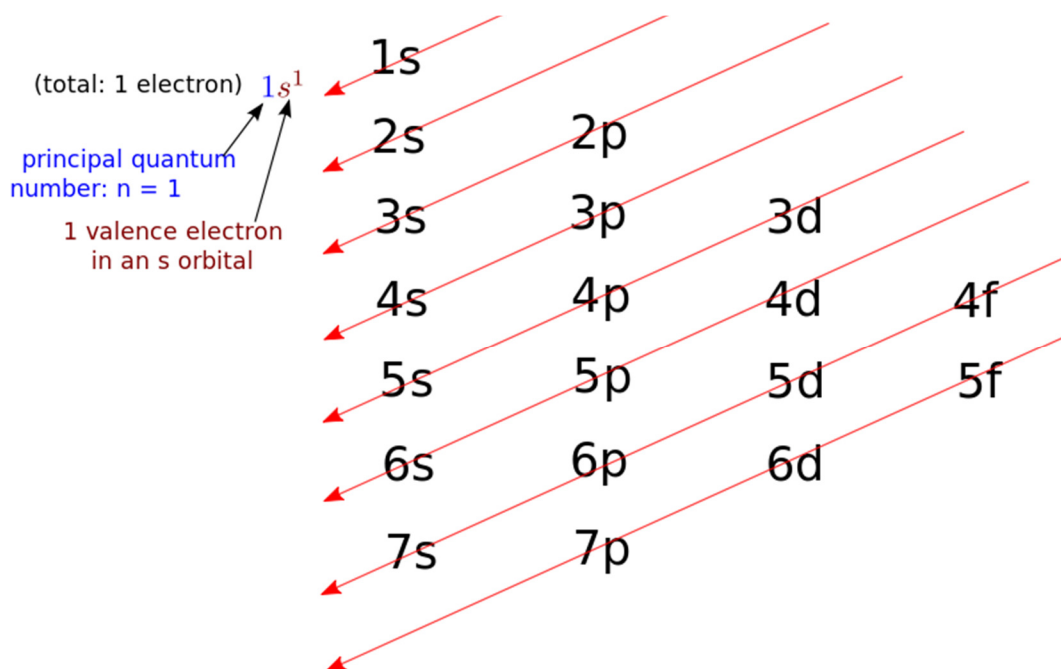
Electronic configuration (hydrogen atom) [27]

BASIC CONCEPTS
  - Atomic orbitals
  - Rules regarding the occupation of atomic orbitals with electrons

LEARNING OBJECTIVES
- To establish the electron configuration of an element
- To correlate the properties of an element with its the position in the periodic table

The energy of electrons in atomic orbitals

The central structure of an atom is the nucleus, which is composed of protons and neutrons. The nucleus is surrounded by electrons. Although all these electrons have the same charge and the same mass, each electron in an atom has a different amount of energy. The lowest energy electrons are found closest to the nucleus, where the attractive force of the positively charged nucleus is greatest. Electrons with higher energy are found in the shells further away from the nucleus.

The formulation of the electronic structure is done by writing the symbols of each type of electron successively according to the distribution in the electronic shells. The main quantum number n is written first, followed by the secondary quantum number l, adding the number of electrons as exponent.

Electronic shells

In an atom, electrons are arranged in energy levels, or shells, around the nucleus of an atom. Electrons that are found in the first energy level are closest to the nucleus and have the lowest energy. Electrons further away from the nucleus will have higher energy. The electron shell of an atom can be occupied by $2n^2$ electrons, where n is the number of that electron shell. For example, the first shell can be occupied by 2 electrons, the second shell can be occupied by 8 electrons, the third electron shell can be occupied by 18 electrons, etc.

Electrons shell	Number of electrons ($2n^2$)
1	2
2	8
3	18
4	32
...	...

For example, fluorine has the atomic number Z= 9, which means that a neutral fluorine atom has 9 electrons. The first 2 electrons are found in the first electron shell and the other 7 are found in the second electron shell.

! The electron configuration of an element shows the arrangement of electrons in shells and subshells.

_____

The electron occupation of the electronic shell of atoms follows the principles:

I. Principle of stability: in the fundamental state electrons will first occupy the energy levels of minimum energy, therefore with the greatest stability.
II. Pauli's exclusion principle: two electrons in an atom cannot have all four quantum numbers identical (in an orbital there are a maximum of two electrons of opposite spin).
III. The principle of maximum multiplicity (Hund's rule): the electrons distribution in degenerate atomic orbitals (of the same energy) must lead to the maximum number of electrons with parallel spin.

I. The principle of stability (the principle of electron occupation of energy sublevels)

The energy ordering of the subshells characterized by the quantum numbers n and l is given by the *(n + l) rule*: the energy of the subshells increases parallel to the value of the sum $(n + l)$, and at equal values of this sum, the sublevel characterized by a smaller value of the principal quantum number n has a lower energy.

The rule *(n + l) minimum* can be illustrated by Goldanski's scheme:

1s							
	2s						
2p		3s					
	3p		4s				
3d		4p		5s			
	4d		5p		6s		
4f		5d		6p		7s	
	5f		6d		7p		

The order of occupation of the electronic subshells will be: **1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f d 7p**

II. Pauli's exclusion principle shows that an atomic orbital ($\Psi_{n,l,m}$) can be occupied by at most two electrons having the opposite spin, and the maximum number of electrons in an energy level n is limited to:

$$2\sum_{l=0}^{l=n-1}(2l+1)=2n^2$$

In other words, there is a maximum of two electrons of opposite spin in an orbital.

$$s = +1/2 \qquad s = -1/2$$
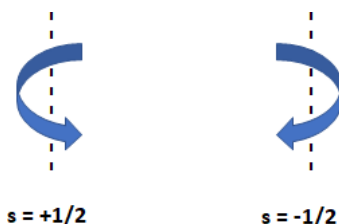
The positive spin electron (s= +1/2) is represented by ↑, and the negative spin electron (s= -1/2) is represented by ↓.

III. Hund's rule states that on same type orbitals, the electrons are arranged in such a way that the sum of the magnetic quantum numbers (in the module) is maximum. Consequently, each atomic orbital of the subshell is initially populated with one electron of the same spin, and after half-occupancy, the atomic orbital is filled with the electron of the opposite spin.

↑↓	↑	↑	right	$2p^4$
↑↓	↑↓		wrong	$2p^4$
↑↑	↑	↑	wrong	$2p^4$

In other words, Hund's rule states that:

Each orbital in a subshell is occupied by a single electron, then filled with the opposite spin electron. All electrons in individually occupied orbitals have the same spin (s= +1/2). The explanation is as follows:

(i). Electrons are negatively charged and therefore repel each other. Electrons tend to minimize electron-electron repulsion by occupying one orbital each, rather than sharing an orbital with another electron.

(ii). Unpaired electrons in singly occupied orbitals have the same (positive) spin. If all the electrons orbit in the same direction, they meet less often than if some of them orbit in opposite directions.

For example, consider the electronic configuration of oxygen ($Z_O=8$; $1s^2$ $2s^2$ $2p^4$): we have 2 electrons coupled in the 1s orbital, 2 electrons coupled in the 2s orbital, and the remaining 4 electrons will be placed in the 2p orbitals.

Following Hund's rule, first an electron with positive spin will be placed in each of the three p-type orbitals, and the fourth electron will have negative spin and form an electron pair in the first of the three p-type orbitals.

$$\uparrow\downarrow \quad \uparrow \quad \uparrow \quad 2p^4$$

The formulation of the electronic configuration is done as follows:

- The quantum numbers n and l are indicated; first the quantum number n is written, followed by the secondary quantum number l.
- The number of electrons is written as an exponent

Example: the configuration **$1s^2 2s^2 2p^5$** shows that the atom has two electrons in the 1s orbital, two electrons in the 2s orbital and five electrons in the 2p orbitals (9 electrons in total, the electronic configuration of the fluorine atom; $Z_F = 9$)

Three types of electronic configurations can be distinguished:
1. Those in which the distinguishing electron is in the outer shell, which may contain 1-8 electrons. These elements are part of the main groups of the periodic table.

ns^1 - group I_A

ns^2 – group II_A

ns^2np^1 - group III_A

ns^2np^2 - group IV_A

ns^2np^3 - group V_A

ns^2np^4 - group VI_A

ns^2np^5 - group VII_A

ns^2np^6 - group $VIII_A$

The electron configuration of the group $VIII_A$ elements being the most stable, the elements in neighboring groups tend to acquire the p^6-type configuration. Thus, elements of groups VII_A, VI_A, and V_A tend to accept 1, 2, and 3 electrons respectively, in order to obtain the stable rare gas configuration of that period (electronegative character). This also explains the electropositive nature of the elements in groups I_A, II_A and III_A, which tend to give up 1, 2 and 3 electrons, respectively, to obtain the stable configuration of the rare gas from the previous period.

2. Those in which the distinguishing electron is found in the penultimate shell (may contain 9-18 electrons). These elements are part of the secondary groups and represent the transition metals.

The electron configurations of these elements are of the type **$ns^2(n-1)d^x$**; two electrons are found in the last n shell, and (1-10) d electrons can be found in the penultimate shell (n-1).

3. Those in which the distinguishing electron is found in the antepenultimate shell (may contain 19-32 electrons).

These elements form the lanthanide group (6th period) and the actinide group (7th period).

The role of electron configurations

When atoms come into contact with each other, the outer electrons of these atoms (valence electrons or valence shell) will interact first. An atom is less stable (and therefore more reactive) when its valence shell is not completely occupied. Valence electrons are largely responsible for the chemical behavior of an element. Elements that have the same number of valence electrons often have similar chemical properties. Electron configurations can also predict the stability of an element. An atom is most stable (and therefore unreactive) when its orbitals are fully occupied. The most stable configurations are those that have full energy levels. These configurations occur

in rare gases. The rare gases (inert or noble – group VIII$_A$) are very stable elements that do not react with any other element.

Based on the electron configuration of an element, predictions can be made about its reactivity. Thus, an element is more reactive when the valence electron shell is incompletely occupied (it will be able to accept/give electrons from other atoms to ensure a stable configuration).

Magnetic properties of elements

Diamagnetic and paramagnetic properties

Whenever two electrons occupy the same orbital, their spin quantum numbers must be different. Whenever two electrons are coupled, they are diamagnetic electrons. Atoms with all diamagnetic electrons are called diamagnetic atoms.
A paramagnetic electron is an unpaired electron. An atom is considered paramagnetic if it has even a single orbital occupied by a single electron. Regardless of the number of coupled electrons, as long as the atom has one unpaired electron, it is considered a paramagnetic atom. Diamagnetic atoms repel magnetic fields. The unpaired electrons of paramagnetic atoms realign in response to external magnetic fields and therefore are attracted to the magnetic field.

Diamagnetism

Whenever two electrons are in the same orbital, their spin quantum numbers must be different. In other words, one of the electrons must be of positive spin, s = +1/2, while the other electron is of negative spin, s = -1/2. This is important for determining the total spin of electrons in an orbital. To decide whether the electrons' spin cancels out, their spin quantum numbers are added. Whenever two electrons are paired in an orbital or their total spin is 0, they are called diamagnetic electrons.
Electron spin is very important in determining the magnetic properties of an atom. If all the electrons in an atom are paired and share an orbital with another electron, then the total spin in each orbital is zero and the atom is diamagnetic.

Paramagnetism

The unpaired electrons in an orbital are called paramagnetic electrons. Therefore, an atom is said to be paramagnetic when it contains at least one paramagnetic electron. As mentioned before, regardless of the number of paired (diamagnetic) electrons, as long as it also has one unpaired (paramagnetic) electron, it is considered a paramagnetic atom.

II. PERIODIC PROPERTIES OF THE ELEMENTS
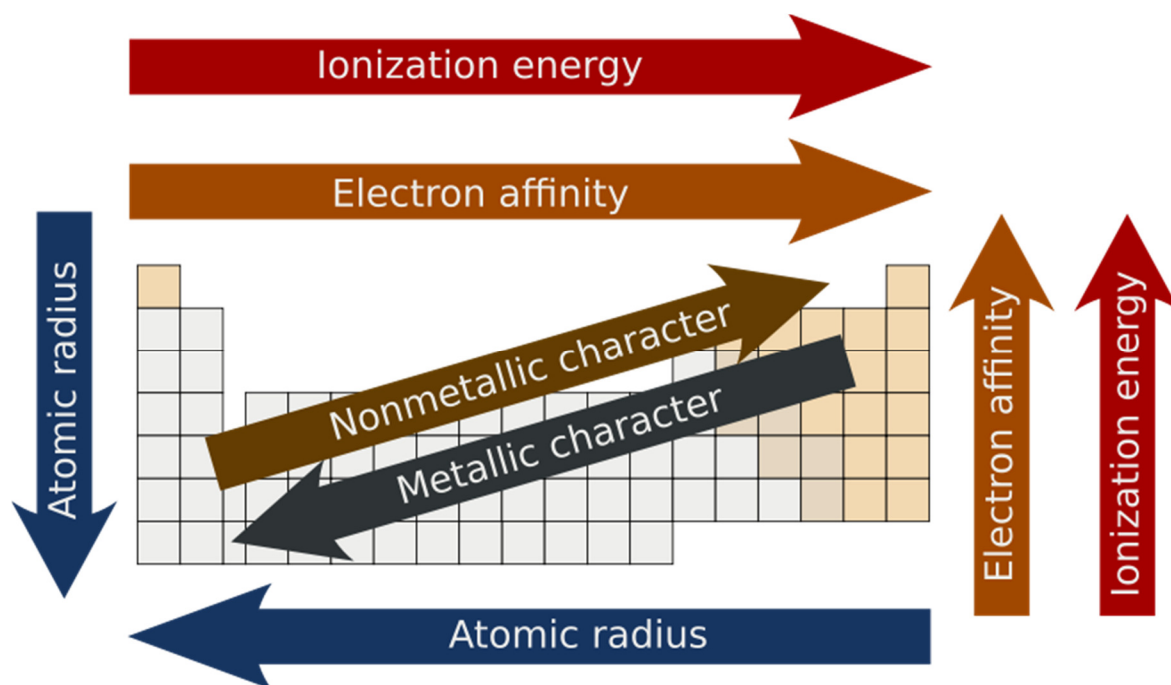
BASIC CONCEPTS
- Atomic radius
- Ionization energy
- Electron affinity

LEARNING OBJECTIVES
- Knowing the notion of periodicity
- Evaluation of the metallic/non-metallic character of an element

_____

Periodic Table of the Elements [1]

The current formulation of the periodic table of elements is due to the development over time of the following fundamental ideas:

- The need to find a natural classification of chemical elements
- The existence of a fundamental property, characteristic of each element, and the chemical behavior of that element
- Recognizing the periodicity of elements according to this fundamental property.

The law of periodicity has known two formulations. The first belongs to Mendeleev (19th century) and is formulated as follows: **the physical and chemical properties of the elements are repeated periodically, depending on their atomic masses.** Moseley (20th century) restated the law of periodicity: **the properties of chemical elements are periodic functions of the atomic number Z.**

The periodic table consists of 18 groups - the vertical columns - (8 main groups and 10 secondary groups) and 7 periods (the horizontal rows).

Period 1: only 2 elements are found, hydrogen (H) and helium (He).

Period 2: contains 8 elements (main group elements), from lithium (Li) → neon (Ne).

Period 3: contains 8 elements (main group elements), from sodium (Na) → argon (Ar).

Period 4: contains 18 elements (main and secondary group elements), from potassium (K) → krypton (Kr).

Period 5: contains 18 elements (main and secondary group elements), from rubidium (Rb) → xenon (Xe).

Period 6: contains 32 elements (of which 14 are lanthanides), from cesium (Cs) → radon (Rn).

Period 7: contains 32 elements (of which 14 are actinides), from francium (Fr) → oganesson (Og) (Og- synthesized element).

_____

Remarks

• **The groups of the periodic table contain elements that have the same electronic configuration of the valence shell, having similar physical and chemical properties.**

• **Valence shell: the farthest electron-occupied shell from the nucleus.**

• **Valence electrons: the electrons in the valence shell.**

• **For elements in groups 1-12, the group number corresponds to the number of valence electrons.**

• **For elements in groups 13-18, the number of valence electrons is calculated by the difference (group number – 10).**

• **The valence electrons of an element in the main groups are the electrons in the ns and np substrates (where n is the largest principal quantum number of the electronic configuration of that element)**

• **The valence electrons of an element in the secondary groups are the electrons in the ns (n-1)d substrates (where n is the largest principal quantum number of the electronic configuration of that element)**

In the periodic table, the elements are arranged in s, p, d and f blocks according to the types of atomic orbitals of the last subshell. Groups are also given the notation "A" and "B". A groups contain elements in which the last subshell is of type s or p. B groups are those in which there are one or two electrons in the s orbital of the last electronic shell, and the orbitals in the previous electronic shell are partially or fully occupied.

For example, group I_A elements lithium, sodium, and potassium have a single electron in their external orbital (ns^1 last subshell of electron configuration). Beryllium and magnesium, in group II_A, have two electrons in their external electron shell, ns^2, while boron and aluminum (group III_A) have three electrons in their external shell, ns^2np^1.
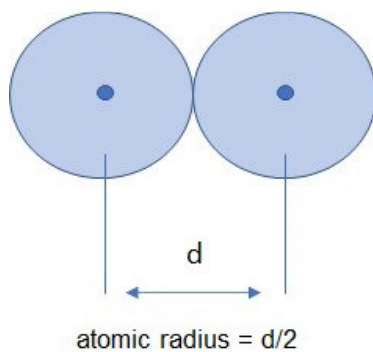
II.1. PERIODIC PHYSICAL PROPERTIES OF THE ELEMENTS

**Periodic physical properties of the elements are:**

1.   Atomic radius and ionic radius

2. Ionization energy

3. Electron affinity

<u>1. Atomic radius</u>

The atomic radius of an element is calculated as half the distance between the nuclei of two adjacent and identical atoms.
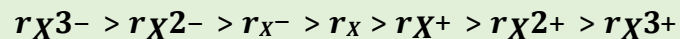

atomic radius = d/2

The atomic radius increase in the group with increasing atomic number and decrease in period with increasing atomic number.

atomic radius increase

PERIODIC TABLE OF ELEMENTS
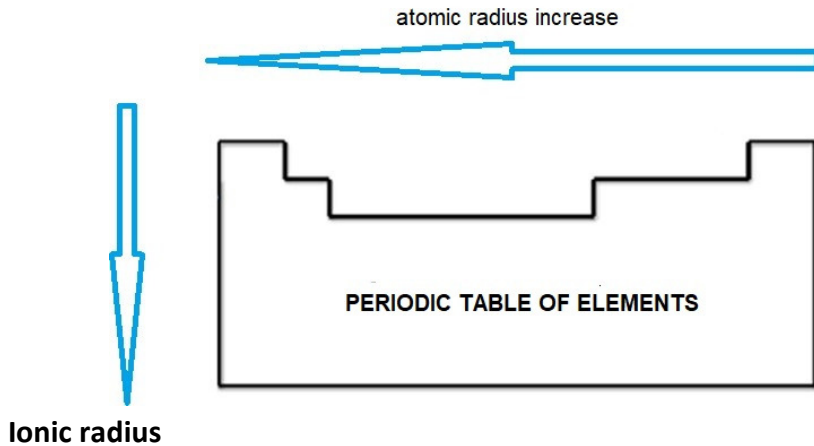
Ionic radius

• **Anionic radius** (always greater than the radius of the atom from which it originates)

• **Cation radius** (always smaller than the radius of the atom from which it originates)

In an isoelectronic series, ionic radii decrease with increasing ion charge:

$$r_{X^{3-}} > r_{X^{2-}} > r_{X^-} > r_X > r_{X^+} > r_{X^{2+}} > r_{X^{3+}}$$

atomic and ionic radius (in picometers)

	Group IA		Group IIA		Group IIIA		Group VIA		Group VIIA	
	Li^+	Li	Be^{2+}	Be	B^{3+}	B	O	O^{2-}	F	F^-
	90	134	59	90	41	82	73	126	71	119
	Na^+	Na	Mg^{2+}	Mg	Al^{3+}	Al	S	S^{2-}	Cl	Cl^-
	116	154	86	130	68	118	102	170	99	167
	K^+	K	Ca^{2+}	Ca	Ga^{3+}	Ga	Se	Se^{2-}	Br	Br^-
	152	196	114	174	76	126	116	184	114	182
	Rb^+	Rb	Sr^{2+}	Sr	In^{3+}	In	Te	Te^{2-}	I	I^-
	166	211	132	192	94	144	135	207	133	206

Figure 17. *Radii of neutral atoms, cations and anions of elements from groups I_A, II_A, III_A, VI_A, VII_A* [28]

_____

The cation, which is an ion with a positive charge, has by definition fewer electrons than protons. The loss of an electron will result in a change in the atomic radius compared to the neutral atom. Thus, there will be a decrease in atomic size because there are now fewer electrons for the protons to pull towards the nucleus and this will result in a stronger attraction of the electrons.

On the other hand, the size of an anion will be larger than the neutral atom (because of the extra electron(s)). The larger number of external electrons will cause a lower attractive force of the nucleus, and thus an increase in the radius.
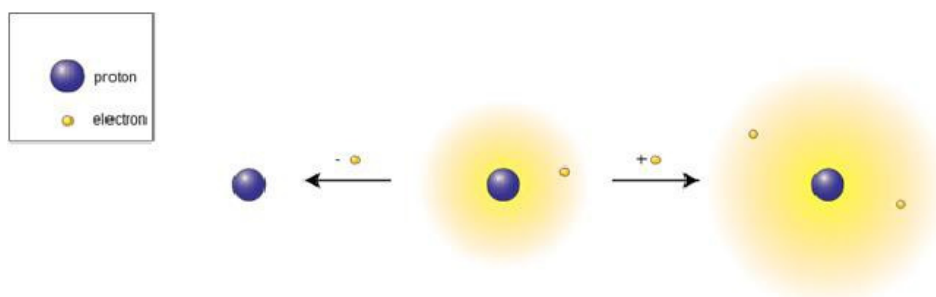
Notation	H^+	H	H^-
Classification	cation	Neutral atom	anion
Number of protons	1	1	1
Number of electrons	0	1	2
Charge	+1	0	-1

   2. The ionization energy represents the minimum energy consumed when removing an electron from an atom in the gas phase: [1]

$$E \rightarrow E^+ + e^-; E_1(eV)$$
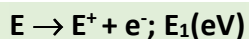
> ➤ the elements with stable configurations (rare gases) have the highest ionization energy
> ➤ alkali metals have the lowest ionization energy

Exceptions: E_I (III$_A$) < E_I (II$_A$) and E_I (VI$_A$) < E_I (V$_A$) (due to stability of s^2 (II$_A$) and p^3 (V$_A$) substrates)

! The ionization energy **increases with increasing effective nuclear charge Z_{ef}.**

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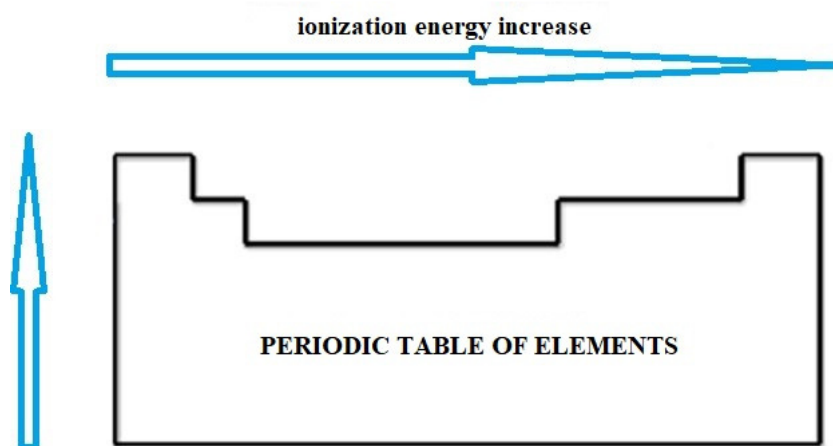
Shielding effect and effective nuclear charge

The shielding effect, approximated by the effective nuclear charge, is due to the internal electrons that interpose between the valence electrons and the nucleus.

The shielding effect describes the decrease in the attractive force between an electron and the nucleus in any atom with more than one electron shell. The more electron shells, the greater the shielding effect on the external electrons. In the hydrogen atom, which has only one electron, the net force on the electron is as great as the electrical attraction in the nucleus. However, when more electrons are involved, each electron (in the nth shell) is exerted not only the electromagnetic attraction from the positively charged nucleus, but also the repulsive forces from other electrons in the $1 \rightarrow (n-1)$ electron shells. This makes the net electrostatic force on the electrons in the external shells significantly smaller. Therefore, these electrons are not bound as strongly as electrons closer to the nucleus.

> ! The shielding effect explains why valence shell electrons are easier to remove from an atom.

Calculation of effective nuclear charge (Z_{eff})

• In an atom, its nucleus (positive charge) exhibits an electrostatic force of attraction towards the electron shells (negative charge).
• In the case of atoms with more electrons, the internal electron shells "screen" the force of electrostatic attraction exerted by the nucleus on the electrons in the valence shell.
• In this case, the positive nuclear charge that manifests itself on the electrons is the **effective nuclear charge Z_{eff}**:

_____

$$Z_{eff} = Z - \sigma \qquad (\sigma - \text{shielding constant})$$

Calculation of the shielding constant (σ)

The calculation of the shielding constant is based on the rules formulated by Slater:

1. **It is written the electronic configuration of the element for which Z_{eff} is calculated.**

2. The electronic configuration is written in the following form (**the electrons in the s and p substrates are considered to be part of the same group**):

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

3. It is identified the subshell of the distinguished electron and all external subshells (located to the right of the respective subshell) are ignored.

4. If **the distinguished electron is found in an s or p orbital**, the following rules are taken into account:

- Electrons from the **same subshell** contribute to shielding with **0,35**, except for electrons from 1s, which shield with 0,30;
- Electrons in **the subshell (n-1) shield with 0,85**;
- Electrons from **subshell farther than (n-1) shield with 1,0**

5. If **the distinguished electron is found in a d or f orbital**, the following rules are taken into account:

- Electrons from **the same subshell contribute to shielding with 0,35;**
- Electrons in all **previous subshells shield with 1,0**

Electron	Other electrons from the same group	Electrons from (ns np)	Electrons from groups with quantum number (n-1)	Electrons from groups with quantum number < (n-1)
[1s]	0.30	-	-	-
[ns, np]	0.35	-	0.85	1
[nd] or [nf]	0.35	1	1	1

_____

3. Electron affinity (A_e) represents **the energy released or absorbed upon acceptance of an electron in the valence shell** and the transformation of an atom into a negative ion: [60]

$$E + e^- \rightarrow E^-$$
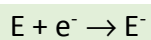
Within the same period, the electron affinity increases with increasing Z.
Within the same group, the electron affinity increases with decreasing Z.

electron affinity increase

PERIODIC TABLE OF ELEMENTS
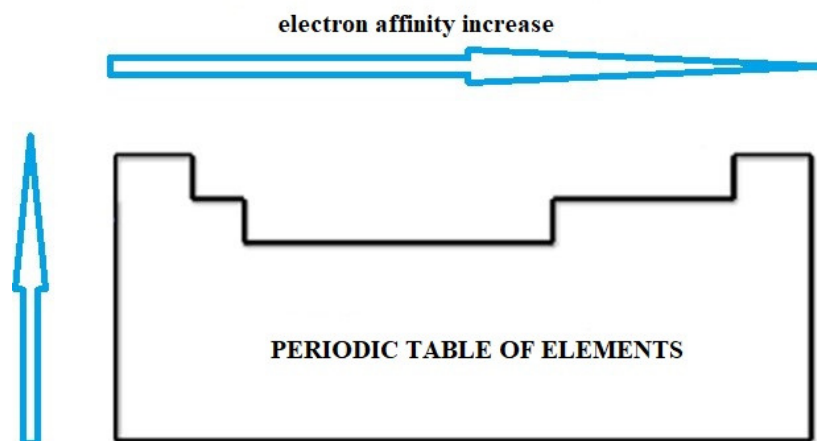
II.2. PERIODIC CHEMICAL PROPERTIES OF THE ELEMENTS

Metallic character (electropositive) [1]

The electrochemical character represents the property of the elements to accept or donate electrons, turning into ions (anions, respectively cations) and varies periodically.

The electropositive (metallic) character of the elements emphasizes their tendency **to donate electrons, forming positive ions.**
- Increases with decreasing ionization energy
- It increases in group from top to bottom (as Z increases) and in period from right to left (as Z and the number of donated electrons decrease).
- Thus, larger group I_A elements have the most pronounced metallic (electropositive) character.

Metals are ordered in **the activity series of metals,** in which the tendency of metal atoms to give up electrons is compared using as a standard the tendency of the hydrogen atom to donate electrons:

K Ba Ca Na Mg Al Mn Zn Cr Fe Ni Sn Pb H Cu Hg Ag Pt Au

more reactive than hydrogen   less reactive than hydrogen

! A pronounced electropositive character determines a greater chemical reactivity of the respective metal.

2. The electronegative (non-metallic) character of the elements emphasizes their tendency **to accept electrons, forming negative ions.**

- Increases with increasing electron affinity;

- Increases in group from bottom to top (as Z decreases) and in period from left to right (as Z and the number of accepted electrons increase).

- the smaller elements from group 17 (VII_A) will have the most pronounced non-metallic (electronegative) character

Thus, **each period begins with an element with a pronounced metallic character and ends with an element with a strong non-metallic character** (with the exception of the rare gases). As a result, **metals** are found placed in the main groups toward **the lower left of the periodic table**, and **nonmetals** are placed in the main groups toward **the upper right of the periodic table**.

• Observation 1: **Secondary groups** are made up **exclusively of metals**.

• Observation 2: the more opposite two elements are in terms of electrochemical character (the further apart they are in the periodic table), the greater their tendency to form chemical combinations.
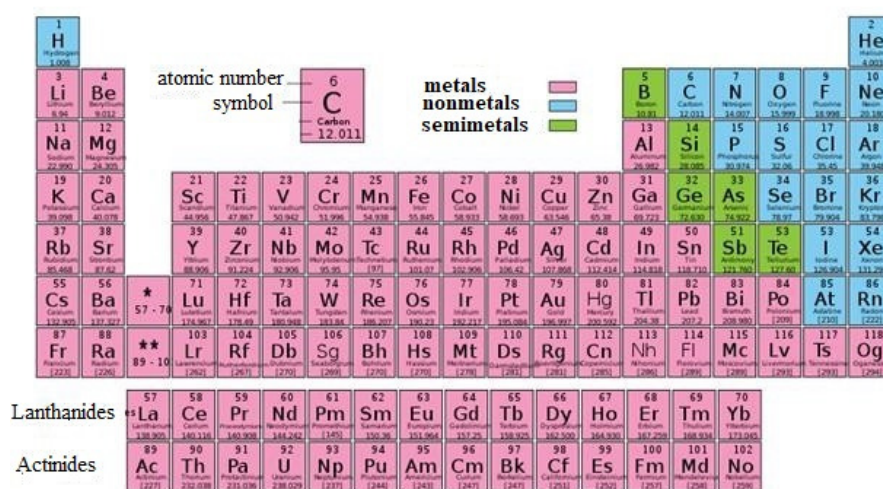
The periodicity of chemical properties is manifested in the composition of chemical combinations, where the valences (oxidation states) of the participating elements are decisive.

3. **Formula of higher oxides**

The maximum valence of the elements has equal values within the same group of the periodic table; it is equal to the group number and increases from 1 (group I_A elements) to 7 (group VII_A elements). Rare gases (group $VIII_A$ elements) do not form combinations with oxygen.

The main group of the periodic table	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
The formula of higher oxides	E2O	EO	E2O3	EO2	E2O5	EO3	E2O7	-

4. Formula of hydrides

The valence towards hydrogen increases from 1 to 4 for elements in main groups I_A-IV_A and then decreases from 3 to 1 for elements in main groups V_A-VII_A.

The main group of the periodic table	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A	$VIII_A$
The formula of hydrides	EH	EH_2	EH_3	EH_4	EH_3	H_2E	HE	-

- If **E = metal**, chemical combinations with hydrogen are called **hydrides**.

- If **E = nonmetal**, chemical combinations with hydrogen are called **acids**.

5. Oxidation state (maximum and minimum)

Oxidation State (O.S.) = the total number of electrons that have been donated by an element (positive O.S.) or accepted by an element (negative O.S.) in that chemical combination.

The elements have a positive oxidation state in chemical combinations with more electronegative elements (they donate their valence electrons).

The main oxidation states of elements from groups I_A-$VIII_A$:

H

$s^1 \rightarrow s^0$ (OS= +1)
$s^1 \rightarrow s^2$ (OS= -1)

Group I_A
$s^1 \rightarrow s^0$ (OS= +1)

Group II_A
$s^2 \rightarrow s^0$ (OS= +2)

Group III_A
$s^2p^1 \rightarrow s^0p^0$ (OS= +3)

_____
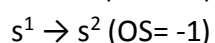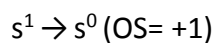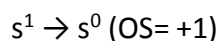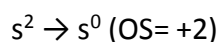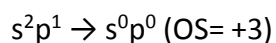
Group IV$_A$

$s^2p^2 \rightarrow s^0p^0$ (OS=+4) (maximum oxidation state)

$s^2p^2 \rightarrow s^2p^6$ (OS= -4) (minimum oxidation state)

Group V$_A$

$s^2p^3 \rightarrow s^0p^0$ (OS= +5) (maximum oxidation state)

$s^2p^3 \rightarrow s^2p^6$ (OS= -3) (minimum oxidation state)

Group VI$_A$

$s^2p^4 \rightarrow s^0p^0$ (OS= +6) (maximum oxidation state)

$s^2p^4 \rightarrow s^2p^6$ (OS= -2) (minimum oxidation state)

Group VII$_A$

$s^2p^5 \rightarrow s^0p^0$ (OS= +7) (maximum oxidation state)

$s^2p^5 \rightarrow s^2p^6$ (OS= -1) (minimum oxidation state)

Remarks:

1. Maximum oxidation state = the number of the respective main group

2. Minimum oxidation state = main group number – 8 (for semimetals and nonmetals only)

3. Metals always have a positive oxidation state (see oxidation states of elements in I$_A$-III$_A$ groups)

III. CHEMICAL BOND
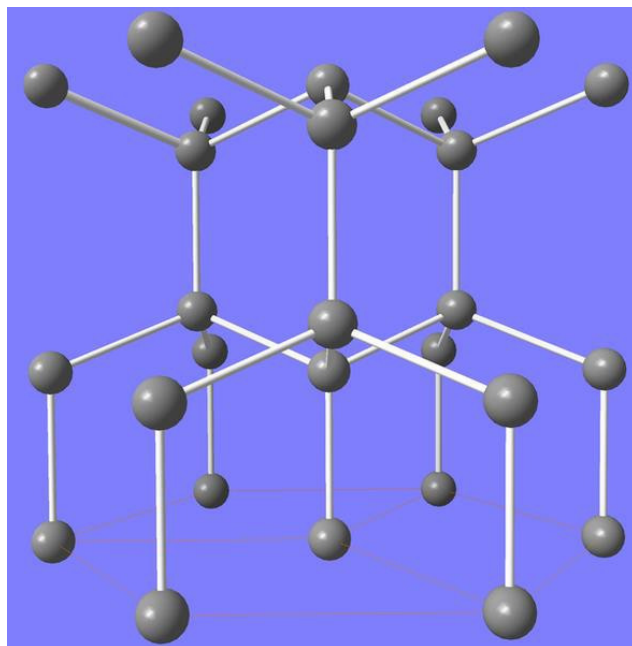
BASIC CONCEPTS

- Lewis structures

- Formation of the ionic bond

- The octet rule

- Covalent compounds: geometry, polarity

- Dipole moment

LEARNING OBJECTIVES

- Correct writing of Lewis structures

- Establishing the bond nature between two elements, ionic or covalent

- Establishing the bond nature according to the electronegativity of the elements

Chemical bond

• The chemical transformations of atoms are due to their tendency to change their external electron shell, to acquire a stable rare gas configuration.

• The electronic configuration of rare gases is very stable. With the exception of the helium atom, whose electron shell consists of two electrons (**doublet**, $1s^2$), in all other rare gases the atoms contain eight electrons in the external electronic shell (**octet**, s^2p^6).

The chemical bond is formed by the interaction between the electrons in the external shell of the atoms (valence electrons).

The formation of the chemical bond is based on the octet rule: the octet of electrons represents the most stable electronic configuration, specific to the $VIII_A$ group elements. The atoms of the other elements will change their electronic shell structure by transferring or sharing electrons, so that they become identical to those of the closest group $VIII_A$ element.

! Exception: When one of the two atoms forming the chemical bond is hydrogen, it will achieve the stable doublet configuration.

The chemical bond can be formed by **transferring electrons** (**ionic bond**) or by **sharing electrons** (**covalent bond**).

III.1. Ionic bond

The ionic bond is achieved by **the transfer of electrons** from atoms that easily donate electrons to atoms that easily accept additional electrons in their shell, turning into ions. Thus, ionic bonds require an **electron donor** (metal) and an **electron acceptor** (non-metal). [60]

Metals: elements from groups I_A, II_A and III_A, elements from secondary groups (transitional metals).
Non-metals: especially the elements from groups VI_A and VII_A.

! In ionic bonds, the metal loses electrons and becomes a cation (positively charged ion), while the nonmetal accepts electrons and becomes an anion (negatively charged ion).

Examples

Let's consider the compounds formed by:

a) Na (group I$_A$ element) and Cl (group VII$_A$ element).

The sodium atom donates its valence electron to the chlorine atom, forming the sodium cation and the chlorine anion.
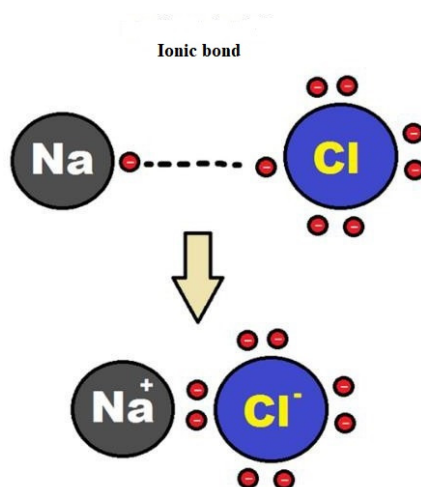
Ionic bond

Figure 18. *Ionic bond* [29]

b) Mg (group II$_A$ element) and Cl (group VII$_A$)

The magnesium atom donates its two valence electrons to the chlorine atoms. Each chlorine atom accepts one electron, so two chlorine atoms are needed to accept the two electrons donated by magnesium. The electron-donating atom will have a positive charge equal to the number of given electrons, and the electron-accepting atom will have a negative charge equal to the number of accepted electrons.

_____
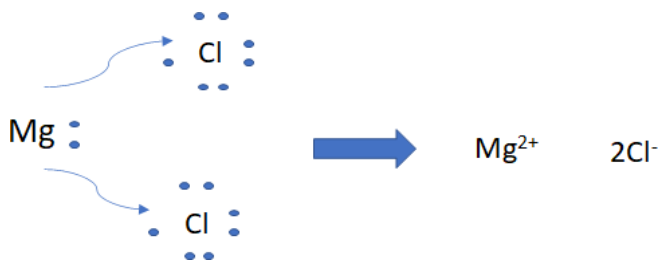
c) Mg (group II$_A$) and O (element of group VI$_A$)

In this case, the magnesium atom donates its two valence electrons to oxygen, turning into a bivalent cation (with two positive charges). By accepting the two electrons, the oxygen atom acquires the octet configuration and transforms into the anion O^{2-}.

Thus, we can say that **the ionic bond:**
    • generates **two ions of opposite charges** (a cation and an anion).
    • the charges of the anion and the cation correspond to the number of given or received electrons.
    • the overall charge of the compound thus formed must be zero.

III.2. Lewis structures

    • **Lewis structures** are **diagrams** that show the bonds between the atoms that compose a molecule, as well as the lone pairs of electrons of each atom in that molecule.

    • The atoms of a molecule can share **two electrons** forming a **simple bond**; the sharing of **four electrons** leads to **double bond**, and the sharing of **six electrons** leads to **triple bond**.

    • **Electrons that are not involved in the formation of a bond are called <u>non-participating electrons.</u>**
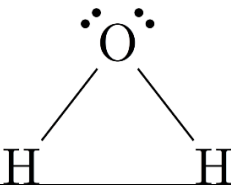
    • The valence electrons of atoms are represented as dots.

    • The central element is the one with less pronounced electronegative character.

_____

I$_A$	II$_A$	III$_A$	IV$_A$	V$_A$	VI$_A$	VII$_A$	VIII$_A$
ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Na	Mg	Al	C	N	O	Cl	Ar

• **The ideal Lewis structur**e is characterized by:

- **the exclusive existence of electron pairs**
- **each atom has the octet of electrons (except for hydrogen, where we will have a doublet).**

Example: consider the H_2O molecule. The oxygen atom (with six external electrons) shares two of these electrons with the electron of the hydrogen atom, thus forming two single O-H bonds. By sharing electrons, the oxygen atom obtains the octet configuration, and the hydrogen atoms the doublet configuration. The electrons of the oxygen atom that are not shared with the hydrogen atom (so they do not participate in the formation of bonds) are called **non-participating electrons.**

Lewis structure of water	In the water molecule, the oxygen atom has two non-participating electron pairs.

III.3. COVALENT BOND

• The covalent bond is achieved by **sharing the electrons** of the two atoms [60].
• The covalent bond occurs between elements that have similar electronegativity and electron affinity (between **two nonmetals** or **a nonmetal and a semimetal**) [60].
• If two atoms have similar electron affinities, none of them will have the tendency to give them; instead, they will share them to achieve their stable octet configuration [60].

Consider the compound PCl$_3$, phosphorus trichloride (P –group V$_A$ element, having 5 valence electrons, Cl –group VII$_A$ element, having 7 valence electrons). The central phosphorus atom

shares one electron with the three chlorine atoms, forming three single P-Cl bonds. The central phosphorus atom will have one pair of non-participating electrons, and each of the three chlorine atoms will have three pairs of non-participating electrons.
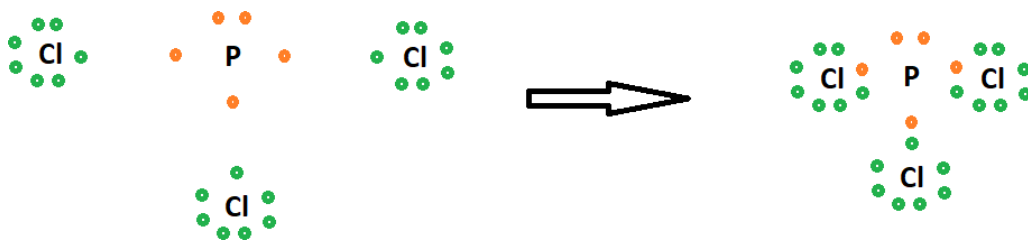
Covalent bonding also occurs in molecules formed by identical atoms (X_2).

For example, in the hydrogen molecule each of the two atoms share their electron, thus obtaining the stable doublet configuration.
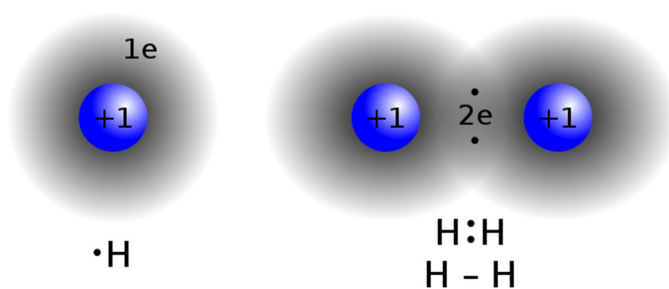
Figure 19. *The covalent bond in the H_2 molecule* [30]
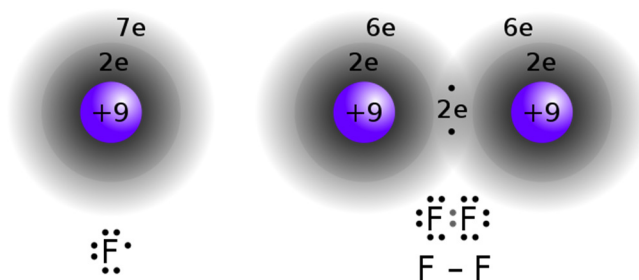
Figure 20. *The covalent bond in the F_2 molecule* [31]

_____

Also, in the fluorine molecule (the fluorine atom has seven valence electrons) each of the two atoms will share one electron, thus obtaining a simple fluorine-fluorine (F-F) covalent bond. The six electrons available to each fluorine atom, which are not involved in the formation of the F-F single bond, are non-participating electrons. Thus, we can say that each fluorine atom in the molecule has three pairs of non-participating electrons [1].

Other examples of covalent bonds are shown in the figures below:

Figure 21. *Lewis structure of ammonia and chemical bonds in NH$_3$* [32]

$$
\begin{array}{c}
H \\
\ddot{} \\
:N:H \\
\ddot{} \\
H
\end{array}
\quad = \quad
\begin{array}{c}
\nearrow H \\
:N-H \\
\searrow H
\end{array}
$$

In the case of the ammonia molecule, three of the five available valence electrons of the nitrogen will be shared with the electron in the hydrogen atom; three single N-H bonds are thus obtained, and the nitrogen atom is left with a pair of non-participating electrons.

(a) O$_2$ molecule; each oxygen atom shares two electrons, thus obtaining a double bond between the atoms and four non-participating electrons per atom;

(b) H$_2$O molecule; the oxygen atom shares one electron with the hydrogen atoms, forming two simple O-H bonds;

(c) HCl molecule; each of the two atoms shares one electron, forming a simple H-Cl bond;

(d) CO$_2$ molecule; the carbon atom shares all four electrons (two for each oxygen atom, obtaining two C=O double bonds);

(e) N$_2$ molecule; nitrogen atoms share three electrons each, obtaining a triple bond N≡N;

(f) NO molecule; the two atoms share two electrons each, obtaining an N=O double bond.

_____
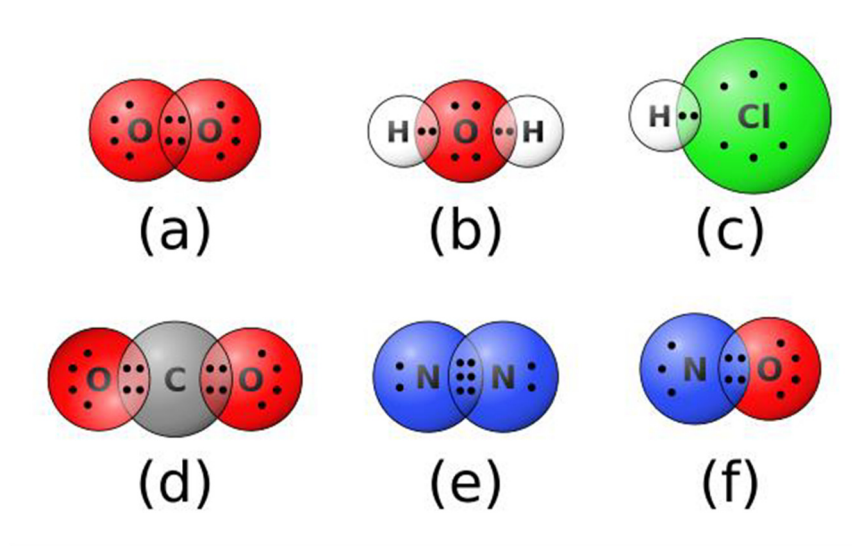
Figure 22. *Covalent bonds* [33]

Special case 1 – hydrogen compounds

> • **Compounds with metals (metal hydrides) have an ionic character** (NaH, MgH_2, etc).
> • **Compounds with non-metals or semi-metals are covalent** (BH_3, NH_3, H_2O, HCl, HF, H_2S, etc.)
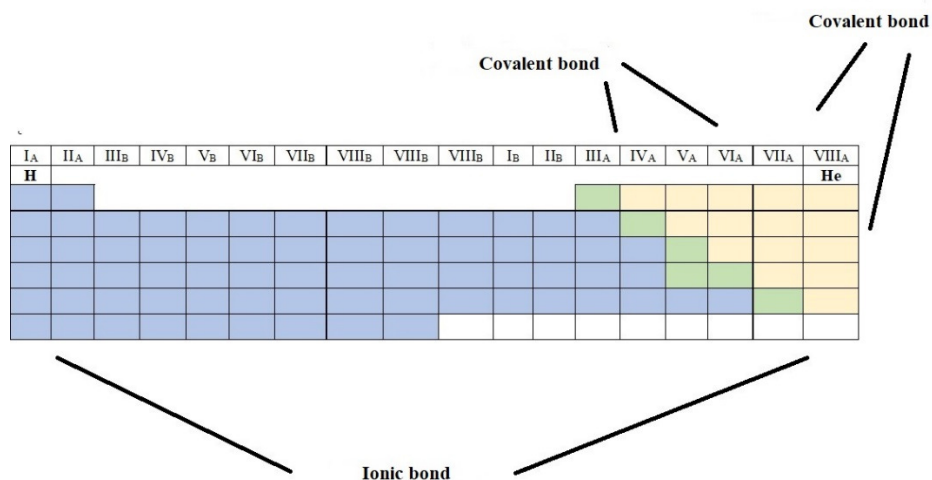
Special case 2 – Lewis acids and Lewis bases

> • **Lewis acid**: a compound whose central atom does not obtain its electron octet (it is electron **deficient**, thus having the ability to **accept electrons**).
Examples: compounds of type EX_3, where E is a group III_A element.

> • **Lewis base**: a compound whose central atom has at least one pair of non-participating electrons (has an **excess** of electrons, thus having the ability to **donate electrons**).
Examples: NH_3, SF_4

The formation of ionic or covalent bonds is summarized in the figure below; an ionic bond implies an opposite character of the two elements (electropositive and electronegative), while the covalent bond involves two elements with an electronegative character [60].

_____

Legend:
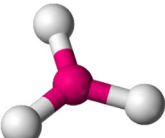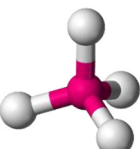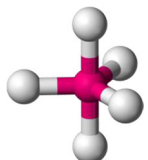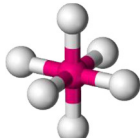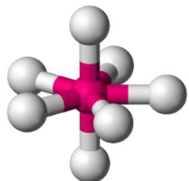
|	
	Metal
	Semimetal
	Non-metal

Ionic compounds	Covalent compounds
- Crystalline solids consisting of ions - High melting points - High boiling points - Good conductors of electricity in aqueous solution or melting - Water-soluble	- gases, liquids or solids consisting of molecules - Low melting points - Low boiling points - Poor electrical conductors (regardless of phase) - Slightly soluble in water

Geometry prediction of covalent compounds

The geometry of covalent compounds is predicted using the **steric number**.

Steric number (SN) = number of atoms bonded to the central atom + number of pair of non-participating electrons of the central atom

Hybridization	Steric number	Geometry
sp	2	
sp^2	3	
sp^3	4	
sp^3d	5	
sp^3d^2	6	
sp^3d^3	7	
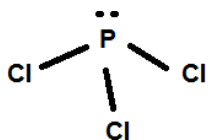
Steric number $(PCl_3) = 3 + 1 = 4$

_____

When determining the geometry of a compound, no distinction is made between single, double or triple bonds.

Examples

- **Linear geometry** (SN = 2): CO_2, $BeCl_2$
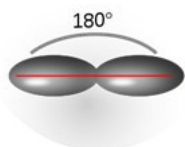
- **Trigonal geometry** (SN = 3): SO_3, BF_3
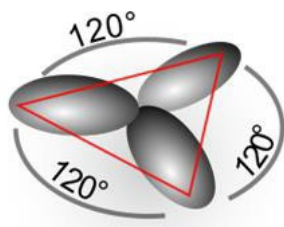
- **Tetrahedral geometry** (SN = 4): CH_4, PCl_3, H_2O
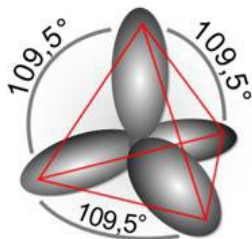
- **Trigonal-bipyramidal geometry** (SN = 5): PCl_5, AsF_5
- **Octahedral geometry** (SN = 6): SF_6, IF_5

III.3.1. COVALENT BOND. THE VALENCE BOND METHOD

The formation of the chemical bond can be explained by:

- **valence bond method**
- the method of molecular orbitals

The valence bond method

- It is based on the linear combination of atomic orbitals.
- Premise: A (single) chemical bond can be formed by **sharing a pair of electrons**.
- Obtaining the pair of electrons takes place by **overlapping an atomic orbital from each of the two atoms participating** in the formation of the bond, with the mention that the overlapping of the orbitals is carried out without their deformation.
- **The overlapping of the orbitals is geometrically conditioned**; atomic orbitals of close energy and concordant symmetry must approach in a perfectly defined direction (where the maximum of the electron's probability density is found). Thus, the phenomenon of **hybridization** of atomic orbitals occurs.

! Atoms of elements from the 2nd period have valence electrons in orbitals of different energies and shapes: 2s and 2p. None of them can achieve complete electron sharing, the optimal configuration being achieved when there is a combination of 2s and 2p orbitals. The orbitals thus formed are called **hybrid orbitals**, and the phenomenon is called **hybridization**.

> ! The phenomenon of hybridization occurs **exclusively** when covalent bonds are formed.

a. sp³ hybridization
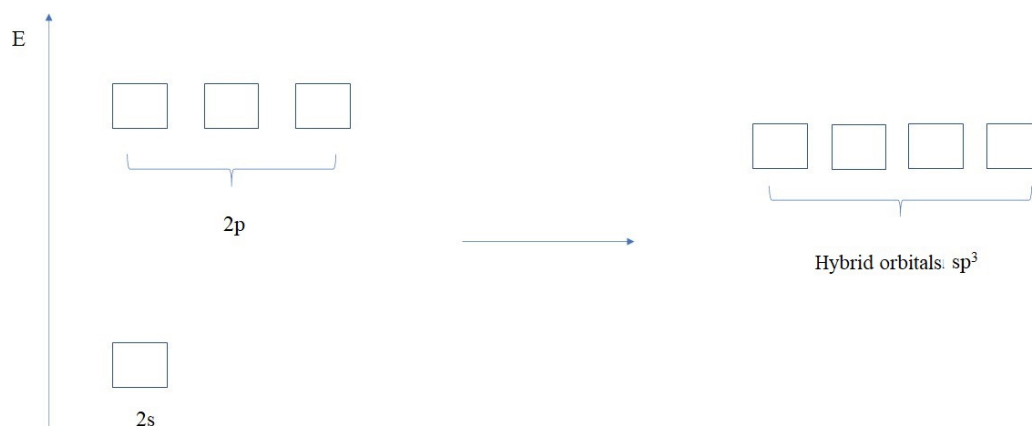
4 sp³ hybrid orbitals (of the same energy) are obtained. The hybrid orbitals formed are composed of ¼ s orbital and ¾ p orbital. The s orbital will increase in energy by ¾ of the energy difference between the two levels, and the energy of the p orbital will decrease by ¼ of the energy difference between the two levels.

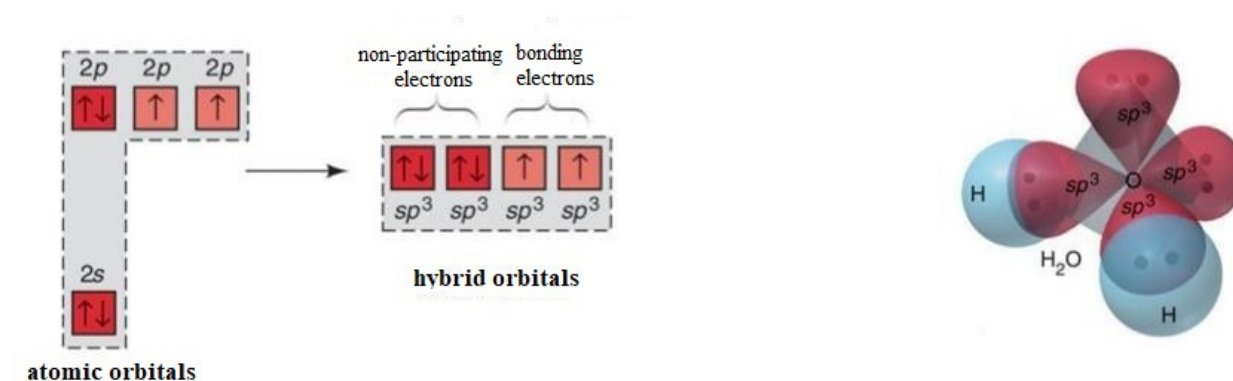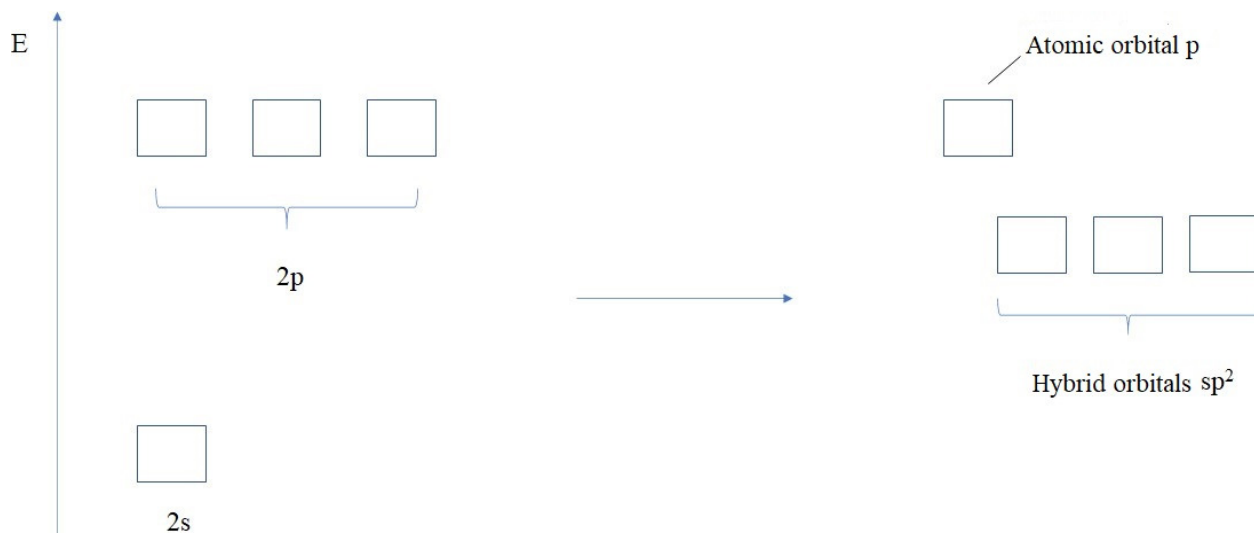**Figure 23**. *sp³ hybridization of H₂O* [34]

b. sp² hybridization

E

Atomic orbital p

2p

Hybrid orbitals sp^2

2s

3 sp² hybrid orbitals (of the same energy) and 1 unhybridized p atomic orbital are obtained. The hybrid orbitals formed are composed of 1/3 s orbital and 2/3 p orbital. The s orbital will increase its energy by 2/3 of the energy difference between the two levels, and the energy of the p orbital decreases by 1/3 of the energy difference between the two levels.
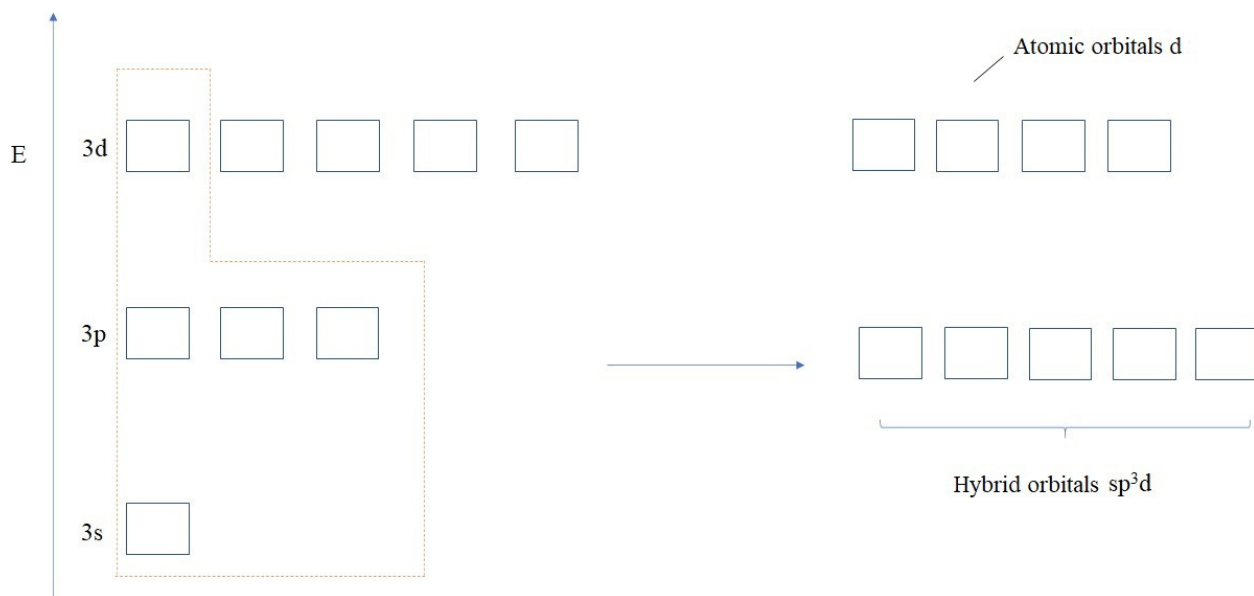
c. sp hybridization

2 sp hybrid orbitals (of the same energy) and 2 p atomic orbitals are obtained. The formed hybrid orbitals consist of ½ s orbital and ½ p orbital. The s orbital will increase its energy by ½ of the energy difference between the two levels, and the energy of the p orbital decreases by ½ of the energy difference between the two levels.

E

Atomic orbitals p

2p

Hybrid orbitals sp

2s
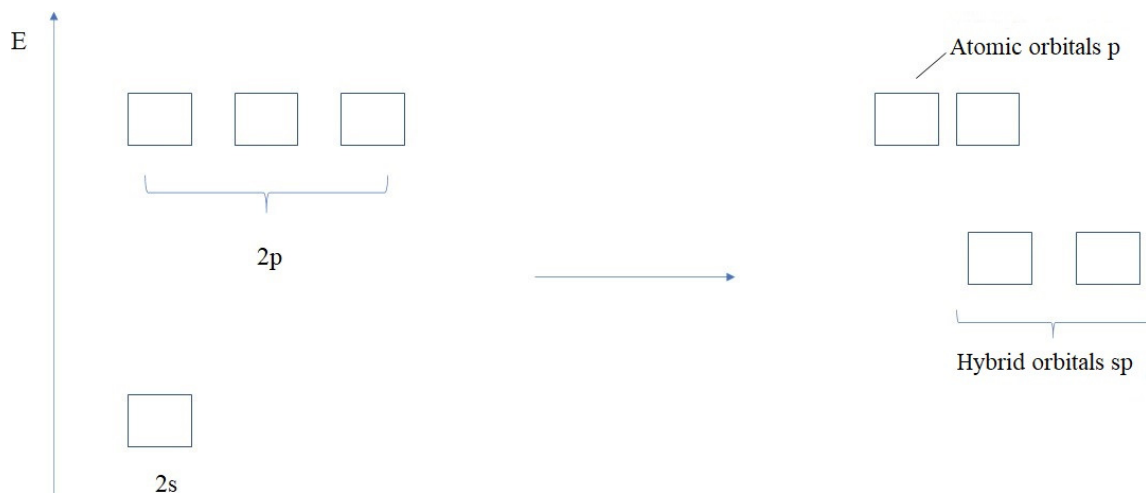
Elements in the 3rd period, which also have d orbitals, can form hybrid orbitals in which they are also involved (maximum 3 d orbitals).
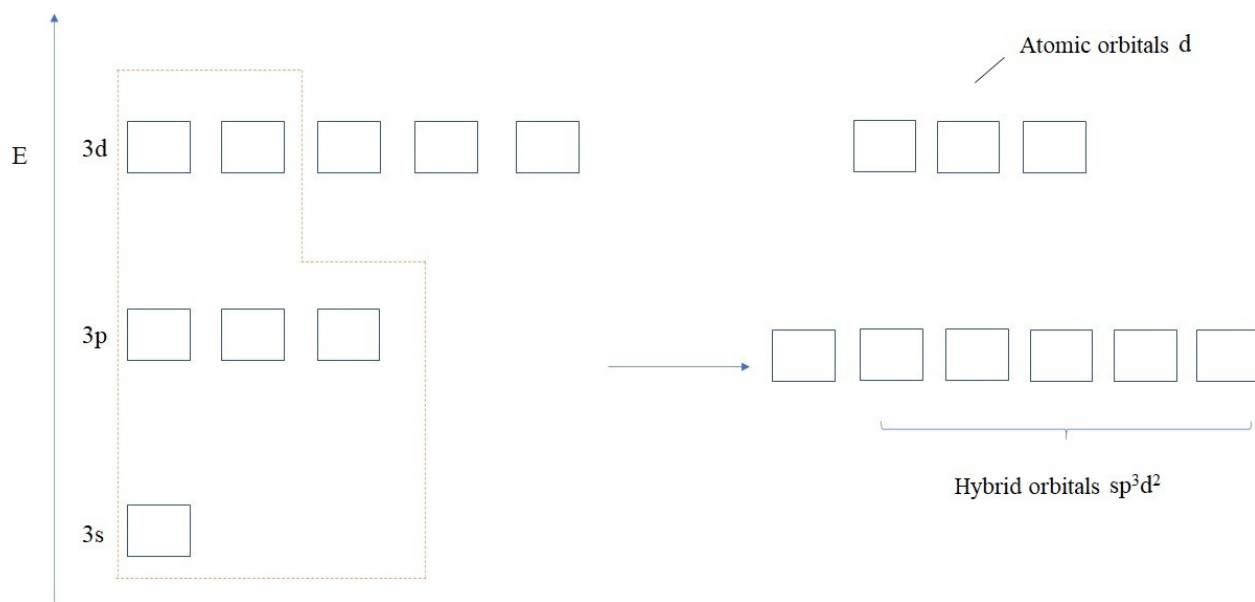
d. sp^{3}d hybridization

5 sp^{3}d hybrid orbitals are obtained, 4 d orbitals remain unhybridized. The obtained geometry is trigonal-bipyramidal.


e. sp^{3}d^2 hybridization

6 sp^{3}d^2 hybrid orbitals are obtained, 3 d orbitals remaining unhybridized. The resulting geometry will be octahedral.

_____

E

3d

Atomic orbitals d

3p

3s

Hybrid orbitals sp^3d^2

f. sp³d³ hybridization

7 sp^3d^3 hybrid orbitals are obtained, 2 d orbitals remaining unhybridized. The obtained geometry is pentagonal-bipyramidal.

E

3d

Atomic orbitals d

3p

3s

Hybrid orbitals sp^3d^3

! Covalent bonds can be σ (sigma) or π (pi) bonds.

_____
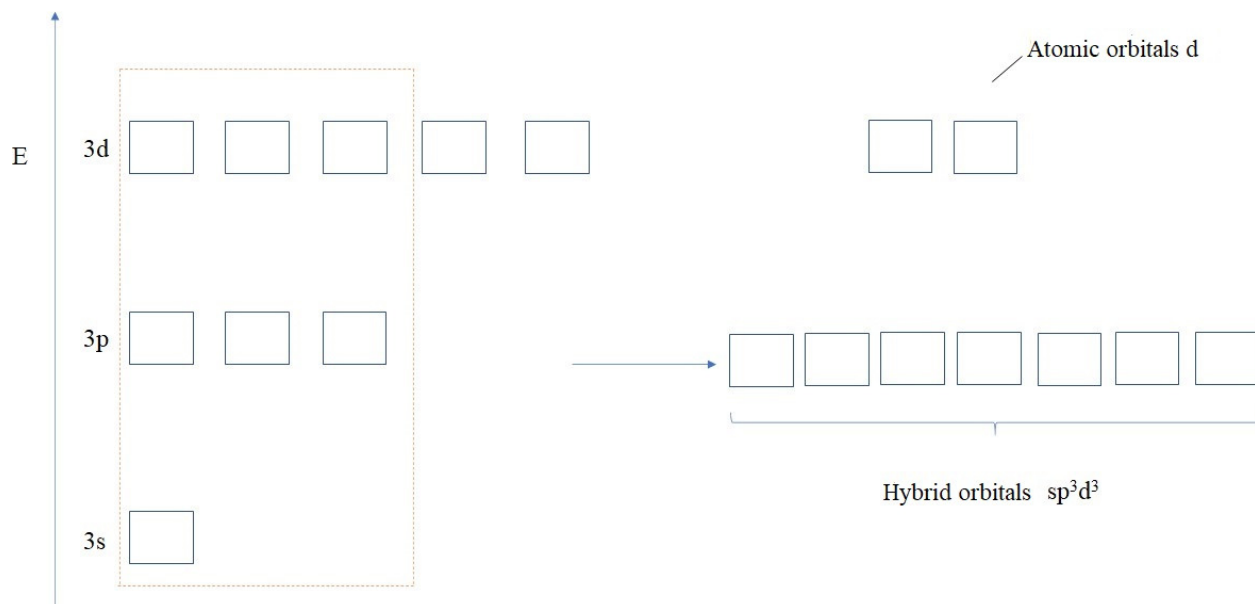
σ (sigma) bond

- **It is established between any of the atomic orbitals**, since the overlap of one lobe from each orbital is required.

! Hybrid orbitals can only participate in the formation of sigma bonds (due to the asymmetric shape).

The probability of finding electrons is maximum in the direction of orbital overlap, and this is the direction of orientation of the lobe, so the sigma bond is oriented in space.
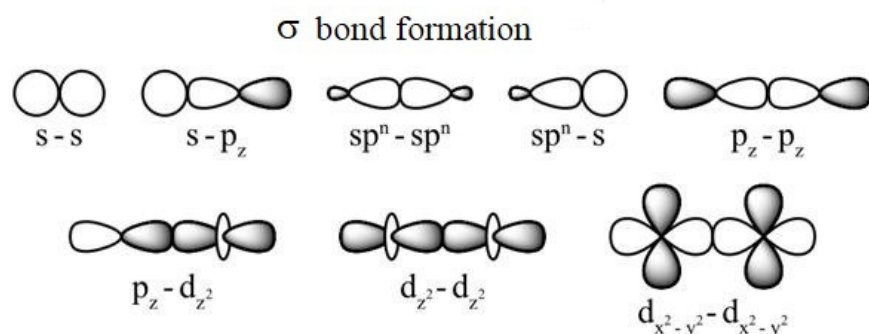

Figure 24. *Sigma bond formation* [35]

π (pi) bond

The π bond is formed when **two lobes from each atomic orbital overlap**.
- It can be formed by **the interaction of p-p, p-d and d-d orbitals**.
- To form a π bond, two p orbitals must approach in a direction perpendicular to their axes.
- To form a π bond, two d orbitals must approach in a direction in their plane.
- To form a π bond, a p-orbital and a d-orbital must approach in a direction in the plane of the d-orbital and perpendicular to the p-orbital.
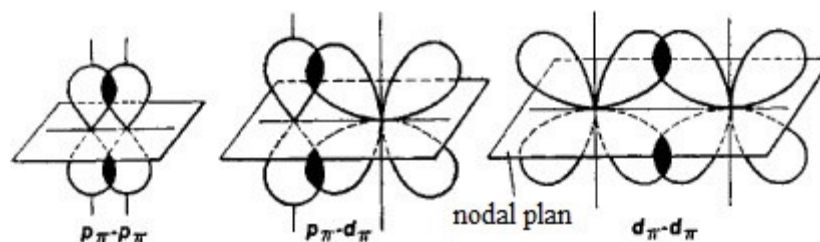

Figure 25. *Formation of the pi bond* [36]

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III.3.2. COVALENT BOND. THE MOLECULAR ORBITAL METHOD

The formation of the chemical bond can be explained by:

- valence bond method
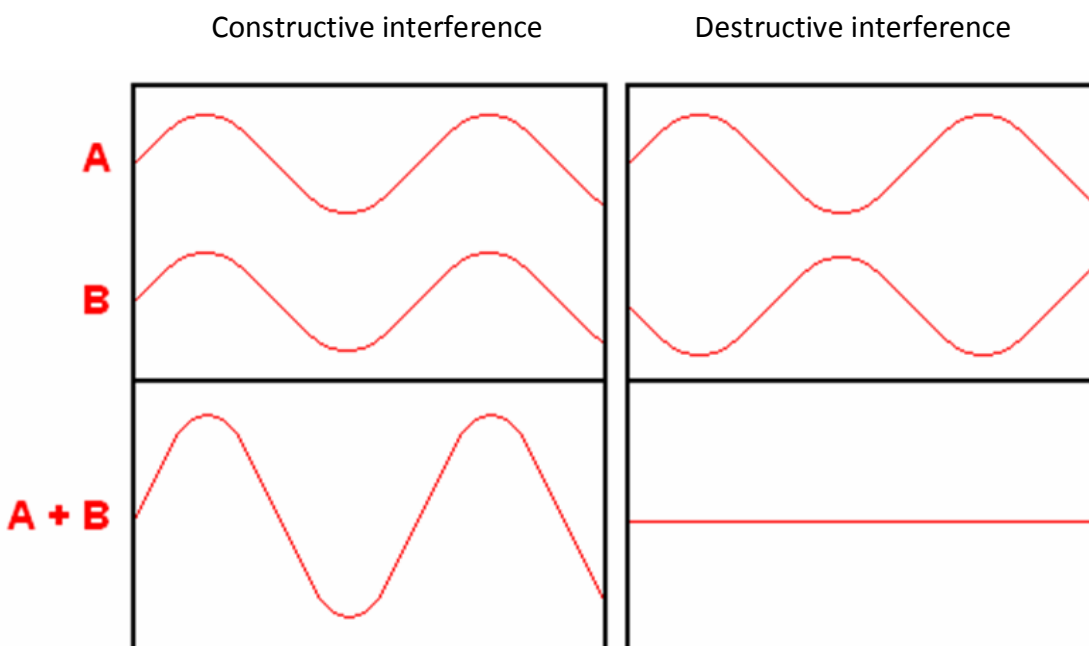- **molecular orbital method**

The method of molecular orbitals is based on the quantum-mechanical description of the wave functions associated with molecules. According to it, the electrons are delocalized in the molecule, they are not directly associated with a specific atom or bond. Thus, the atomic orbitals (A.O.) interact forming new orbitals, called **molecular orbitals** (M.O.).

Atomic orbitals – describe the position and energy of electrons in atoms

Molecular orbitals – describe the position and energy of electrons in molecules

Molecular orbitals - they are extended on the molecule, not localized to a specific atom

The formation of molecular orbitals takes place by combining the two atomic orbitals (the interference of the two wave functions).
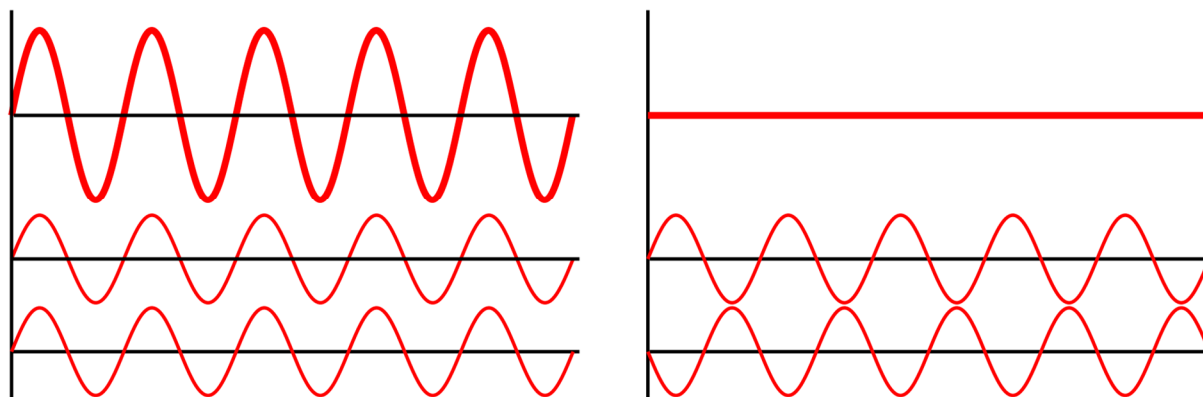
Constructive interference   Destructive interference

_____

Figure 26. *Wave interference (constructive – left; destructive – right)* [37]

In the case of constructive interference, a **bonding molecular orbital** of lower energy than that of the initial atomic orbitals will be formed.

In case of destructive interference, an **antibonding molecular orbital** of higher energy than the initial atomic orbitals will be formed.

> ! **The number of molecular orbitals obtained must be equal to the sum of the atomic orbitals of the 2 atoms**.
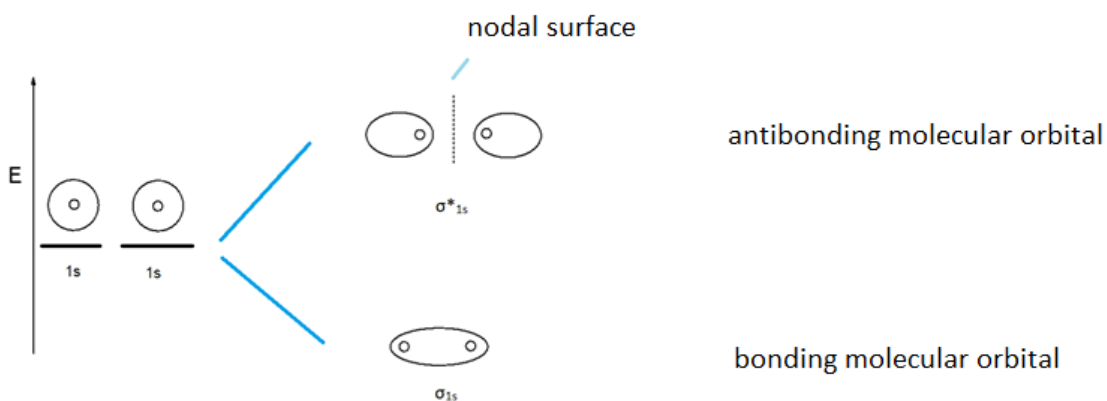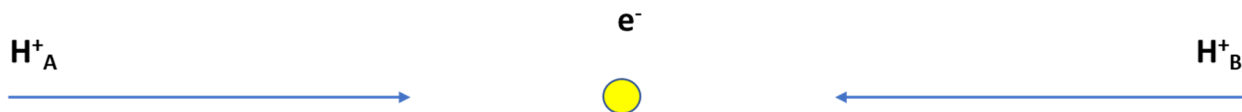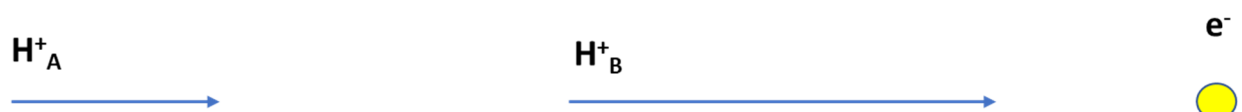

Figure 27. *Formation of hydrogen molecular orbitals* [38]

The bonding molecular orbital σ_{1s}, obtained by summing the atomic orbitals, corresponds to the constructive interference of the wave functions.

_____

H^+_A → e^- ← H^+_B

! Constructive interference: high electron density between the two nuclei, which causes the energy of the molecular orbitals to decrease. The electron-nucleus electrostatic attraction reduces the repulsions between the two positively charged nuclei.

In the case of the σ^*_{1s} antibonding molecular orbital, the electrons are found outside the space between the two nuclei, which allows the establishment of repulsion forces between the positively charged nuclei. For this reason, the σ^* orbital has a higher energy than the 1s atomic orbitals.

H^+_A → H^+_B → e^-

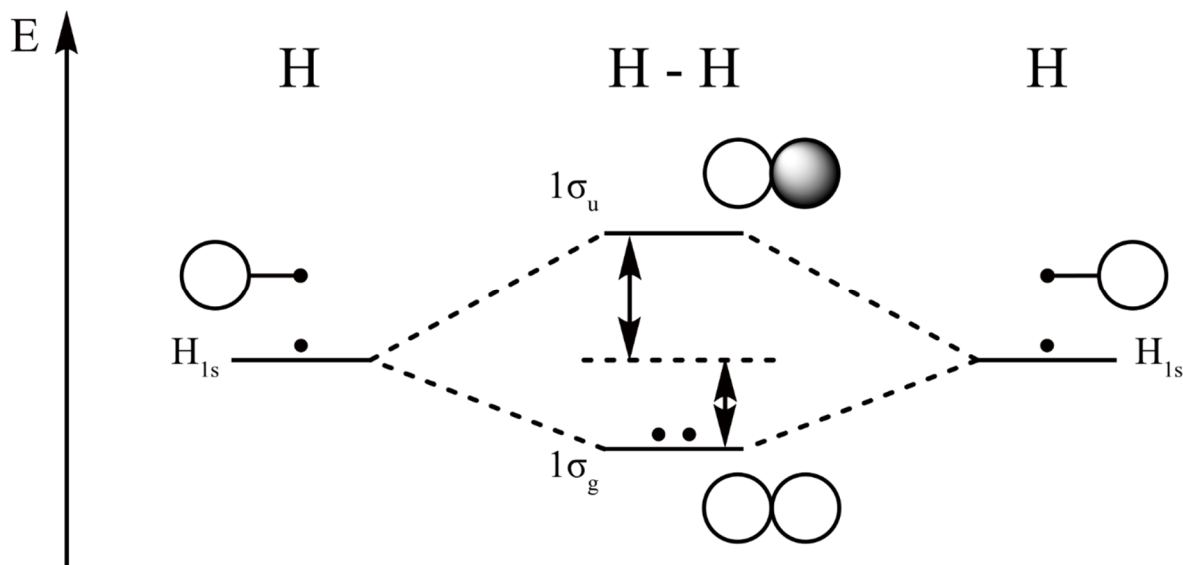The energy diagram of the H_2 molecule is shown in the following figure:

Figure 28. *Molecular orbital diagram of dihydrogen* [39]

The electron occupation of molecular orbitals is based on the same principles that underlie the occupation of the electronic shell:

✓ Molecular orbitals are occupied in **order of increasing energy**

✓ An orbital can be occupied by a **maximum of two electrons of opposite spin**

✓ Every orbital in a subshell is **singly occupied with one electron** before any one orbital is doubly occupied

Bond order

The bond order (bond multiplicity) represents the effective number of bonds made by atoms in the molecule.

$$Bond\ order = \frac{1}{2}(n - n^*)$$

n – number of electrons on bonding molecular orbitals

n* - number of electrons on antibonding molecular orbitals

The following situations may be encountered:

Bond order = 0   → the molecule does not exist

Bond order = 1, 2, 3   → stable molecule

Bond order = 0.5, 1.5, 2.5 → unstable molecule

Energy diagrams of period 1 diatomic molecules are shown in the figures below:

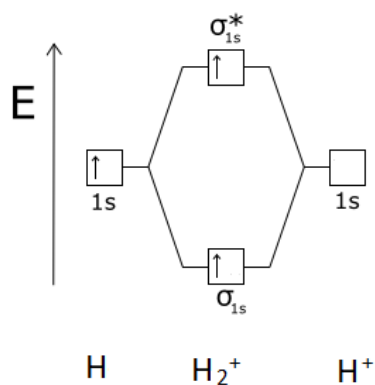**H₂⁺ (bond order 0.5)**

Figure 29. *Energy diagram of H₂⁺ molecule* [39]

He$_2^+$ (bond order 0.5)
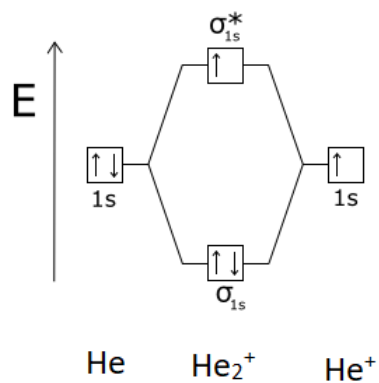

Figure 30. *Energy diagram of He$_2^+$ molecule*[40]
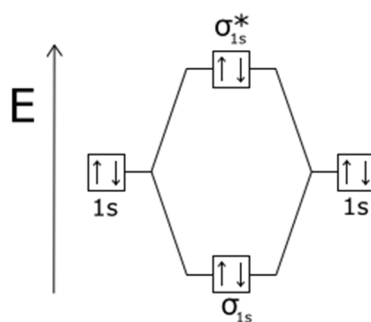
He$_2$ (bond order 0)

Figure 31. *Energy diagram of He$_2$ molecule* [40]

Period 2 diatomic molecules

By linear combination of two 2s atomic orbitals two molecular orbitals will be obtained: σ_{2s} and σ^*_{2s}.

Linear combination of six 2p atomic orbitals will yield six molecular orbitals: two sigma orbitals (σ_{2p} and σ^*_{2p}) and four pi orbitals (two π_{2p} orbitals and two π^*_{2p} orbitals).
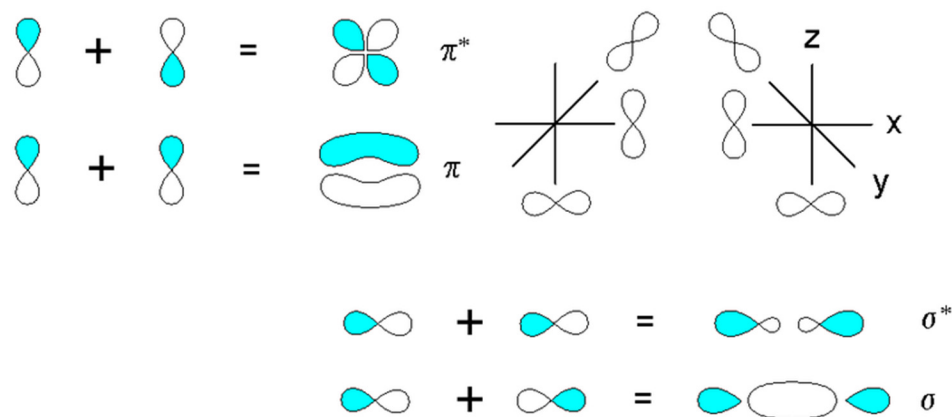

Figure 32. *Formation of sigma and pi molecular orbitals from p-type atomic orbitals* [41]

The energy diagram of the elements from the 2nd period (block p) is shown in the following figure:
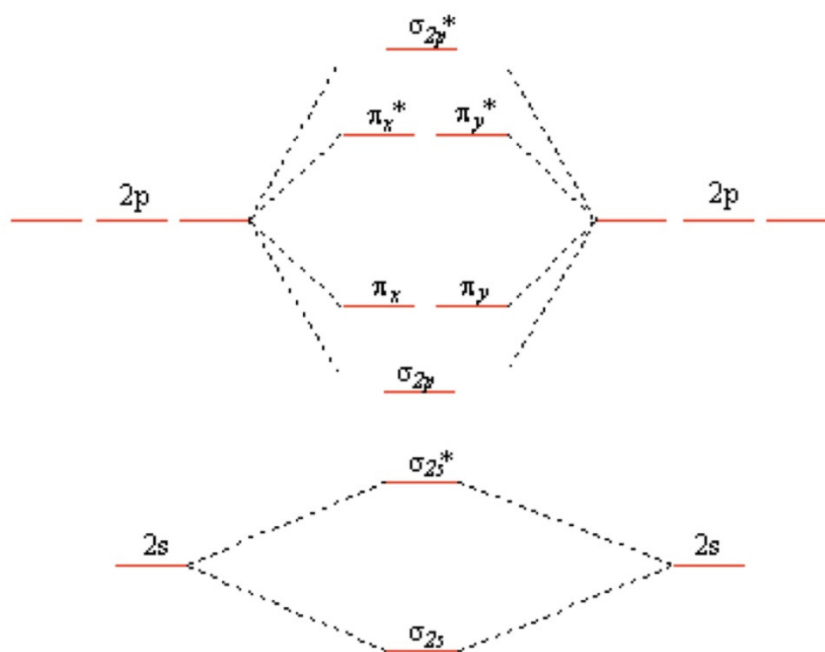

Figure 33. *Energy diagram of the p block elements from the 2nd period* [42]

_____

Consider the O_2 diagram. The electron configuration of the oxygen atom is $1s^2\ 2s^2\ 2p^4$; we will discuss the electrons in the valence shell, $2s^2\ 2p^4$. The twelve electrons of the O_2 molecule will be arranged as follows: each pair of electrons occupies the molecular orbitals σ_{2s}, $\sigma*_{2s}$, σ_{2p} and the two π_{2p} orbitals, and the remaining two electrons will each occupy an orbital $\pi*_{2p}$.
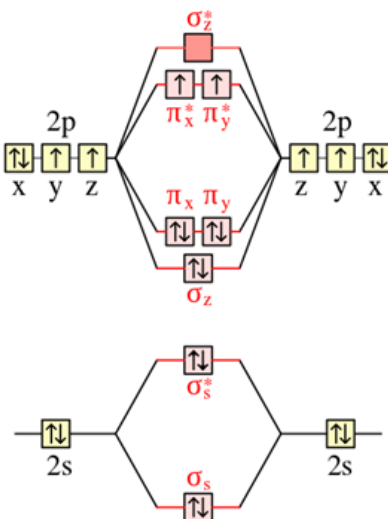
atomic orbital   molecular orbital   atomic orbital

Figure 34. *Energy diagram of the oxygen molecule* [43]

Covalent bonds can be:

- **Non-polar:** the electrons are equally shared between two atoms

- **Polar**: the electrons are uneven shared between two atoms, when the bonding electrons move to the more electronegative atom

- **Coordinate**: both electrons come from the same atom, that donates them to an acceptor (an electron deficient species).

Polarity of covalent bonds

In the case of a covalent bond between two atoms of the same type (which will have the same electronegativity), the electrons will be **equally distributed between the two atoms** (non-polar molecules).

In the case of a covalent bond between two atoms with different electronegativity, **a delocalization of the electrons will result**, leading to partially positive and partially negative charges for the two atoms (thus a dipole moment appears).

Dipole moment

Let's consider the diatomic molecule AB, where the B atom is more electronegative than the A atom.

The molecule will be polarized like this:

$\mu = \delta \cdot d(AB)$, where: μ – dipole moment (Debye); δ – partial charge; $d(AB)$ – length of the AB bond

➢ The dipole moment is a physical vector quantity associated with a polarized spatial distribution of electrical charges.

➢ In most molecules we can talk about a positively charged pole and an opposite pole, with a partial negative charge.

➢ The dipole moment of such a molecule is equal to the vector sum of the dipole moments of all bonds in the molecule and will be symbolized as:

Observations
- If a molecule is symmetrical, the dipole moment vectors of the polar bonds will cancel each other → nonpolar molecule.
- If in a molecule characterized by one of the seven types of geometries previously presented, the central atom has at least one pair of non-participating electrons, the molecule will be polar.

_____

Coordinate bond

- Occurs when the bond between two atoms is made by means of a pair of electrons that comes from one atom.

The covalent bond that forms with a pair of electrons given by a single atom is called a coordinate bond. The atom or ion that donates the non-participating pair of electrons is called the donor, and the atom or ion that accepts this pair of electrons is called the acceptor.

Therefore, the coordinate bond appears when the donor has a lone pair of electrons and the acceptor lacks two electrons to complete the electron shell.
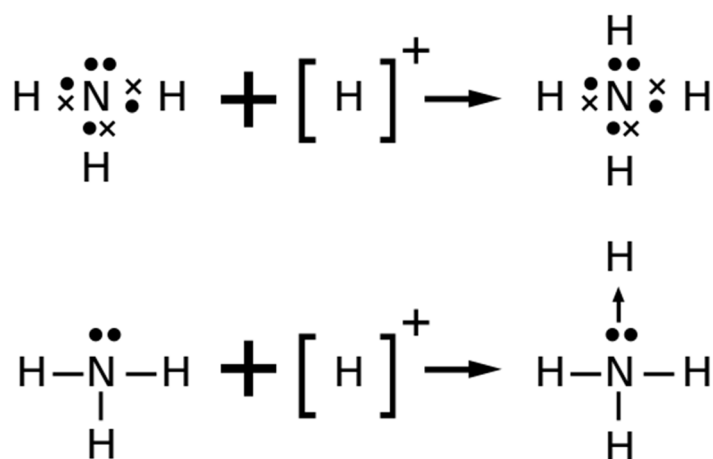

Figure35. *Coordinate bond in ammonium ions NH$_4^+$* [44]

Figure 36. *Coordinate bond in NH$_3$-BF$_3$ adduct* [45]

_____

III.4. Intermolecular forces

The properties of chemical systems are strongly influenced by the forces acting between the molecules/atoms/ions of these systems.

Intermolecular bonds (forces) can be classified into:

III.4.1. Ion-dipol forces

Definition: The force of attraction between a polar molecule and an ion in its vicinity is called the ion-dipole force.

Example: when NaCl is dissolved in water, it dissociates into Na^+ and Cl^- ions; the attractive force between Na^+ and the O atom of water (with $-\delta$ charge) in water is an ion-dipole force. This fact is due to the fact that polar molecules are also dissolved in a solvent of the same type (polar).
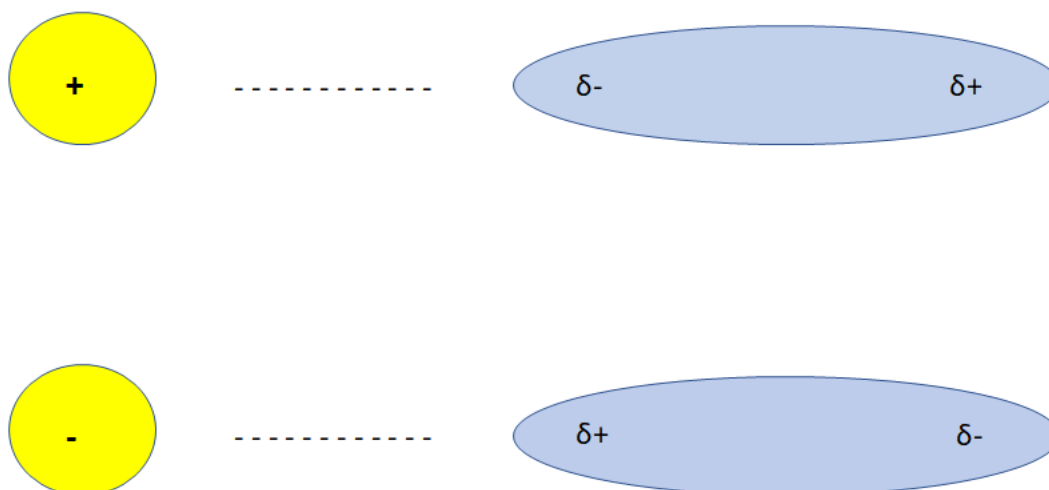
Figure 37. *Ion-dipol interactions*

III.4.2. Ion – induced dipole forces

Definition: The force of attraction between a nonpolar molecule and an ion found in its vicinity is called the ion-induced dipole force. In this case, the ion can attract or repel the electrons of the nonpolar molecule, thus inducing a temporary dipole in the nonpolar molecule.

_____

Example: hemoglobin is a protein found in red blood cells, having the role of carrying oxygenated blood. The structure of hemoglobin contains the Fe^{2+} ion, which has the role of attracting O_2 through an ion- induced dipole force.
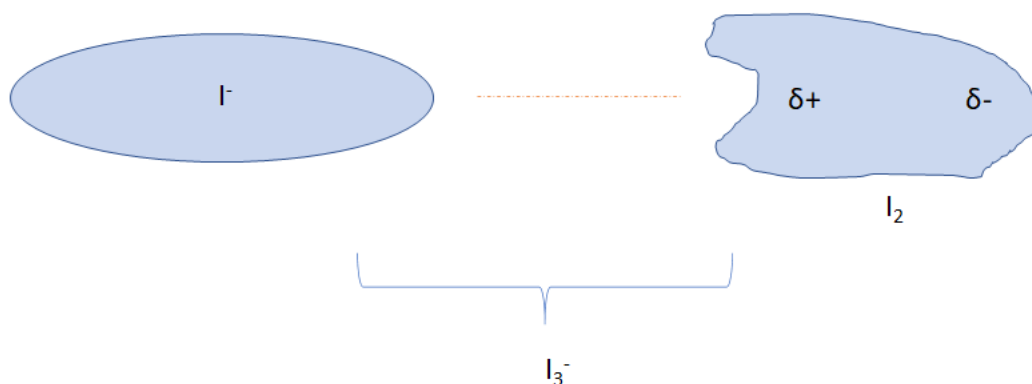

Figure 38. *Ion – induced dipole interactions*

III.4.3. Hydrogen bonds

Definition: The force of attraction between the non-participating pair of electrons of an electronegative element and a hydrogen atom that is covalently bonded to one of the N, O or F atoms is called a hydrogen bond.

Any of the N, O or F atoms have a much more pronounced electronegativity than the H atom, so they will attract the bonding electrons towards them; thus a negative partial charge appears on these atoms, while the hydrogen atom will have a positive partial charge. The molecules will orient themselves so that the hydrogen atom ($+\delta$) is in close proximity to the more electronegative atom (F, O, N), and the force of attraction that occurs between the pair of non-participating electrons of the more electronegative atom and the hydrogen atom represents the hydrogen bond.

Examples: In H_2O, there is a hydrogen bond between the oxygen atom of one molecule and the hydrogen atom of another water molecule. Analogously, in NH_3 there is a H bond between the nitrogen atom of one molecule and the hydrogen atom of another NH_3 molecule.

The hydrogen bond that forms between H_2O molecules will be stronger than that between NH_3 molecules because the oxygen atom in water has two pairs of unpaired electrons available to form hydrogen bonds. In the case of NH_3, there is only one lone pair of electrons, so the hydrogen bond will be weaker than in water.

_____

N-H ···· :N–   O-H ···· :N–   F-H ···· :N

N-H ···· :O–   O-H ···· :O–   F-H ···· :O

N-H ···· :F–   O-H ···· :F–   F-H ···· :F
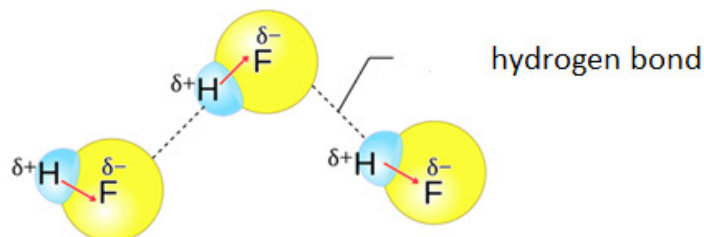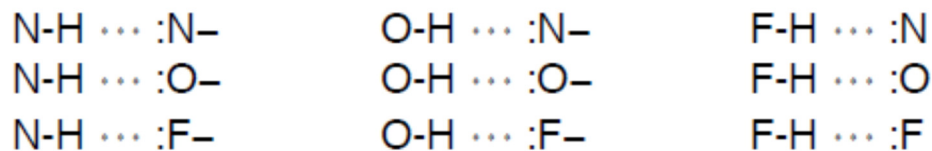
Figure 39. *Hydrogen bonds between HF molecules* [46]
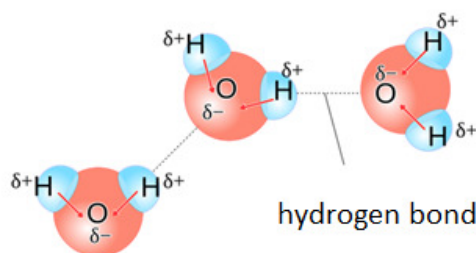
Figure 40. *Hydrogen bonds between water molecules* [47]

III.4.4. Dipole-dipole interactions

Dipole-dipole interactions occur due to an unequal distribution of electrons, which results in a partially positive charge (+δ) and a partially negative charge (-δ) in a polar molecule that is, on the whole, neutral. Polar molecules tend to orient themselves in space so that the side with partial positive charge +δ is in the vicinity of the negative partial charge –δ of another molecule. Thus, the forces of repulsion between molecules are minimized and the forces of attraction between them are maximized.

Figure 41. *Dipole-dipole interactions* [48]

III.4.5. Dipole – induced dipole interactions (Debye)

This type of forces occurs between molecules with a permanent dipole and those with an induced dipole (between a polar molecule and a molecule that can be polarized in the presence of a polar compound).

Observation: large atoms and molecules are more easily polarizable than the smaller ones.

Polar molecules tend to displace the electrons of a non-polar compound so that regions of partially negative or negative charge (induced polarity) appear. The molecules will then orient themselves in such a way as to maximize the attractive forces between the molecules.

Example: Ar and HCl. When the (non-polar) argon atom and the polar HCl molecule are in close proximity, the side with partial negative charge of HCl will repel the argon electron cloud, which will move in the opposite direction, inducing a temporary dipole moment in the argon. Both compounds will rearrange themselves so as to maximize the attractive forces.
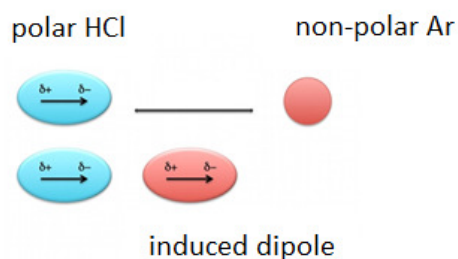
Figure 42. *Dipole – induced dipole interactions*

III.4.6. London dispersion forces

London dispersion forces are the weakest intermolecular forces.

Definition: The London dispersion force is a temporary attractive force that occurs when the electrons of two adjacent atoms are arranged to form temporary dipoles.

In turn, this temporary dipole can act on a second atom or molecule, leading to the appearance of another temporary dipole (due to the repulsion between the electrons), which leads to an electrostatic attraction between the two atoms or molecules.

unequal electron distribution   attractive forces
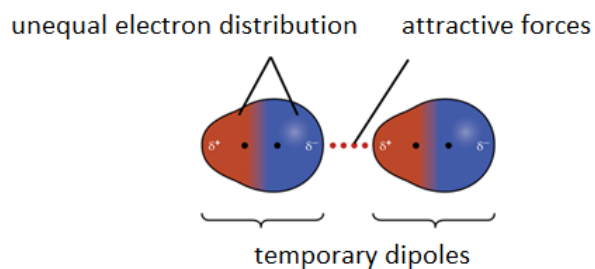
temporary dipoles

Because of the continuous movement of electrons, an atom or molecule can develop a temporary dipole when the electrons are asymmetrically distributed around the nucleus.

The strength of intermolecular forces is shown in the following figure:

Intermolecular forces   Intramolecular forces

weak   medium   strong

dispersion   hydrogen bonds   covalent bonds

dipole-dipole   ion-dipole   ionic bonds
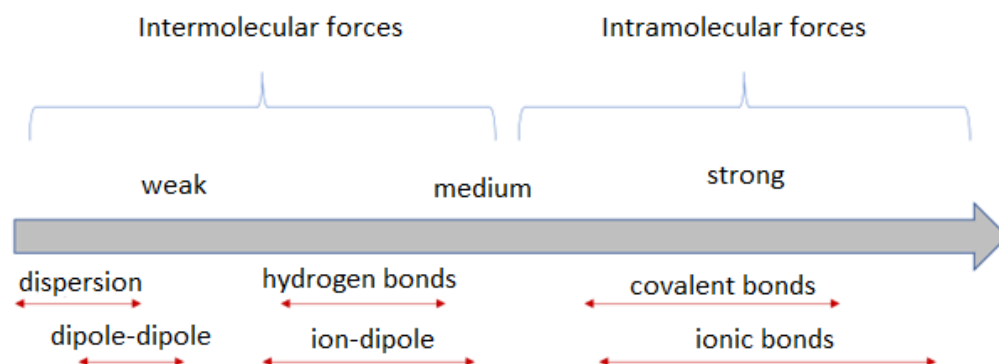
Phenomena that depend on intermolecular forces:

- Boiling and melting points (boiling and melting points increase with the strength of intermolecular bonds)
- Solubility in polar/non-polar solvents (polar compounds dissolve in polar solvents, non-polar compounds dissolve in non-polar solvents).

IV. STOICHIOMETRIC CALCULATIONS

BASIC CONCEPTS
Calculations based on chemical reaction equations
The notion of limiting reactant
Calculating the yield of a chemical reaction

LEARNING OBJECTIVES
Correct writing and balancing chemical reactions
Using chemical reaction equations to calculate the number of moles of reactants/ products
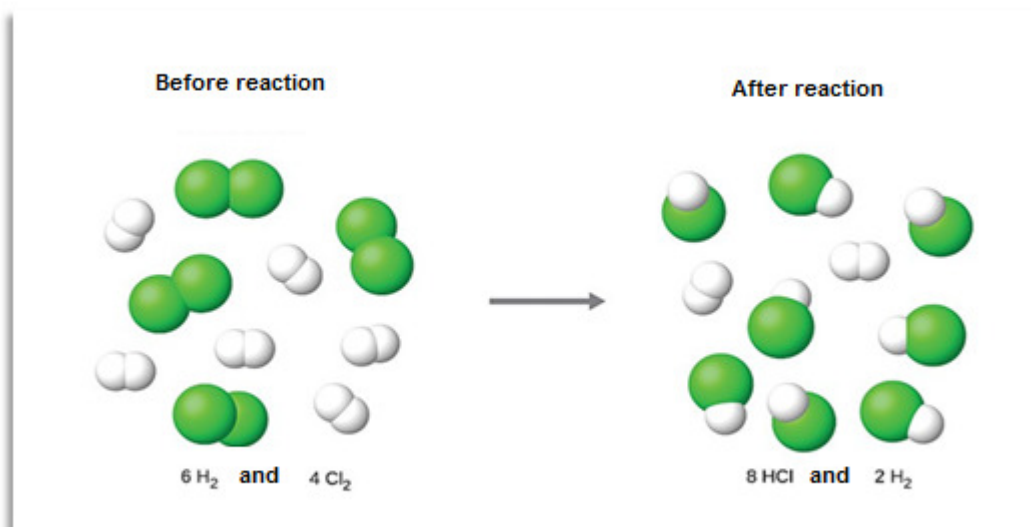Identify the limiting reactant in a reaction

Illustration of the limiting reactant concept: Cl_2, in the reaction between 6 moles of H_2 and 4 moles of Cl_2 [49]

_____

      Stoichiometry deals with the study of quantitative relationships between substances and their reactions.

When we write the equation for a chemical reaction, we use the following general rules [50]:

1. The substances undergoing the reaction are called reactants, and their formulas are placed on the left side of the equation.

2. The substances generated in the reaction are called reaction products and their formulas are found on the right side of the equation.

3. (+) signs separate the individual formulas of reactants and reaction products, and an arrow (⟶) separates reactants and products on the left and right side of the equation, respectively.

4. The relative number of reactant species and reaction products are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is usually omitted.

> ! It is customary to use the smallest possible (whole number) coefficients in a chemical equation.

The physical state of reactants and products in chemical equations is very often indicated by an abbreviation; common abbreviations are **s** for solids, **l** for liquids, **g** for gases, and **aq** for substances dissolved in water. These notions are illustrated in the following reaction:

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$
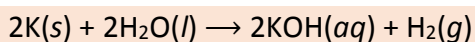
This equation represents the reaction that occurs when potassium reacts with water. Potassium (solid) reacts with water (liquid) to produce hydrogen (gas) and potassium hydroxide (ionic compound, solid in pure form, water soluble).

      Stoichiometry deals with establishing the quantitative ratio between the components of chemical combinations or chemical reactions. Thus, starting from the chemical equations of the reactions, the proportions between the reactants and the reaction products can be calculated.

      To solve the stoichiometry problems, the following are needed:

      - correct writing of the chemical reaction equation;

      - establishing the mass or molar ratios between the substances participating in the reaction;

      - formulating the necessary proportions from which to calculate the required quantities.

1. Calculation of the number of moles

The number of moles (**v**) is calculated as the ratio between the mass of a compound (m, in grams) and its molecular mass (μ, g/mole).

$$v = \frac{m}{\mu} \text{ (moles)}$$

If we know the volume of a gas, the number of moles can be calculated with the formula:

$$v_{gas} = \frac{V}{22.4}, \text{ where V is the volume of the respective gas (liters)}$$

2. Limiting reactant and excess reactant

Definition: The limiting reactant of a chemical reaction is that reactant that is completely consumed when the chemical reaction is complete. The amount of product formed in that reaction is limited by this reactant because the reaction cannot proceed without it. If one or more other reactants are present in amounts greater than that required to react with the limiting reactant, they are considered **excess reactants**.

Consider the reaction: $N_2 + 3H_2 \rightarrow 2NH_3$

$$\underset{x}{\overset{1}{N_2}} + \underset{y}{\overset{3}{3H_2}} \rightarrow \underset{z}{\overset{2}{2NH_3}}$$

_____
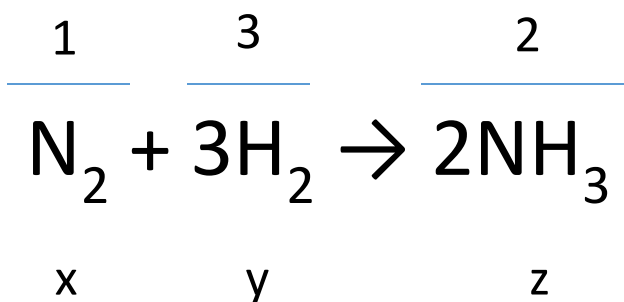
The following situations are encountered:

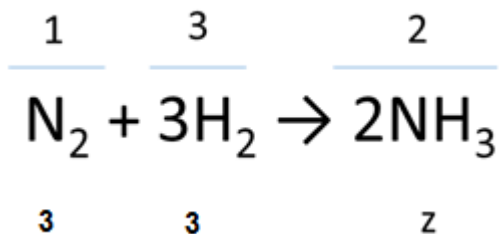|	N_2		H_2	
If:	$\dfrac{x}{1}$	>	$\dfrac{y}{3}$	N_2 – excess reagent H_2 – limiting reagent
If:	$\dfrac{x}{1}$	<	$\dfrac{y}{3}$	N_2 – limiting reagent H_2 – excess reagent
If:	$\dfrac{x}{1}$	=	$\dfrac{y}{3}$	We have no limiting reactant and no excess reactant, the reaction is complete

Suppose 3 moles N_2 and 3 moles H_2 react.

$$\overset{1}{\underline{}} \quad \overset{3}{\underline{}} \qquad \overset{2}{\underline{}}$$
$$N_2 + 3H_2 \rightarrow 2NH_3$$
$$\overset{}{}3 \qquad 3 \qquad\quad z$$

$N_2 \left(\dfrac{3}{1}\right) > H_2 \left(\dfrac{3}{3}\right) \rightarrow$ **N_2 - excess**, *H_2 – limiting reagent*.

We calculate the amount of N_2 that will react as a function of the limiting reactant:

$$\overset{1}{\underline{}} \quad \overset{3}{\underline{}} \qquad \overset{2}{\underline{}}$$
$$N_2 + 3H_2 \rightarrow 2NH_3$$
$$a \qquad 3 \qquad\quad z$$
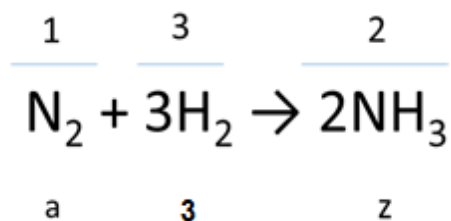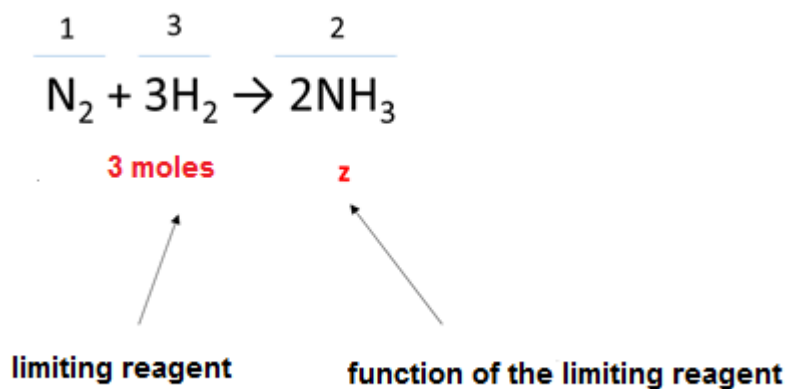
$$a = \frac{3 \cdot 1}{3} = 1 \ mole \ N2$$

We calculate the amount of excess N_2:

$$v_{N_2}(excess) = v_{initial} - v_{necessary} = 3 - 1 = 2 \ moles$$

> **!** The amount of reaction product that is obtained is always calculated as function of the limiting reactant.

$$\overset{1}{\underline{}} \quad \overset{3}{\underline{}} \quad \overset{2}{\underline{}}$$

$$N_2 + 3H_2 \rightarrow 2NH_3$$

3 moles   **z**

limiting reagent   **function of the limiting reagent**

$$z = \frac{3 \cdot 2}{3} = 2 \ moles \ NH_3$$

3. Reaction yield

The **yield** (η) of a reaction is calculated as the ratio between the practical amount of product obtained in the reaction and the amount that should have been obtained theoretically, if the transformation had occurred completely.

$$\eta = \frac{c_p}{c_t} \cdot 100 \ (\%)$$

Example: by decomposing 50 g of $CaCO_3$, 6.72 l of CO_2 were obtained. Calculate the yield of the decomposition reaction.
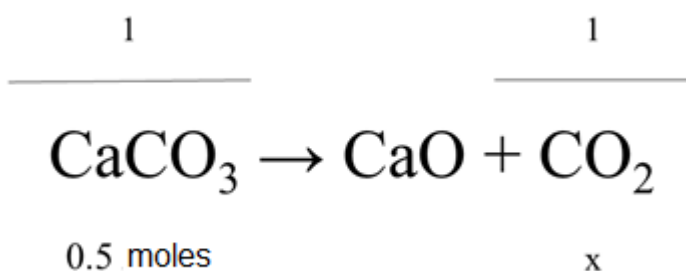
μ_{CaCO3} = 100 g/mole

_____

<u>Answer</u>

1. We write the equation of the decomposition reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

2. We calculate the number of moles of $CaCO_3$ entering the decomposition reaction:

$$v_{CaCO_3} = \frac{50}{100} = 0.5 \; moles$$

3. We calculate the number of moles of CO_2 we should get (theoretically) from the decomposition reaction:

$$\frac{1}{CaCO_3} \rightarrow CaO + \frac{1}{CO_2}$$

0.5 moles   x

$$x = \frac{0.5 \cdot 1}{1} = 0.5 \; moles$$

$$vCO_2(theoretical) = 0.5 \; moles$$

4. We calculate the number of moles of CO2 that was practically obtained in the reaction:

$$vCO_2(practic) = \frac{6.72}{22.4} = 0.3 \; moles$$

5. We calculate the yield of the decomposition reaction:

$$\eta = \frac{v_{practic}}{v_{theoretical}} \cdot 100 = \frac{0.3}{0.5} \cdot 100 = 60\%$$

V. NOTIONS OF CHEMICAL THERMODYNAMICS

Chemical thermodynamics studies the stability conditions of chemical systems and the laws according to which they transform to reach the state of maximum stability, i.e. the state of chemical equilibrium.

Thermodynamics notions

The energy of a system can take different aspects, such as kinetic energy, potential energy, chemical energy, or electrical energy. Physical and chemical transformations are always accompanied by energy transformations, the study of which is the object of thermodynamics.

The energy of the atoms and molecules that form the substances is given by the sum of the translational kinetic energy of the moving molecules, the rotational and vibrational energy of the atoms, the internal potential energy influenced by the position of the nuclei and electrons.

From a thermodynamic point of view, it is not the absolute value of energy that is important, but the energy variations that accompany a process.

A chemical system is defined as a portion of matter containing a defined amount of one or more substances under given conditions.

Chemical thermodynamics deals with the study of the stability conditions of chemical systems and the laws according to which they transform to reach the state of maximum stability, that of chemical equilibrium.

The first principle of thermodynamics

Variations in the total energy of a system

The amount of energy contained in a chemical system depends on its mass, chemical nature and physical parameters (temperature, pressure, volume); this amount of energy is constant as long as the system does not undergo any transformation. This total energy is called internal energy and is denoted by E. The internal energy of a chemical system consists of: the kinetic energy of molecules, atoms and electrons; the potential energy; the energy of electric and magnetic fields. The absolute value of the internal energy of a system is not known; what is of interest is the change in total energy when the system undergoes a change. Thus, there is no physical or chemical process in which energy can be created or destroyed, the various types of energy can only be transformed (for example, in the process of electrolysis, electrical energy is transformed into chemical energy).

_____

The change in internal energy of a system when the trasnformation from state A to state B occurs is:

$$\Delta E = E_B - E_A$$

The first law of thermodynamics says that the total energy remains the same when it changes from one state to another; thus, the change in internal energy ΔE will be equal to the difference between the energy q absorbed from the environment (as heat) and the energy W lost as mechanical work:

$$\Delta E = q - W$$

$$dE = dq - dW$$

The first law of thermodynamics can be rephrased as follows: the change in internal energy is equal to the sum of the energies given or taken to the system in the form of mechanical work or heat.

The law of conservation of energy states that although energy can be transformed from one form to another, it can neither be created nor destroyed; in other words, when an amount of one type of energy is produced, an exactly equivalent amount of another type of energy must disappear. Thus, the equivalence between mechanical work and heat is a direct consequence of the law of conservation of energy.

The universal validity of the law of conservation of energy underlies the first law of thermodynamics, which states that the total energy of an isolated system remains constant as long as no changes occur in the system.

Thermochemistry concepts

Heat of reaction

Any chemical reaction is related to a change in the internal energy of the participating substances. Because different substances contain different amounts of energy, the total energy of the products of a chemical reaction may be different from the total energy of the reactants, so the process may be accompanied by the absorption or release of energy in the form of heat.

The process will be exothermic if a reaction takes place with release of heat.

The process will be endothermic if a reaction occur with absorption of heat.

The change in heat that occurs in a chemical reaction is called the heat of reaction.

Standard enthalpy of formation (denoted $\mathbf{\Delta H_f^0}$) represents the change of enthalpy during the formation of one mole of substance from the constituent elements in their standard states. By convention, the standard enthalpy of formation of the elements is considered zero.

The heat of formation of a substance means the increase in caloric content, ΔH, when one mole of substance is formed from the constituent elements. For the exact definition of the heat of formation, the standard states - 25°C temperature and 1 atm pressure - are considered.

The first fundamental law of thermochemistry:

- The amount of heat required to decompose a chemical combination into its component elements is equal to the amount of heat released when this combination is formed from its components.

For example, if 22.3 kcal are required for the formation of one mole of lead sulphide, the decomposition of the same amount of PbS will also release 22.3 kcal.

The second law of thermochemistry:

- The thermal effect of a chemical reaction that occurs at constant pressure or constant volume is the same, regardless whether the chemical reaction occurs in one or many steps.

V.1. CHEMICAL EQUILIBRIUM

In most chemical reactions, the conversion of reactants into reaction products is not total/complete. Thus, when reactants are mixed in stoichiometric amounts, they do not completely transform into reaction products. Reactions in which the reactants do not completely transform into the reaction products and can proceed in both directions are called reversible reactions.

A reversible reaction can be represented as follows:

$$mA + nB \leftrightarrows pC + qD$$
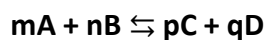
The double arrow indicates that the reaction is reversible - that is, both the forward and reverse reactions occur simultaneously. In discussions of chemical equilibrium, the substances that appear on the left side of the balanced chemical equation are called "reactants" and those on the right side are called "reaction products." In reality, the reaction can go both ways. When A and B react to form C and D at the same rate as C and D react to form A and B, the system is at equilibrium.

Chemical equilibrium exists when two opposite reactions occur simultaneously at the same reaction rate.

Chemical equilibria are dynamic equilibria, that is, molecules are continuously reacting, even though the overall composition of the reaction mixture does not change. In a system at equilibrium, we say that the equilibrium is shifted to the right if there is a greater proportion of compounds C and D than A and B; analogously, the equilibrium is shifted to the left if there is a greater proportion of A and B compared to C and D.

Reactions that occur simultaneously in both directions, so that both reactants and products are present, lead to a final state of no chemical transformation: a chemical equilibrium.

In a chemical reaction, not only its development is important, but also the time required to reach the equilibrium. This problem is especially important in technology; the faster a reaction proceeds, the greater the amount of end products obtained in a given time.

For a general reaction:

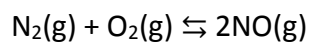**mA + nB ⟷ pC + qD**, the equilibrium constant has the expression:

$$K = \frac{[C]^p \cdot [D]^q}{[A]^m \cdot [B]^n}$$

At equilibrium, the ratio of the product of the concentrations of the final compounds to the product of the concentrations of the initial compounds is constant at a given temperature.

The equilibrium constant K is defined as the product of the equilibrium concentrations (mol/liter) of the reaction products, each raised to the power corresponding to its coefficient in the balanced reaction, divided by the product of the equilibrium concentrations of the reactants, each raised to the power corresponding to its coefficient in the balanced reaction.

The numerical values of the equilibrium constants are determined experimentally.

Examples:

$N_2(g) + O_2(g) \leftrightarrows 2NO(g)$

$$K = \frac{[NO]^2}{[N_2] \cdot [O_2]} = 4.5 \times 10^{-31}$$

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$
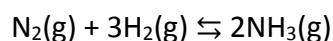
$$K = \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3} = 3.6 \times 10^8$$

The thermodynamic definition of the equilibrium constant involves activities rather than concentrations. The activity of a component of an ideal mixture is the ratio of its concentration or partial pressure to the standard concentration (1 M) or pressure (1 atm).

We can consider the activity of each species as a dimensionless quantity whose numerical value can be determined as follows:

1. For any pure liquid or pure solid, the activity is considered to be equal to 1.

2. For components of ideal solutions, the activity of each component is considered the ratio of its molar concentration to the 1 M standard concentration, so the units cancel.

3. For gases in an ideal mixture, the activity of each component is taken to be the ratio of its partial pressure to a standard pressure of 1 atm, so the units cancel again.

The order of magnitude of the equilibrium constant is a measure of the extent to which the reaction proceeds. For any balanced chemical reaction, the value of the equilibrium constant K is **(1)** constant at the given temperature, **(2)** varies with temperature, **(3**) does not depend on the initial concentrations.

A value of the equilibrium constant K much greater than 1 indicates that the "numerator concentrations" (reaction products) are much greater than the "denominator concentrations" (reactants); it follows that, at equilibrium, most of the reactants have been converted into reaction products.

On the other hand, if the value of the constant K is relatively small, equilibrium is established when most of the reactants remain unreacted and only small amounts of reaction products are formed.

Factors influencing chemical equilibrium

The position of chemical equilibrium can be shifted under the influence of pressure, temperature and concentration.

Pressure variation: if in a gas phase reaction the pressure is increased, the equilibrium shifts to the side where a smaller number of molecules are formed, and vice versa. When both sides of the chemical equation have the same total number of molecules, the change in pressure does not affect the chemical equilibrium.

Temperature variation: when heating a system in equilibrium, the equilibrium moves in the direction of the endothermic reaction; upon cooling, in the direction of the exothermic reaction.

Concentration variation: if the concentration of one of the substances participating in the reaction increases, then the balance shifts in the direction of consumption of that substance.
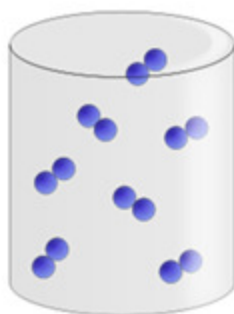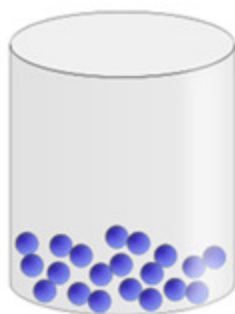
VI. STATES OF AGGREGATION

LEARNING OBJECTIVES

Knowing the main differences between aggregation states
Knowing the concept of phase transformation
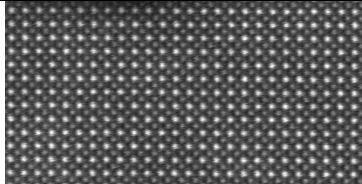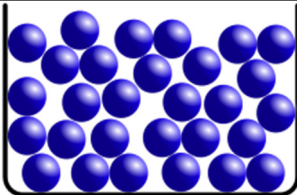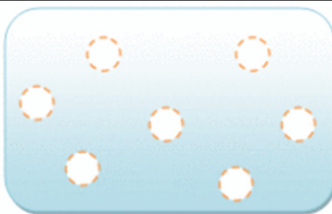Knowledge of the notions of melting, sublimation, evaporation

Gas   Liquid   Solid

States of aggregation

Gases, liquids, and solids are made up of microscopic particles, but the behavior of these particles differs in the three phases.

Structure of crystalline **solid**	The structure of a classical monatomic **liquid**. Atoms have many close neighbors in contact, but they are found in a particular order.	The spaces between **gas** molecules are very large. Molecules can move freely and quickly.

The particles in a:

- Gas: they are separate, without any particular arrangement.
- Liquid: they are close, without any particular arrangement.
- Solid: they are close, arranged in a well-defined pattern.

The following table summarizes the properties of gases, liquids, and solids and identifies the microscopic behavior responsible for each property [51].

Gas	Liquid	Solid
takes the shape and volume of the container; particles can move freely;	it takes the shape of the container part it occupies; particles can move/slide over each other;	retain a fixed volume and shape the particles do not move
compressible;	not easily compressible	not easily compressible
flows easily	flows easily	does not flow easily

VI.1. PHASE DIAGRAMS

If the appropriate temperature and pressure changes are made, any substance can be brought into one of three states of aggregation: gaseous (G), liquid (L) or solid (S). The fourth state of aggregation, plasma, is not characteristic for substances under usual conditions.

Following the dependence of the vapor pressure for a substance as a function of temperature and neglecting the transformations that can occur in the solid state, we obtain the equilibrium diagram of the state of matter transformations. The general shape of the curve is shown in figure 43.
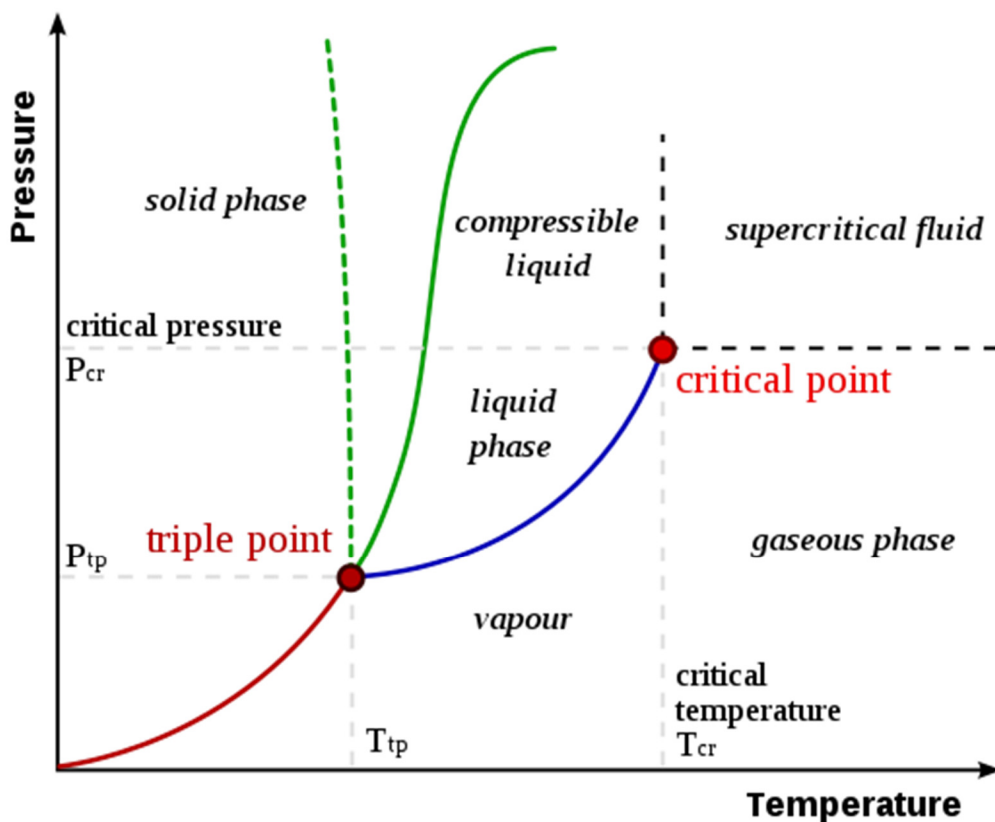

Figure 43. *Phase diagram* [52]

The three curves divide the plan into three areas. Each domain will define the existence of an aggregation state. Thus:
-   any substance is found in a solid state (S) at a sufficiently low temperature, but at a high pressure;

- at high temperature and low pressure, the substance is found in gaseous state of aggregation (G);
- - the liquid state (L) can only be achieved in a reduced range of pressure and temperature.

The curves in the diagram define the coexistence in equilibrium of two states of aggregation, therefore, the conditions of state transformations.

The curve represented in red defines sublimation (S → G) and desublimation (G → S), respectively.

The green curve defines melting (S → L) and solidification (L → S), respectively.

The blue curve defines vaporization (L → G) and condensation (G → L), respectively.

The point where the three curves meet (T) is a characteristic of the substance and is called **the triple point**. For the pressure and temperature corresponding to the triple point, the three states of aggregation of the substance coexist in equilibrium. If we look at the equilibrium diagram of state transformations, we can see that at a lower pressure than the corresponding to the triple point, the substance cannot change to a liquid state, no matter the temperature increase.

The vaporization curve ends at a point called the critical point, which is also a characteristic of the substance. At higher temperatures than the one corresponding to the critical point, the substance cannot be brought into a liquid state, no matter the pressure. It is thus confirmed that the liquid state is an intermediate state between the solid state and the gaseous state, having a strictly delimited domain of existence.

The shape of the equilibrium diagram of state transformations corresponds to most substances. There are a few exceptions, (H_2O, Ge, Bi, etc.) for which the melting curve (T) has a negative slope (dotted line in the diagram). These substances have an abnormal behavior, they reduce their volume in the melting process, having a more rarefied ordered arrangement in the solid state.

Since the composition of substances remains constant in the process of state transformations, it is considered a physical process. Often the statement is not justified because, once the state of aggregation is changed, the nature of the bonds between the particles that form the substance changes.

2. Brief characterization of the gaseous state

All states of aggregation can be characterized by an equation of state, i.e. by a relation between the thermodynamic quantities that define them. To establish the equation of state, it is necessary to develop a mathematical model capable of describing that state of aggregation.

The model that describes the gaseous state is that of an ideal gas:

- the particles that constitute a gas are point-shaped (without volume) and they move freely (there are no interactions between them, so the potential energy is zero) in the entire volume in which the studied system is found.
- the particles enter into an elastic collision both with each other and with the walls of the vessel (so their kinetic energy is conserved and its value depends only on the absolute temperature value).

The homogeneity of a gaseous system is a statistical homogeneity; that is, the probability of occupying a point of the system is the same for all its points and it depends on the degree of particle occupation of the given space.

The defining law for the gaseous state is given by the **Mendeleev-Clapeyron equation**:

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

p = gas pressure (atm)
V = volume (L)
T = absolute temperature (K)
R = the universal gas constant
ν = the number of moles of the substance, which can be determined using the relationship:

$$\nu = \frac{N}{N_A} = \frac{m}{M} = \frac{V_0}{V_{0M}}$$

N = number of particles (atoms, ions, molecules)
N_A = Avogadro number (N_A = 6,023 · 10^{23} particles/mol)
m = the mass of the substance (g)
M = molar mass of the particle with kinetic individuality (g/mol)
V_0 = the volume occupied by the gas (L)
V_{0M} = the volume occupied by one mole of gas under normal conditions (p_0 = 1 atm, T_0 = 273 K); V_{0M} = 22,4 L

3. Brief characterization of the liquid state

There is no model for describing the liquid state. Depending on the temperature, liquids have properties comparable to solids or real gases. Thus, in the vicinity of the melting temperature, liquids have a short-range ordered structure and a binding force between particles comparable to that of the solid state.

Liquids differ from solids by two properties: *fluidity* and *isotropy*.

Fluidity represents the property of liquids to flow, that is, the existence of a translational movement of some ordered fragments of the system, relative to each other. This means that liquids do not have their own shape, but they do have their own volume, so the equation of state for liquids is:

$$V = f(T)$$

This proves that liquids are practically **incompressible**. In principle, with the increase in temperature, the fluidity of the liquid increases (viscosity is the quantitative measure of fluidity; being inversely proportional to fluidity, viscosity decreases). An inverse variation of viscosity with temperature is observed.

Isotropy is the characteristic of a system to have the same value for a property in all directions. Conversely, **anisotropy** shows that the system has different values for a property if its determination was made for different directions. The absence of long-range order in liquids makes the system as a whole statistically homogeneous, so that its behavior is isotropic.

In the vicinity of the critical temperature, the values of the properties of a liquid are comparable to those of the gas that forms from the liquid. The liquid state is intermediate between the solid and gaseous states. This state (liquid) is not characteristic of mineral substances either. Among the elementary substances, only two are liquids: Br_2 and Hg. Among the other substances, under normal conditions, those that have low molecular mass and polar molecules are in the liquid state (HNO_3, H_2SO_4 etc).

4. Brief characterization of the solid state

It is the characteristic state of aggregation for mineral substances. About 95% of known mineral substances are solids.

The equation of state shows that solids are not only incompressible (like liquids) but have their own shape: at a constant temperature, the distance between two points of a solid body is constant.

4.1. Amorphous solids

There are compounds which, although they satisfy the equation of state, are not considered solids because they do not have a fixed melting temperature. They are called amorphous solids. Amorphous solids that satisfy the equation of state for solids represent a thermodynamically metastable state. In the amorphous state there is a higher degree of order than in the liquid state, but it is not a long-range order.

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4.2. Crystalline solids

The crystalline solid is the solid that has an ordered distribution of the constituent particles, whose properties can be described with the help of a model - the model of the ideal crystal. The solid state corresponds to a real physical homogeneity and not statistical as in the case of the gaseous state. In other words, for the solid state, for any point in the system, the occupancy probability can only have values:

P = 1 – point occupied by a particle

and

P = 0 - "empty" (unoccupied) point

The ordered distribution of particles in three-dimensional space constitutes the crystalline lattice of the substance.

The smallest portion of the crystal lattice, which, by translation in the three directions of space forms the lattice, is called **the lattice unit**.

The unit of a crystal lattice can only be a convex, regular polyhedron, with two-by-two parallel faces and the corners occupied by particles of the same type.

Depending on the imposed geometric relationships, there are seven crystallographic systems: cubic, square, rhombic, hexagonal, trigonal, monoclinic and triclinic. All these systems can be obtained by the deformation of two fundamental polyhedra:

- the cube for which the geometric properties are:
    $a = b = c$ and $\alpha = \beta = \gamma = 90^0$

- the hexagonal prism for which the geometric relations are:
    $a = b \neq c$ and $\alpha = \beta = 90^0$ and $\gamma = 120^0$
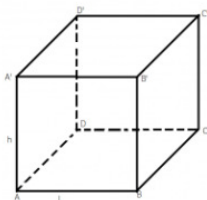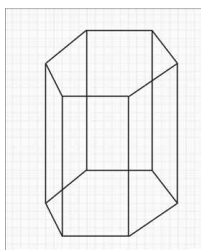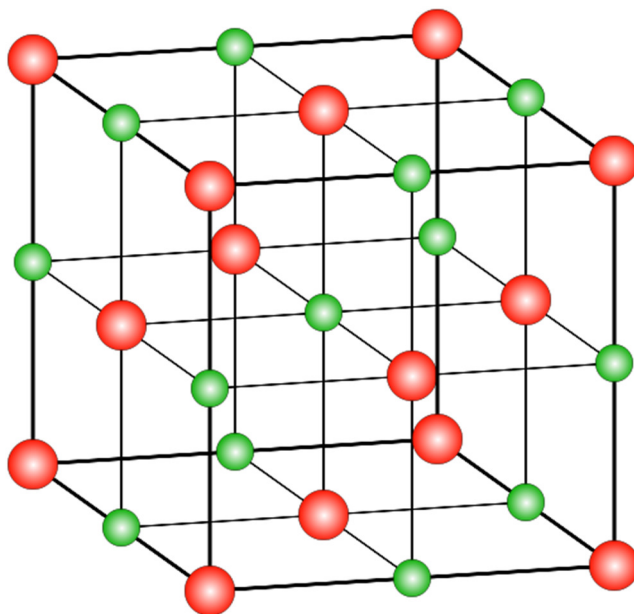

Cube	Hexagonal prism

VII. THE CRYSTALLINE SOLID

LEARNING OBJECTIVES

Description of the metal bond
Knowledge of the notions of conductor, semiconductor
Knowing the types of crystal lattices

VII.1. METALLIC BOND

General properties of the metals

Metals have several unique qualities, such as the ability to conduct electricity and heat, low ionization energy, and low electronegativity (they will donate electrons to form cations). Their physical properties include metallic luster, malleability, and ductility.

Most metals have very compact crystal structures involving either face-centered cubic lattices, face-centered lattices, or hexagonal lattices. Thus, each atom in a metal is usually surrounded by 8 or 12 equivalent neighboring atoms. An important information regarding the nature of chemical bonding in metals is provided by their ability to conduct electricity. Electrons can pass through a metal wire without causing any obvious change in the physical and chemical properties of the metal. Thus, modern theories of metallic bonding assume that the valence electrons are completely delocalized; that is, they occupy molecular orbitals belonging to the metal crystal as a whole. These delocalized electrons are often referred to as "electron gas". The positive metal ions obtained by the loss of valence electrons are found in this electron gas. Each ion is held in place by the attraction exerted by the gas of negatively charged electrons and by the forces of repulsion between the positive ions.
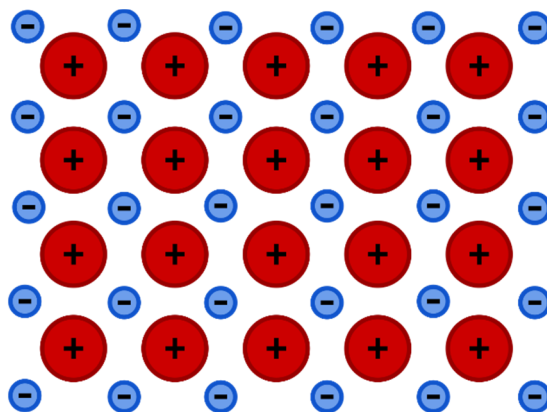
Figure 44. *Metallic bond* [53]

Through the interaction of two atomic orbitals, for example the 3s orbitals of two sodium atoms, two molecular orbitals are obtained, a bonding orbital and an antibonding orbital (similar to the formation of a covalent bond according to the molecular orbital method). If N atomic orbitals interact, N molecular orbitals are formed.

For example, in a single metal crystal containing one mole of sodium atoms, overlapping 6.022×10^{23} 3s atomic orbitals will yield 6.022×10^{23} molecular orbitals. The energy separating the bonding and antibonding molecular orbitals decreases as the overlap between the atomic orbitals decreases.

The interactions between the sodium atoms found in a mole result in a series of closely spaced molecular orbitals (σ_{3s} and σ^*_{3s}). They form an almost continuous band of orbitals that belongs to the crystal as a whole. One mole of Na atoms contributes 6.022×10^{23} valence electrons, so the 6.022×10^{23} molecular orbitals are half occupied.

The ability of sodium metal to conduct electricity is due to the ability of any of the highest-energy electrons in the 3s orbital to move into a vacant orbital of slightly higher energy in the same band when an electric field is applied. The resulting net electron flow is in the direction of the applied electric field.
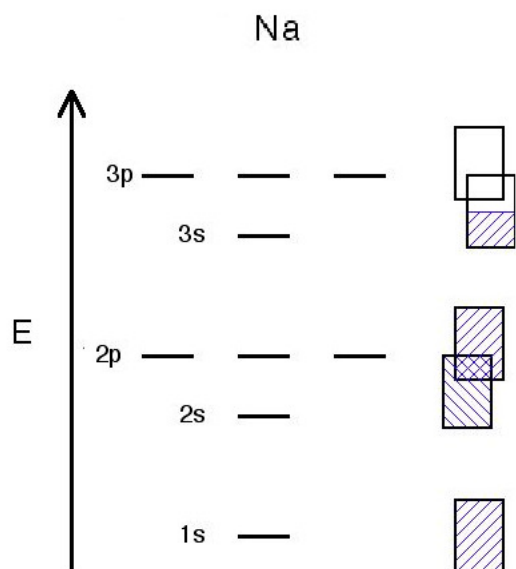

Sodium band structure

The unoccupied band of lowest energy is called the **conduction band** and the band occupied by electrons having the highest energy is called the **valence band**.

VII.2. IONIC STRUCTURES

Most monoatomic ions behave as positively or negatively charged spherical particles, and the attraction exerted on oppositely charged ions is the same in all directions. Consequently, ionic compounds have stable structures (1) when the ions are surrounded by as many oppositely charged ions as possible and (2) when the cations and anions are in contact with each other. Structures are determined by two main factors: the relative sizes of the ions and the ratio of the number of positive to negative ions in the compound.

In simple ionic structures, the anions (which are larger in size than the cations) are arranged in a matrix-like arrangement. Cations usually occupy one of two types of gaps left between anions. The smallest gap is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this gap are arranged at the corners of a tetrahedron, so the gap is called a **tetrahedral gap**. The larger type of gap is found at the center of six anions (three in a single layer and three in an adjacent layer) located at the corners of an octahedron; this is called an **octahedral gap**.

Cubic crystallization system: the basic unit is shaped like a cube. Three types of cubic crystals are known: simple cubic, body-centered cubic, face-centered cubic.
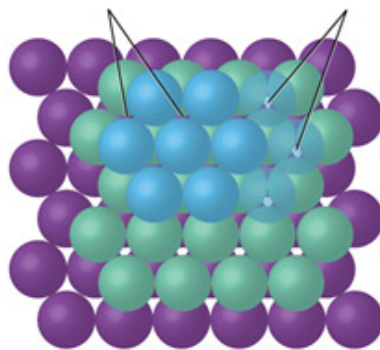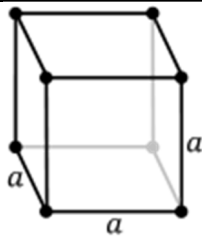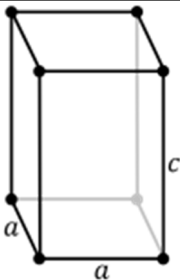

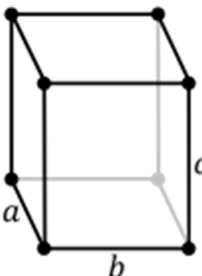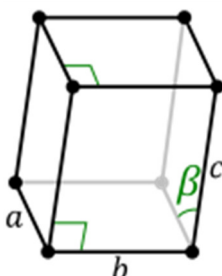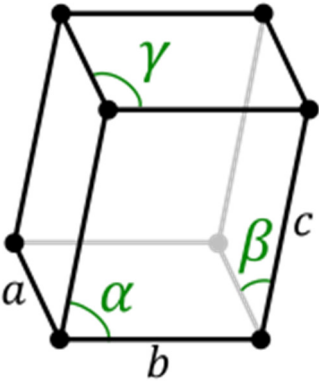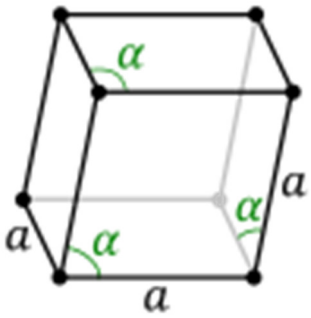| simple cubic [54] | body-centered cubic [55] | face-centered cubic [56] |
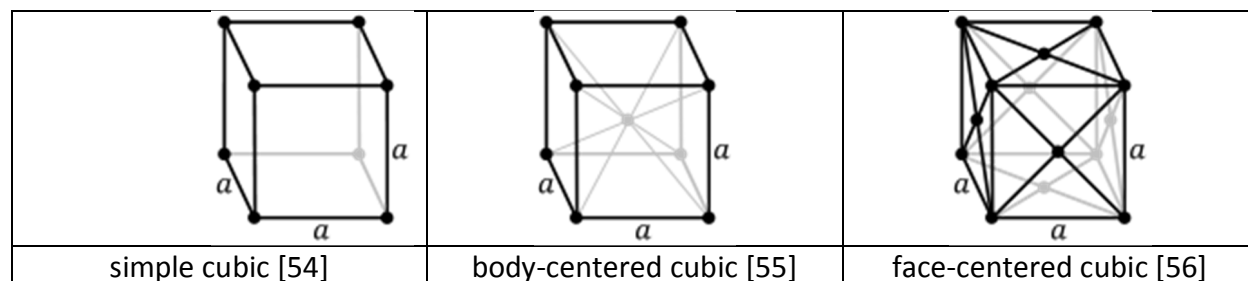
**Figure 45**. *Tetrahedral and octahedral gaps* [57]

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Simple cubic system: the arrangement of atoms corresponds to the corners of the cube. Each atom is then divided equally between eight adjacent cubes, and thus the unit cell contains only one atom in total (1/8×8).

Body-centered cubic system: The arrangement of atoms corresponds to the corners of the cube and the center of the cube. Thus, the unit cell will contain two atoms (1/8 × 8 + 1).

Face-centered cubic system: The arrangement of atoms corresponds to the corners of the cube and the faces of the cube. Thus, the unit cell will contain four atoms (1/8 × 8 + ½ × 6).

The known crystallization systems are: cubic, tetragonal, rhombic, monoclinic, triclinic, rhombohedral, and hexagonal.

Cubic crystal system	Tetragonal crystal system [58]
Rhombic crystal system [59]	Monoclinic crystal system [60]
Triclinic crystal system [61]	Rhombohedral crystal system [62]

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Hexagonal crystal system [63]
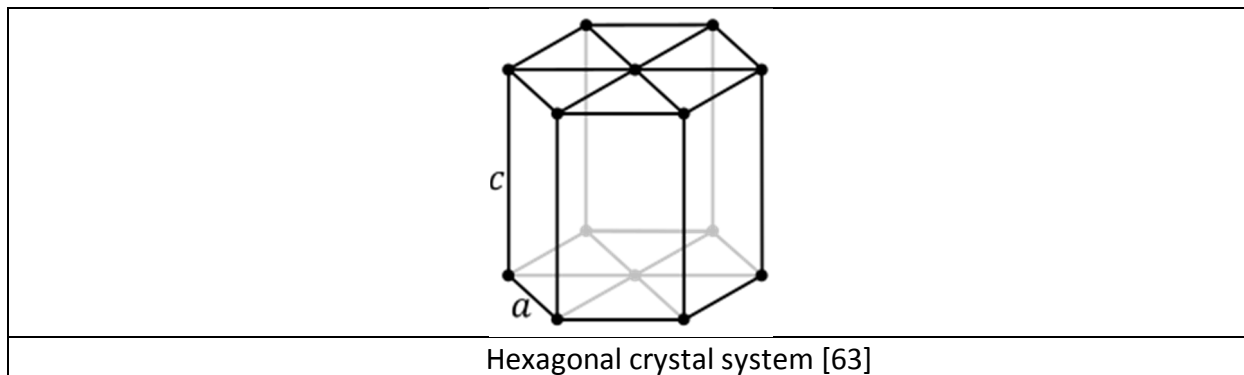
Geometrical characteristics:

System	Sides	Angles
Cubic	a=b=c	$\alpha=\beta=\gamma$
Tetragonal	a=b≠c	$\alpha=\beta=\gamma$
Rhombic	a≠b≠c	$\alpha=\beta=\gamma$
Monoclinic	a≠b≠c	$\alpha=\gamma=90$, $\beta≠90$
Triclinic	a≠b≠c	$\alpha≠\beta≠\gamma$
Rhombohedral	a=b=c	$\alpha=\beta=\gamma≠90$
Hexagonal	a=b≠c	$\alpha=\beta=90$, $\gamma=120$

The notion of solid state of crystalline substances refers to the state characterized by a **certain regularity in the distribution of the atoms or molecules**.

Thus, the crystal can be considered the basic structural element of matter in the solid state. Each solid substance forms crystals with a specific shape, characteristic of that substance. Crystals are classified based on their symmetry. This symmetry depends on certain symmetry elements: the center, planes and axes of symmetry.

Each crystalline substance has its own spatial lattice, characterized by the position of the particles and the distances between them. The smallest portion of a lattice that has all the characteristics of the network structure is called an elementary cell.
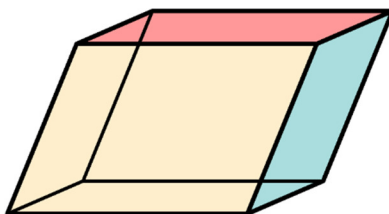

Figure 46. *Elementary cell* [64]

In the case of heteroatom lattices, the ordering of the ions in the lattice takes into account two factors:

- Principle of electroneutrality (the number of positive charges must equal the number of negative charges)

- Radius ratio r_{cation}/r_{anion}

The crystalline lattice AB

a. CsCl lattice ($r_{cation}/r_{anion} \approx 1$) is a simple cubic lattice.

The anions are found in the corners of the cube:

$8 \cdot \frac{1}{8} = 1 \ ion$ (Cl⁻)

The ion of the opposite sign will occupy the center of the cube:

$1 \cdot 1 = 1 \ ion$ (Cs⁺)

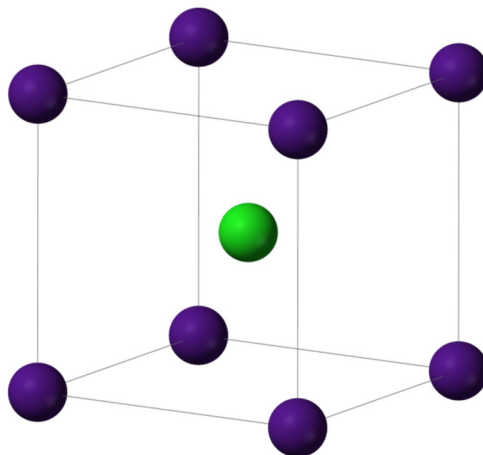**Figure 47**. *Elementary cell of cesium chloride* [65]

b. NaCl lattice (r_{cation}/r_{anion} < 0.7) is a face-centered cubic lattice. Both the anion and the cation of the respective substance can be chosen as a benchmark. Ions are found at the corners and faces of the cube:

Example: cations are located at:

Corners: $8 \cdot \frac{1}{8} = 1$

Faces: $6 \cdot \frac{1}{2} = 3$

In total, there will be 4 cations Na^+. Anions will be distributed in:

Edges: $12 \cdot \frac{1}{4} = 3$

Center: $1 \cdot 1 = 1$

There are four Cl^- anions. The empirical formula is $(NaCl)_4$.
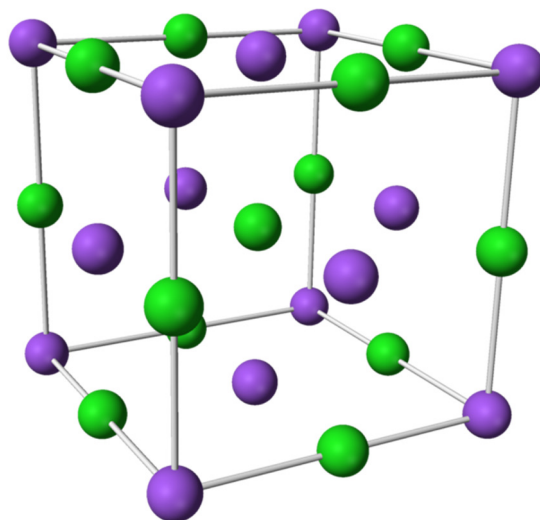
Figure 48. *Elementary cell of sodium chloride* [66]

c. ZnS lattice (rc_{ation}/r_{anion} < 0.414) is a face-centered cubic lattice. Both the anion and the cation of the respective substance can be chosen as a benchmark. Ions are found at the corners and faces of the cube. The four sulfide anions S^{2-} are found:

Corners: $8 \cdot \frac{1}{8} = 1$

Faces: $6 \cdot \frac{1}{2} = 3$

Cations will be found in the tetrahedral gaps of the unit cell:

$4 \cdot 1 = 4$ cations Zn^{2+}

The empirical formula is $(ZnS)_4$.

_____

Figure 49. *Elementary cell of zinc sulfide* [67]

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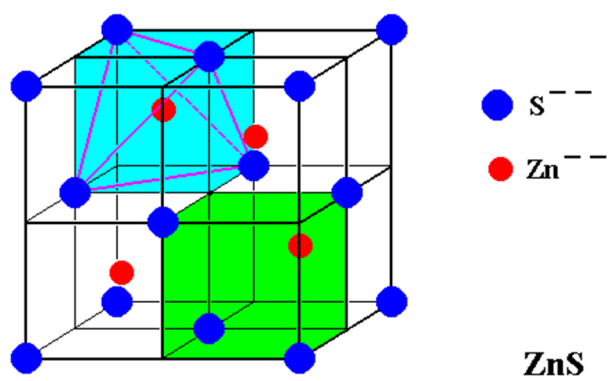1. Raluca Pop, *Chimie anorganică. Note de curs*, Editura V. Babeș, Timișoara, **2019**.

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