University Ferhat ABBAS Setif 1
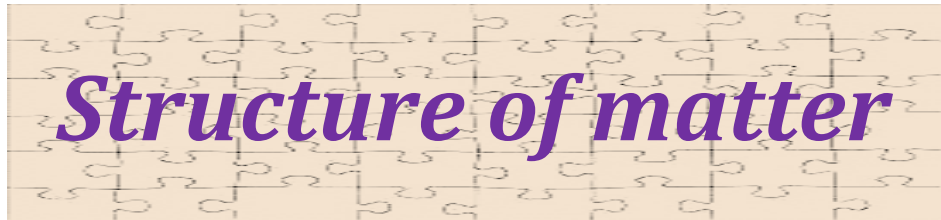
Faculty of Technology

Department of Basic Education in Technology

Course handout

Structure of matter

Realized by: *Dr. GOUISSEM Linda*

2022-2023
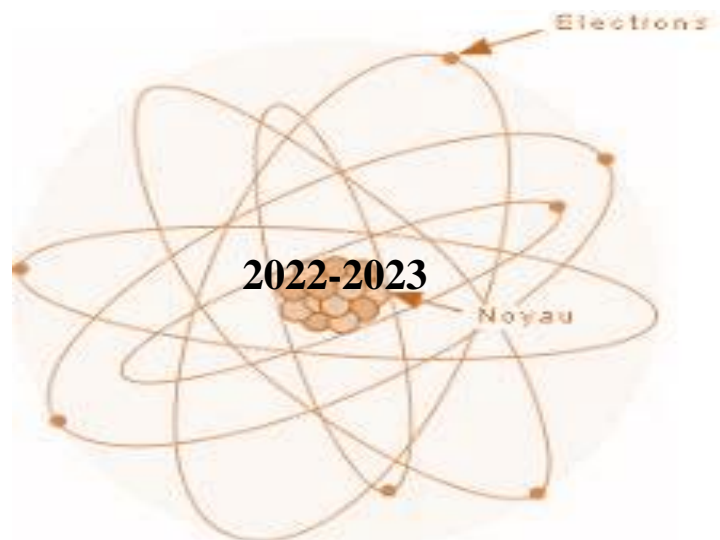
Foreword

This document has been specially designed to meet the needs of first-year engineering students. Its content aims to provide an in-depth presentation of the fundamental concepts revolving around the structure of matter, a captivating branch of general chemistry. Divided into six carefully crafted chapters, this document takes readers on an intellectual journey. It begins by exploring the basic building blocks of the atom (neutrons, protons, electrons) while highlighting the crucial experiments that led to their identification. Gradually, he unveils the subtleties of molecule formation through a diverse palette of chemical bonds, paving the way to a profound understanding of the very genesis of matter.

Table of contents

Chapter I: Fundamental notions

Chapter II:Principal constituents of matter

Chapter IV:Periodic classification of the elements

Chapter V: Chemical bonds

Chapter VI:Radioactivity-nuclear reactions

Chapter I:
Fundamental notions

I-1- State and macroscopic characteristics of states of matter

There are three states of matter: solid, liquid and gas. These three states are distinguished by their compressibility and deformability.

State of matter	Compressibility	Density	Deformability
Solid	Low	High	Low
Liquid	Low	High	High
Gas	High	Low	High

I-2- Change of state of matter

The transition from one state of matter to another is called a change of state. This change is brought about by a change in volume, temperature and/or pressure.
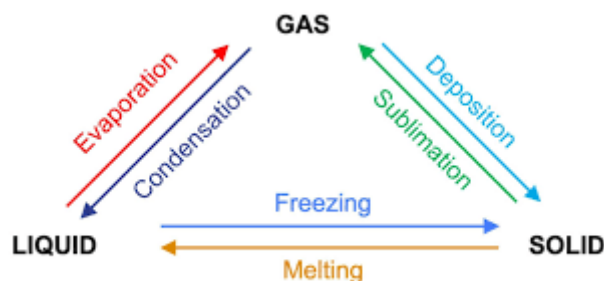
I-3- Different constituents of matter

Matter is made up of elementary particles assembled by more or less strong bonds.

I-3-1- Atom

In chemistry, the atom is the smallest component of matter (from the Greek ATOMOS, which cannot divide). It is the basic element that can combine with others to form matter.

$$ATOM \Rightarrow MOLECULE \Rightarrow MATIER$$

We call:

- Nucleide, a set of identical nuclei (same A, same Z, therefore same N).
  Example: the nuclide $^{12}_{6}C$

- Isotopes, nuclei with the same Z but different A (i.e. different N).

- Isotones, nuclei with the same N, but different A and Z.

- Isobars, nuclei with the same A, but different Z.

1

An atom can gain or lose one or more electrons. It then ceases to be neutral and becomes an ion.

Examples:

♦ The Na^+ ion (one electron lost by the sodium atom $_{11}$Na.

♦ The Br^- ion (one electron gained by the bromine atom $_{35}$Br).

I-3-2- Molecule

A molecule is a basic structure of matter. It is the electrically neutral chemical assembly of at least two atoms, different or not, which can exist in a free state, and which represents the smallest quantity of matter possessing the characteristic properties of the substance in question.

I-3-3- Mole and Avogadro number

The mole, denoted 'n', is a quantity of matter, convenient on a macroscopic scale. It applies to any elementary entity: atoms, particles (electrons, protons, molecules, ions...). Its unit is **mol**.

The Avogadro number, or Avogadro constant noted '$\aleph_A$' is defined as the number of elementary entities in a mole of matter.

By convention, its value corresponds to 12 grams of carbon 12.

$$\aleph_A = 6.022 \text{ x } 10^{23} \text{ mole}^{-1}$$

I-4- Atomic mass unit (a.m.u.)

A special unit has been defined, allowing atomic masses to be expressed simply: the atomic mass unit (a.m.u.). This unit represents one-twelfth of the mass of the nuclide $^{12}_6C$ used as a reference.

1 a.m.u. $= \dfrac{1}{12}$ x m$^{12}_6$C ....(1).

A mole of $^{12}_6C$ contain $\aleph_A$ atoms $\longrightarrow$ 12 g,

One carbon atom $\longrightarrow$ m = x

Hence: m $= \dfrac{12}{\aleph_A}$ ....(2).

Replacing expression (1) in expression (2)

we obtain: 1 u.m.a. $= \dfrac{1}{12}$ x $\dfrac{12}{N_A} = \dfrac{1}{\aleph_A} = \dfrac{1}{6,22 10^{23}}$

> 1 a.m.u. $= 1,6605402 . 10^{-24}$ 10^{-24} g $= 1, 6605402 . 10^{-27}$ Kg

2

I-4-1- Atomic molar mass

The atomic molar mass corresponds to the mass of one mole of atoms, and each atom is made up of electrons and a nucleus made up of nucleons. If an atom's atomic number is 'Z' and its number of nucleons is 'A', then it is made up of: **Z electrons; Z protons; A - Z neutrons.**

The mass of the atom can be considered as the sum of the masses of these particles, but the following approximations can be made:

- The mass of the electrons ($9.109 \cdot 10^{-31}$ kg) is negligible compared to that of the nucleons ($1.67 \cdot 10^{-27}$ kg), especially if we limit ourselves to a precision of 3 significant digits, to the nearest $0.01 \cdot 10^{-27}$ kg.

- Since the mass of a proton and a nucleon are the same, the mass of a nucleon is approximately $1.67 \cdot 10^{-27}$ kg.

We can therefore approximate the mass of an atom to that of the nucleons in its nucleus.

- ❖ Since a ^{12}C atom has a mass of exactly 12 a.m.u., this means that 12 nucleons have a mass of 12 a.m.u., so we can deduce that each nucleon has a mass of 1 a.m.u.. Since most chemical elements exist in the form of several isotopes, a mole of an element's atoms is generally made up of atoms of different masses. The mass of a mole of these atoms is the average mass taking into account the relative natural abundances of the different isotopic nuclides.

Example:

$^{14}_{7}$N : atomic mass 14.00307; abundance 99.636%.

$^{15}_{7}$N : atomic mass 15.00011; abundance 0.364%.

So the atomic mass of nitrogen = 14,00307x 0,99636 + 15,00011 x 0,00364 = 14,0067

The atomic mass of: **N = 14,0067 u.m.a.**

The atomic molar mass of nitrogen is equal to **14.0067 g.** Generally, IL is rounded to **14 g.**

Note:

- ➢ Do not confuse atomic mass and mass number (which is always a whole number);
- ➢ The number of nucleons A (mass number) of an atomic chemical species also corresponds to its molar mass expressed in g/mol.

I-4-2- Molecular mass

Molecular mass, noted 'M', is the sum of the atomic masses of the different atoms making up a molecule.

Example:

- The molecular mass of H_2O is: Mm (H_2O) = 2 M (H) + M (O)

$$Mm (H_2O) = (2 \times 1) + (16) = 18 \text{ g/mol.}$$

- The molecular mass of NaCl is: Mm (NaCl) = M (Na) + M (Cl)

$$Mm (NaCl) = 23 + 35 = 58 \text{ g/mol.}$$

I-4-3- Molar volume

The molar volume (V_{mol}) of a substance is the volume occupied by one mole of that substance. It can be determined for any substance in any phase (gas, liquid, solid).

$$V_{mol} = \frac{V}{n} \quad [\text{m}^3\text{/mol } \textbf{Or} \text{ l/mol}]$$

Where: V is the volume (m^3 **or** l) ;

     n is the quantity of substance (in moles)

For gases: V_{mol} = 22.414 l/mol under standard conditions (T= 25 °C, P =1 atm).

I-5- Weight law conservation of mass, chemical reaction

"Nothing is lost, nothing is created, everything is transformed". (Lavoisier)

In general, an equation can be written to show the balance of a chemical reaction:

$$\text{REAGENTS} \longrightarrow \text{PRODUCTS}$$

This assessment equation obeys two laws:

- ♥ In a chemical reaction, elements are conserved;
- ♥ In a chemical reaction, the mass of reactants lost is equal to the mass of products formed (Lavoisier's Law).

Examples:

$$\textbf{Fe + S} \longrightarrow \textbf{FeS}$$
$$\textbf{2Al + Fe}_2\textbf{ O}_3 \longrightarrow \textbf{2Fe + Al}_2\textbf{ O}_3$$
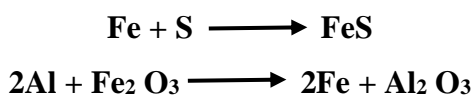
I-6- Qualitative aspects of matter

I-6-1- Pure substances, homogeneous or heterogeneous mixtures

Matter can be found in the form of mixtures (homogeneous or heterogeneous) or pure substance. A pure substance is characterized by its physical (melting temperature, boiling temperature, density, etc.) or chemical properties. There are two categories of pure substance.

```
                          ┌──────────┐
                          │  Matter  │
                          └──────────┘
                    ┌───────┴────────┐
              ┌───────────┐      ┌────────────┐
              │ substance │      │  Compound  │
              └───────────┘      └────────────┘
              ┌─────┴──────┐       ┌─────┴─────┐
```

| Simple: same element types (Cl_2, O_2, H_2, Fe) | Composite: several elements types (H_2O, $FeCl_2$, HCl, S_2O_4) |

| Homogenous: a single phase (water + alcohol) | Heterogeneous: two phases (water + oil) |
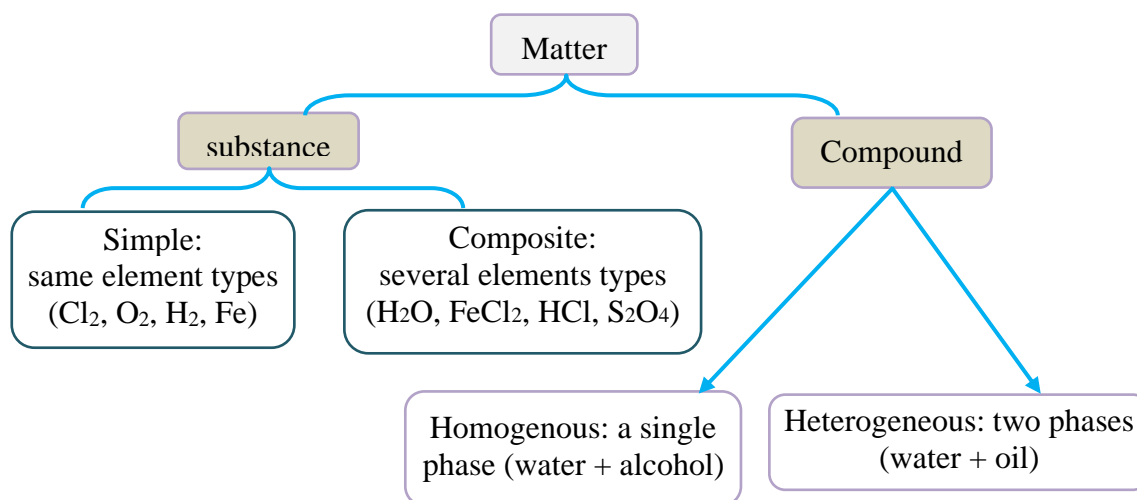
I-6-2- Solutions

A solution is a homogeneous mixture of two or more pure chemical species (without any chemical reaction). It is made up of: a solvent and one or more solutes. The solvent: this is a dispersing medium; it is the liquid in which the solution is made. It is usually the substance found in greatest quantity.

- ✓ **The solute:** this is the dissolved (dispersed) body; it can be a solid (sugar, salt), a liquid (HCl) or a gas (O_2, N_2).
- ✓ **A solution:** is called aqueous when the solvent is water.
- ✓ Dilution involves increasing the ratio of solvent/solute. The solution is made less concentrated than the initial solution by adding solvent. The initial solution is called the **mother solution** and the diluted solution is called the **daughter solution**.

During dilution, the quantity of dissolved chemical species does not vary:

Therefore: $n_{mother} = n_{daughter}$ conservation of mass

Now: $n_{mother} = C_0 . V_0$ and $n_{daughter} = C_1 . V_1$

Hence :

$$C_0 . V_0 = C_1 . V_1$$

 ✓ Saturation involves increasing the solute/solvent ratio to the solubility limit.

I-7- Quantitative aspects of matter

I-7-1- Number of moles

The mole number, noted 'n' is the quotient of the mass of substance and its molar mass.

$$n = \frac{m}{M} \quad [mol]$$

Where: m is the mass of the solute;

M is the molar mass of the solute.

I-7-2- Molar concentration (Molarity)

Molar concentration or molarity (C_M or M): this is the quantity of material dissolved in one liter of solution.

$$C_M = \frac{n}{Vsol} \quad [mol/l \ Or \ M]$$

I-7-3- Molar concentration (Molality)

Molar concentration or molality (C_{molal}) expresses the quantity of solute contained in one kilogram of solvent.

$$C_{molal} = \frac{n}{m \ (solv.Kg)} \quad [mol/Kg]$$

I-7-4- Weight or mass concentration

The weight (mass) concentration (C_m) is the number of grams dissolved in one liter of solution.

$$C_m = \frac{m}{Vsol} \quad [g/l]$$

I-7-5- Weight or mass fraction

The weight or mass fraction 'w_i' of component 'i' is the ratio of the mass mi of this component to the total mass of the mixture:

$$W_i = \frac{m_i}{\Sigma m_i}$$

Note: $\sum_i^n w_i = 1$

I-7-6- Molar fraction

The mole fraction 'χ_i' of component 'i' is the ratio of the number of moles 'n_i' of this component to the total number of moles in the mixture.

$$\chi_i = \frac{n_i}{\Sigma n_i}$$

Note: $\sum_{i}^{n} \chi i = 1$

I-7-7- Normal concentration (Normality)

Normal concentration or normality 'N' is the number of gram equivalents of an acid, base, reducing agent or oxidizing agent contained in one liter of solution.

$$N = \frac{number\ of\ gram\ equivalents}{1\ littr\ of\ solution} \quad ; \qquad N = \frac{m}{Meq\ .V}$$

Where: Meq: equivalent mass;

The relationship between normality and molarity is as follows:

$$N = C_M\ .\ Z\ \ [N]\ Or\ [eq.gr/l]$$

+ In the case of an acid: Z is the number of H^+ protons involved;

Example: HCl (Z=1); H_2SO_4 (Z=2); H_3PO_4 (Z=3).

+ In the case of a base: Z is the number of OH^- ions involved;

Example: NaOH (Z=1); $Ca(OH)_2$ (Z=2).

+ In the case of salts: Z is the number of metal cations multiplied by the valency of the metal.

Example: Na_2SO_4 (Z=2 × (+1) =2).

+ In the case of redox reactions, Z is the number of electrons given up or captured.

Example: $KMnO_4 + 5e^- \longrightarrow Mn^{2+}$ (Z=5),

I-7-8- Volumetric mass and density

I-7-8-1- Volumetric mass

The Volumetric mass (ρ) of a substance is the ratio of its mass to its volume.

$$\rho_i = \frac{m_i}{V_i}\ \ [\frac{unité\ de\ masse}{unité\ de\ volume}]$$

I-7-8-2- Density

Density is the ratio between the density of a substance and the density of a comparable substance.

$$d = \frac{\rho_i}{\rho_0}$$

Where: ρ_i is the density of the substance;

ρ_0 is the density of the comparison substance.

♠ For gases, the comparison substance is air;

$$d = \frac{M}{29}$$

♠ For liquids and solids, the comparison substance is water: $\boldsymbol{\rho_0 = 1g/cm^3}$.

International system units (SI)

Physical quantities	Symbol	Unit	Symbol
Mass	M	kilogram	Kg
Length	L	Meter	M
Time	T	second	S
temperature	T	degree Kelvin	K
amount of substance	N	Mole	Mol
electric current	I	ampere	A

I-8- Law of dilute solutions: Raoul's law

his law relates the ideality of a solution in equilibrium to its vapour phase, which is itself in a condition of ideality: in an ideal solution, the vapour pressure of each component is proportional to its mole fraction.

$$P_i = \chi_i \times P_t$$

With: P_i is the partial pressure;

P_T is total pressure.

Chapter II:

Principal constituents of matter

Introduction

In 1831, Faraday established the principles of magnetic induction (creation of an electric current in a conductor placed in a magnetic field). He coined the terms electrode, electrolyte, anode, cathode and ion.

Like the discovery of induction, Faraday's name is attached to the "laws of electrolysis". Faraday established the quantitative laws of the chemical action of electric current. He is the author of the discipline: cathode (current output electrode), anode (current input electrode), ion, particle that moves towards the anode (anion) or cathode (cation). He measured the intensity of an electric current by inventing the voltameter, an electrolyze whose electrodes are capped with graduated gas tubes. His work advanced the notions of the atom and atomic weight, later put forward by other researchers. In recognition of this, the unit representing the charge of a "mole" of electrons was given the name "Faraday".

II-1- Faraday experiment

Faraday's law states that the amount of substance released during electrolysis at an electrode is proportional to time and electric current (equivalent to charge). It can be represented as follows:

$$m = \frac{Q \cdot M}{F \cdot Z}$$

In the simple case of constant-current electrolysis, Q = I.t ;

So :

$$m = \frac{M \cdot I \cdot t}{F \cdot Z}$$

Where: m is the mass of the substance released at the electrode in grams ;

Q is the total electric charge passed through the substance ;

I is the intensity of the electric current;

F is Faraday's constant ($F = 96485$ C mol^{-1});

M: the molar mass of the substance;

Z: the valence of the substance.

II-2- Constituents of matter

The term matter refers to everything that makes up the objects around us, everything that has mass and volume.

Matter is made up of elementary particles called atoms.

The atom has a more complex structure, consisting of a nucleus and electrons. Some important dates:

- 1881: Discovery of the electron (J. J. Thompson, cathode rays).
- 1908: Rutherford experiment on particle-matter interaction, which led to the proposal of the planetary model of the atom (1911).
- Bohr model (1913).
- Schrödinger model (1930).

<div align="center">

Different characteristics of an atom

Electron charge	$q_e = -1{,}6022.10^{-19}$ C
Electron mass	$m_e = 9{,}1095.10^{-31}$ kg
Proton charge	$q_p = 1{,}6022.10^{-19}$ C
Proton mass	$m_p = 1{,}6726.10^{-27}$ kg.
Neutron charge	$q_n = 0$ C
Mass of neutron	$m_n = 1{,}6749.10^{-27}$ kg.

</div>

II-2-1- Electrons

The electrons evolve around the nucleus, in a very large volume compared to the volume of the nucleus.

II-2-1-1- Crooks experiment

The tube is filled with a low-pressure gas. A high voltage is applied between the cathode and the anode. At the cathode, this voltage gives rise to a beam of electrons that travel in a straight line, as long as they don't collide with any gas atoms. On the right, a cross-shaped piece of metal partially blocks this flow of electrons, creating a shadow at the right end. The remaining electrons strike the bottom of the tube, making it partially luminescent. In the bend below the tube, the gas is illuminated by the deflected electrons collected by the anode.
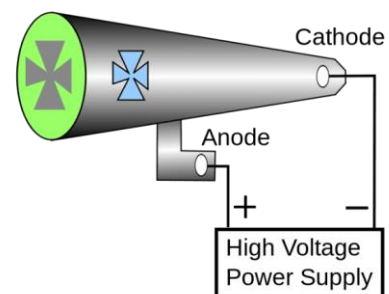
Experiments with Crooks tubes have demonstrated with certainty the existence of the electron.

II-2-1-2- J. J. Thomson experiment

The aim of this experiment is to determine the electron's 'e/m' ratio. The experiment consists in studying the trajectory of a thermionically emitted electron beam with velocity v in a tube with an adjustable electric and magnetic field.

The electron's trajectory is bent towards the P1 plate due to the effect of the electrostatic force. We deduce that the direction of this force is towards plate P1.
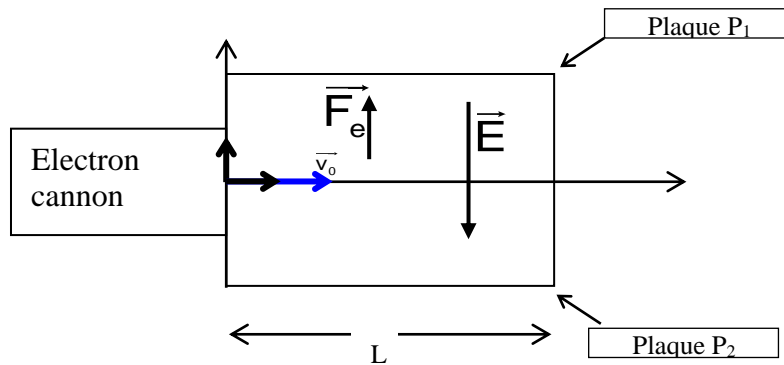

It is stated that the electric field $\vec{E}$ is perpendicular to the two plates and we know that:

$$\overrightarrow{F_e} = -\, e.\, \vec{E}$$

Thus, the direction of the field $\vec{E}$ is opposite to that of the force $\overrightarrow{F_e}$.

We apply Newton's second law to the electron system.

$$\overrightarrow{F_e} = m_e \; x \; \frac{dV}{dt} = m_e .\, \vec{a}$$

$$\left. \begin{array}{c} \\ \\ \overrightarrow{F_e} = -\, e.\, \vec{E} \end{array} \right\} \Longrightarrow \vec{a} = \frac{-\, e.\vec{E}}{m_e}$$

By projection along the axes of the reference frame, we obtain: $\vec{a} \begin{cases} a_x = 0 \\ a_y = \frac{e.E}{m} \end{cases}$

Since: $a = \dfrac{dV}{dt}$; the antiderivative of this expression leads to: $\vec{v} \begin{cases} v_x = 0 + C_1 \\ v_y = \frac{e.E}{m_e}.t + C_2 \end{cases}$

Where: C_1 and C_2 are integration constants that depend on the initial conditions.

At : t = 0; we have: $\overrightarrow{v_0} \begin{cases} v_{0x} = v_0 \\ v_{0y} = 0 \end{cases}$, we deduce that : $C_1 = v_0$ and $C_2 = 0$.

So: $\vec{v} \begin{cases} v_x = v_0 \\ v_y = \dfrac{e.E}{m_e}.t \end{cases}$ When we integrate a second time, we arrive at:

$$\begin{cases} x = v_0 . t + C_3 \\ \\ y = \dfrac{e.E}{2.me} . t^2 + C_4 \end{cases}$$ At: t = 0, we have: $\begin{cases} x_0 = C_3 = 0 \\ \\ y_0 = C_4 = 0 \end{cases}$ So: $\begin{cases} x = \overrightarrow{v_0} . t \dots\dots(1) \\ \\ y = \dfrac{e.E}{2.me} . t^2 \dots\dots(2) \end{cases}$

From equation (1), we have at: $t = \dfrac{x}{v_0}$ which we transfer to equation (2). The result is:

$$y = \frac{e.E}{2.m_e} \cdot \frac{x^2}{v_0^2}$$

When the electron travels the length 'L', we can write

$$\boxed{y = \frac{e.E}{2.m_e} \cdot \frac{l^2}{v_0^2}} \implies \boxed{\frac{e}{m_e} = \frac{2.y.v_0^2}{E.l^2}}$$

II- 2-1-3- Millikan experiment

The aim of Millikan's experiment is to measure the electric charge 'q' of an oil droplet and thus deduce the value of the elementary electric charge 'e'.

The principle of the experiment is as follows: a very small, electrically-charged droplet of oil is subjected to the force of gravity, which causes it to fall. If this drop occurs in air, it is also subject to other, more or less negligible forces.
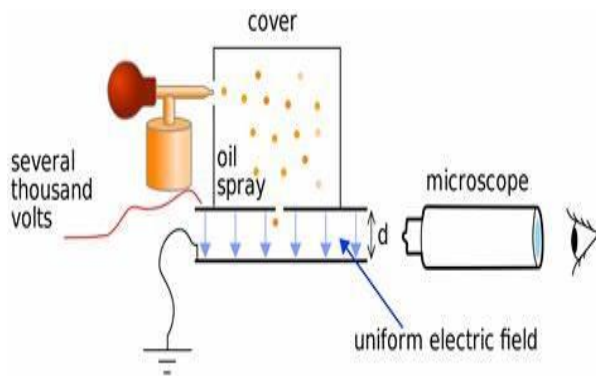
If the fall takes place in an electric field.

By varying the value of this field, it is possible to create a force on the droplet that is sufficient to compensate for the gravitational force and stop or slow down the fall.

➢ **Vertical droplet fall**

The droplet has uniform rectilinear motion. According to Newton's first law and neglecting Archimedes' thrust, the forces exerted on the droplet are compensated by the friction force 'F_t' and the droplet's weight 'P' :

$\vec{P} + \vec{F}_t = \vec{0}$; by projection, we get:
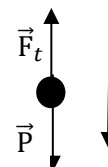
$$P - F_t = 0 \implies P = F_t \implies m.g = 6.\pi.\eta.r.v \ \ldots(1)$$

Where: m is the mass of the droplet ;

       r is the radius of the droplet ;

      g is the acceleration of gravity;

      η is the coefficient of viscosity of air;

      v: droplet speed.

On the other hand, we have the density 'ρ' of the droplet, which is equal to:

$$\left.\begin{array}{l} \rho = \dfrac{m}{V} \\[2em] V = \dfrac{4}{3}\pi.r^3 \end{array}\right\} \implies m = \rho . V = \rho . \dfrac{4}{3}\pi.r^3 \ldots(2) \qquad \text{(V is the volume of the droplet)}$$

Replacing (2) in (1) gives :

$$\rho.\dfrac{4}{3}\pi.r^3.g = 6.\pi.\eta.r.v \implies \rho.\dfrac{2}{3}.r^2.g = 3.\eta.v$$

So: $\qquad \boxed{r = \sqrt{\dfrac{9.\eta.v}{2.\rho.g}}}$

> ➢ **Droplet ascent**

In a simple model, an oil droplet is subjected to the following forces:

- ▪ Its weight: $\vec{P} = m.\vec{g} = 4/3.\pi.r^3.\rho.\vec{g}$
- ▪ Friction force: $\vec{F}_t = 6\pi\eta r\vec{v}$
- ▪ Electrical power: $\vec{F}_e = q.\vec{E}$.
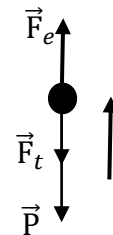
The movement of the droplet is upward we can write :

$$\vec{P} + \vec{F}_t + \vec{F}_t = m.\vec{a} \ ; \text{ by projecting this equation we obtain:}$$

$$-P - F_t + F_e = 0 \implies -4/3\,\pi\,r^3\rho\,g - 6\,\pi\,\eta\,r\,v + q\,E = 0$$

$$\boxed{q = \dfrac{\frac{2}{3}\pi\,r^3\,\rho\,g + 3\,\pi\,\eta\,r\,v}{E}}$$

Millikan concluded that the electrical charges he observed were multiples of an elementary charge, 'e', the charge of the electron, with a value of $1{,}602.10^{-19}$ Coulomb. This

value subsequently enabled him to determine other physical constants, including Avogadro's number and the mass of the hydrogen atom.

Knowing the value of **'e'** and that of $\frac{e}{m}$, we can then deduce the value of 'm' the mass of the electron, where it is equal to : $9.108.10^{-31}$ kg.

## II-2-2- Proton: Goldstein experiment

A cathode pierced with a channel is placed in a discharge tube, and the radiation is highlighted on the fluorescent screen: these are the channel rays.

It has been shown that these channel rays are made up of positive particles. These are the positive ions obtained by stripping electrons from the molecules of the gas contained in the enclosure.
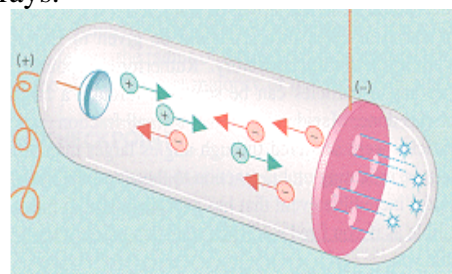
The positive ions, attracted by the cathode and given sufficient kinetic energy, pass through the channel and strike the fluorescent screen. This demonstrates the existence of the positively charged proton.

The number of protons is represented by the atomic number 'Z'.

II-2-3- Neutron: Chadwick experiment

The elements bore 'B' and beryllium 'Be' were bombarded with an **α** particle (the He nucleus). These elements, particularly Be, emitted a highly penetrating form of radiation, much more energetic than **γ** rays.

The energy of the radiation emitted by 'Be' was measured, as were the energies (and therefore speeds) of the protons coming from the kerosene. Applying the laws of conservation of energy and momentum, it was shown that the particles emitted by the 'Be' are neutral particles with roughly the same mass as the proton. The neutron is discovered.
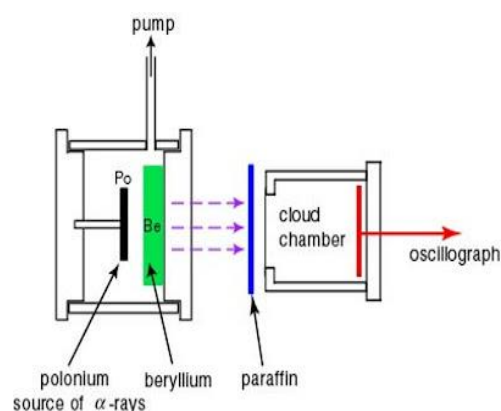
The neutron is a particle with zero electric charge. Neutrons are present in the nucleus, bound to protons by the strong interaction.

The process involved in the experiment was explained as:

$$\ce{^{4}_{2}He + ^{9}_{4}Be -> ^{12}_{6}C + ^{1}_{0}n}$$
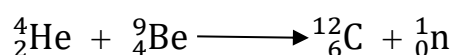
II-3- Rutherford's planetary method

The experiment is performed in a vacuum. Radioactive material (Ra) emitting 'α' particles (He^{2+}), is placed in a lead (Pb) box with a small hole, the 'α' particle beam passes through this hole and is directed towards a very thin gold foil (6000 Å). It was found that:

o   Most particles pass through the gold foil without being deflected or damaging it;
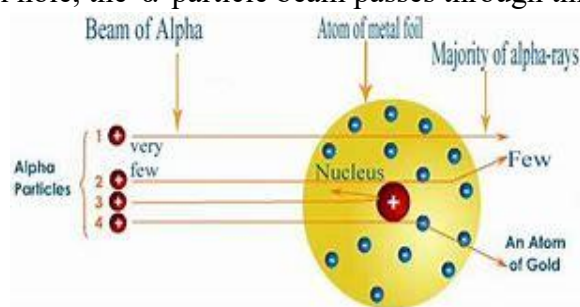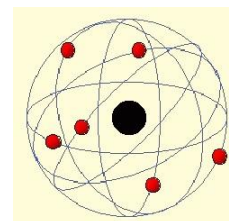
o   Some particles are slightly deflected and others are thrown back.

Rutherford concluded that the atom is not solid. The atom is made up of a positively-charged nucleus, which contains the majority of the atom's mass, and electrons, which rotate around it.

The size of the atom's radius is of the order of 10^{-10} m, (this differs from one atom to another), and that of the nucleus of the order of 10^{-15} m. The ratio between the size of the atom and the size of the nucleus is of the order of 105. So the radius of the atom is 100,000 times greater than the radius of the nucleus, which means that: the atom is essentially made up of vacuum.

II- 4- Presentation and characterization of the atom

An atom is characterized by its 'Z' and 'N' values. A pair of these two values defines a nuclide. A nuclide 'X' is identified by the following symbolism:

$$\begin{array}{l} \text{nombre de masse} \quad A \\ \text{nombre atomique} \quad Z \end{array} X$$

Where: X is the symbol of the element in question;
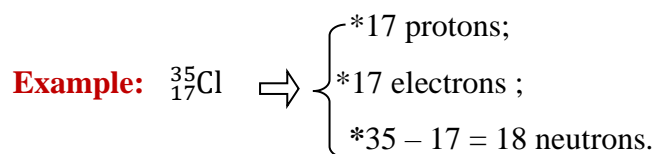
A is the mass number;

Z is the atomic number.

We have: **A = Z + N**

Where: N is the number of neutrons;

An atom is electrically neutral overall: the nucleus containing 'Z' protons (positive charge) is surrounded by 'Z' electrons (negative charge).

Example: $^{35}_{17}\text{Cl}$ $\Rightarrow$
$\begin{cases} \text{*17 protons;} \\ \text{*17 electrons ;} \\ \text{*35 – 17 = 18 neutrons.} \end{cases}$

II-5- Isotopies and relative abundance of different isotopes

II-5-1- Isotopes

An isotope is a simple substance with the same atomic number 'Z' as another, but a different atomic mass 'A'.

The differences between isotopes of the same element 'X' are due to the difference in the constitution of the nucleus: it's the number of neutrons 'N' that differs from one isotope of one element to another.

Examples:

* Carbon isotopes: $^{12}_{6}\text{C}$; $^{13}_{6}\text{C}$; $^{14}_{6}\text{C}$.

♦ Oxygen isotopes : $^{16}_{8}\text{O}$; $^{17}_{8}\text{O}$; $^{18}_{8}\text{O}$.

• Chlorine (Z = 17) has 9 isotopes (A = 32 to 40). The two mains (most abundant) are $^{35}_{17}\text{Cl}$ and $^{37}_{17}\text{Cl}$. Three isotopes occur naturally (isotopes 35, 36 and 37), including radioactive $^{35}_{17}\text{Cl}$. The others are artificial.

Isotopes of the same element have identical chemical properties, as they have the same number of electrons. However, the nuclei of isotopes of the same element do not contain the same number of neutrons. The proportion of neutrons in a nucleus can make it unstable, and therefore radioactive. The ratio of stable to unstable isotopes therefore varies over time. This variation is the basis of dating methods (the best-known is carbon-14 dating).

II-5-2- Relative abundance

Relative abundance is the percentage by number of atoms, for a given element, of each isotope in relation to all (natural) isotopes.

II-6- Isotope separation and atomic mass determination

* Mass spectrometry (Bainbridge spectrograph)

The discovery of isotopes results from the analysis of channel rays using the electrical and magnetic deflection method. Electric and magnetic fields are placed in such a way that ions of the same $\frac{e}{m}$ values are focused on a short line, whatever their speed
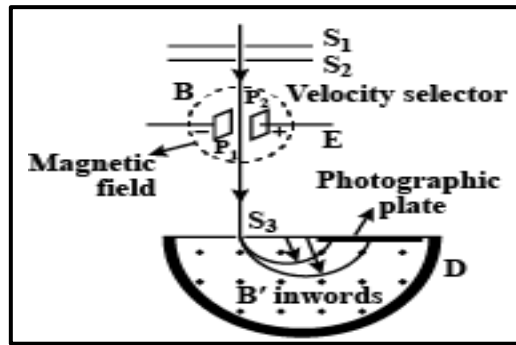
- ♠ The particle is subjected to a magnetic force: $\vec{F}_{mag} = q.v.\vec{B}$
- ♠ Electric power: $\vec{F_e} = q.\vec{E}$

At the exit of the melt, we have : $F_{mag} = F_e \Rightarrow q.v.B = q.E$; So : $v = \frac{E}{B}$ …..(1)

Due to the selector, all particles have a velocity 'v'.

The ions are deflected in a semicircle at constant speed in a uniform circular motion, resulting in a centrifugal force 'Fc' that is balanced by the magnetic force.

With: $Fc = m . \frac{v^2}{R}$;

Where: m is the mass of the isotope;

R is the radius of the semicircle formed by the isotope's trajectory.

Since: $F_{mag} = Fc => q.v.B = m . \frac{v^2}{R} \Rightarrow R = \frac{m.v}{q.B}$ ….. (2)

And by replacing equation (1) in equation (2) ;

We obtain: $R = \frac{m.E}{q.B^2}$;

- # So, for isotope 1: $R_1 = \frac{m_1.E}{q.B^2}$;

- # For isotope 1 : $R_2 = \frac{m_2.E}{q.B^2}$; with: $m_2 > m_1$

So, particles with the same charge but different mass movements move in a circle with a different radius. As a result, they collide with the detection plate at different points. With a distance 'd', between the point of impact and the opening of the speed selector.

With: $d = 2(R_2 - R_1)$;

We can then write: $d = 2 (\frac{m_2.E}{q.B^2} - \frac{m_1.E}{q.B^2}) = 2\frac{E}{q.B^2}(m_2 - m_1)$;

17

We have: $m_2 - m_1 = \dfrac{q..d.B^2}{2.E}$ (by multiplying by N_A) ; $(m_2 - m_1).N_A = \dfrac{q.d.B^2}{2.E} . N_A$

At the end, we obtain:

$$M_2 - M_1 = \frac{q.d.B^2}{2.E} . N_A$$

Where: $M = m . N_A$; ($\mathbf{N_A}$: Avogadro number)

* Determination of average mass

The mass of a mole of these atoms is the average mass, taking into account the relative

natural abundances of the various isotopic nuclides.

$$M_{moy} = \frac{\sum M_i . \chi_i}{100}$$

Where: M_{moy}: average mass of the element ;

M_i: Atomic mass of the isotope ;

χ_i : Percentage of the isotope; $(\sum \chi_i = 1)$.

Example:

Silver has two isotopes, ^{107}Ag with a relative abundance of 51.8% and 109Ag with a relative abundance of 48.2% . Calculate the average mass of silver.

$M_{moy} = \dfrac{\sum M_i . \chi_i}{100} = \dfrac{107 .51{,}8 + 109 .48{,}2}{100} = 107{,}96$

The average mass of silver is 108 u.m.a.

II-7- Binding and cohesive energy of the nucleus

II-7-1- Binding energy

A system at rest has an energy due to its mass, called mass energy. It is defined by :

$$E_L = m . C^2$$

Where: E_L is the binding energy (J) ;

m is the mass (kg) ;

C is the speed of light in a vacuum (m.s^{-1}); $C = 3.0.10^8$ m.s^{-1}

When the mass of a system varies, so does its energy. Thus, we have:

$$\Delta E_l = \Delta m . C^2$$

So, if the mass of a system decreases, its energy decreases and the system supplies energy to the external environment.

Mass defect

By measuring the mass of nuclei at rest and those of nucleons, scientists have discovered that the mass of a nucleus is always less than the sum of the masses of the nucleons that make it up. This difference in mass is called the mass defect 'Δm'. For an element $_Z^A X$, the mass defect is calculated as follows:

$$\Delta m = Z \cdot m_P + (A\text{-}Z) \cdot m_N - m_{noyau}$$

Example :

Calculating the binding energy of a Helium nucleus ($_2^4 H_e$) :

Species	proton	neutron	nucleus
mass (a.m.u)	1,0076	1,0096	4,0015

1- Calculation of mass default :

$\Delta m = Z \cdot m_P + (A\text{-}Z) \cdot m_N - m_{noyau}$

$\Delta m = 2 \cdot 1,0076 + (4\text{-}2) \cdot 1,0096 - 4,0015 = 0,0329$ a.m.u.

Knowing that : 1 a.m.u $\longrightarrow$ 1,66. 10^{-27} kg ;

So : 0,0329 u.m.a. $\longrightarrow$ 5,4614 10^{-29} kg

$\Delta m = 5,4614 \ 10^{-29}$ kg

2- Calculation of binding energy (in joules) :

$\Delta E_l = \Delta m \cdot C^2 = 5,4614.10^{-29} \cdot (3.10^8)^2$

$\Delta E_l = 4,9153. \ 10^{-12}$ J

3- Calculation of binding energy (in calories):

Knowing that: 1 calorie $\longrightarrow$ 4,18 J ;

So: 1,176. 10^{-12} calorie $\longleftarrow$ 4,9153. 10^{-12} J

$\Delta E_l = 1,176. \ 10^{-12}$ calorie

4- Calculating the binding energy (in electronvolts):

Knowing that: $1 \, eV \longrightarrow 1,6. \, 10^{-19} \, J$;

So: $3,072. \, 10^7 \, eV \longleftarrow 4,9153. \, 10^{-12} \, J$

$$\Delta E_l = 3,072. \, 10^7 \, eV$$

5- Calculation of binding energy (in mega-electronvolts)

Knowing that : $1 \, eV \longrightarrow 10^{-6} \, MeV$;

So: $3,072. \, 10^7 \, eV \longleftarrow 30,72 \, MeV$
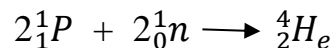
$$\Delta E_l = 30,72 \, MeV$$

* Binding energy per nucleon

Binding energy per nucleon is equal to the binding energy of the nucleus divided by the number of nucleons in the nucleus:

$$\Delta E \, /nucléon = \frac{-E_l}{A} = \frac{\Delta E}{A}$$

II-7-2- Nucleus cohesion energy

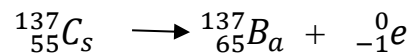Consider the formation of a helium nucleus from nucleons according to the following reaction:

$$2{}_1^1 P \ + \ 2{}_0^1 n \longrightarrow {}_2^4 H_e$$

The reaction is accompanied by a loss of mass 'Δm' which is transformed into energy 'ΔE'

$\Delta E = - E_l = \Delta m.C^2$; with $\Delta m = \sum m_{produits} - \sum m_{réactifs}$

Example:

Consider the following reaction:

$$ {}_{55}^{137} C_s \longrightarrow {}_{65}^{137} B_a \ + \ {}_{-1}^{0} e $$

Species	${}_{55}^{137} C_s$	${}_{65}^{137} B_a$	${}_{-1}^{0} e$
mass (a.m.u.)	136,876 92	136,875 11	$5,485 \, 80.10^{-4}$

The change in mass 'Δm' during the decay of a ${}_{55}^{137} C_s$ nucleus

$\Delta m = \sum m_{produits} - \sum m_{réactifs} = [m \, (Ba) \ + m \, (e)] - m \, (Cs)$

$\Delta m = 136,87511 + 5,48580.10^{-4} - 136,87692 = - 1,2614. \, 10^{-3}$ a.m.u.

$\Delta m = - 1,2614. \, 10^{-3} . 1,66. \, 10^{-27} = -2,094. \, 10^{-30}$ kg

$$\Delta m = 2,094. \, 10^{-30} \, \text{kg}$$

20

The mass change of the system is negative, so the reaction is accompanied by a loss of mass. The corresponding mass energy change is written :

$\Delta E = \Delta m \cdot C^2 = -2,09 \cdot 10^{-30} \cdot (3 \cdot 10^8)^2$

$$\Delta E = -1,88 \cdot 10^{-13} \text{ J} \; ; \; \Delta E = -1.17 \cdot 10^6 \text{ eV.}$$

Note that $\Delta E < 0$, so cesium transfers energy of 1.17 MeV outwards.

II-8- Stability of nuclei

II-8-1- Determination of the cohesion energy per nucleon

The binding energy per nucleon represents the average energy required to tear a nucleon from a nucleus. It is a yardstick of a nucleus' stability.

The stability of nuclei is directly linked to the ratio $\Delta E/A$ (binding energy per nucleon). The greater this ratio, the more stable the nucleus.

A large nucleus, such as uranium, has a high binding energy, but its nucleons are less tightly bound than those of an iron nucleus, because uranium's binding energy per nucleon is lower than that of iron.
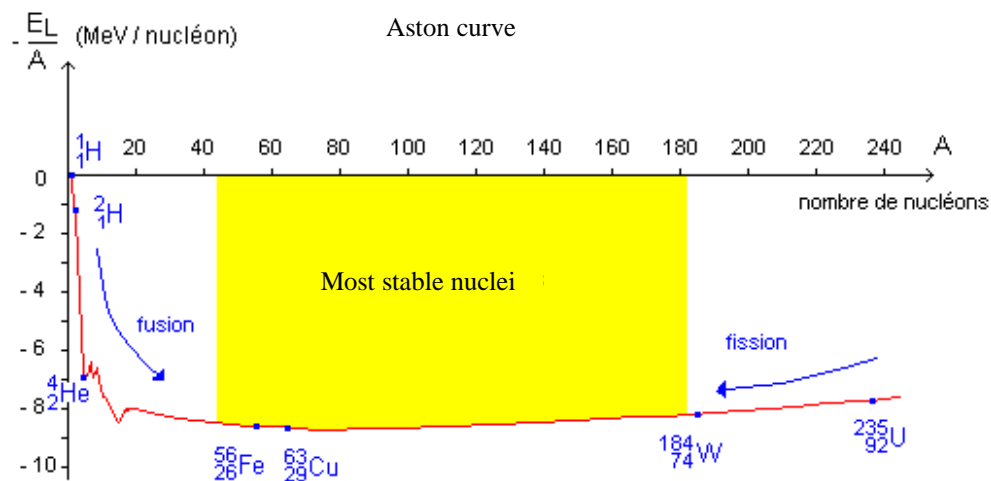
From the curve, known as the Aston curve ($-E/A = f(A)$), we can see that:

- The average binding energy per nucleon is around 5 to 9 MeV (except for very light nuclei).

  * The curve is fairly regular, with a maximum of 8.7 MeV for nuclei close to iron ($A \approx 56$), and remains close to 8.0 MeV/nucleon.

- The curve increases rapidly for light atoms ($A < 30$), with peaks for nuclei with even numbers of neutrons and protons $^4_2 He$; $^{12}_6 C$; $^{16}_8 O$ (very stable).

🔸 It reaches a maximum for 'A' values between 40 and 100, then decreases very slowly to 7.6 MeV/nucleon for uranium 238.

The tendency of elements to evolve towards greater stability explains why it is possible to produce nuclear energy by two processes that are in fact the opposite of each other, and why there are 2 types of nuclear reaction: fission and fusion.

1- **Fission:** This is the splitting of a heavy nucleus into more stable medium-sized nuclei, releasing a large amount of energy.

Examples:

$$^{235}_{92}U \ + \ ^{1}_{0}n \ \longrightarrow \ ^{139}_{56}B_a \ + \ ^{86}_{36}K_r \ + 11^{1}_{0}n$$
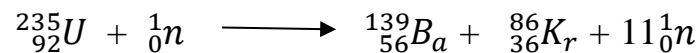
2- **Fusion:** The combination of two light nuclei (A < 10) to produce a heavier nucleus, releasing considerable energy.

Example:

$$^{2}_{1}H \ + \ ^{2}_{1}H \longrightarrow \ ^{4}_{2}H_e \ + E \qquad\qquad ^{3}_{1}H \ + \ ^{1}_{1}H \longrightarrow \ ^{4}_{2}H_e \ + E$$

Where: E is the energy.

II-8-2- Stability and number of nucleons

The representation of known nuclei in an 'N=f(Z)' graph highlights the stability line, populated by stable nuclei. Unstable nuclei undergo a series of radioactive decays until they become stable:

🔸 Below the stable nuclei, in blue, are those too rich in neutrons. These nuclei return to the stability line through β- decay, which transforms a neutron into a proton within the nucleus.

🔸 Above the stable nuclei, we find, in red, nuclei too rich in protons. These nuclei return to the stability line through β+ decay or electron capture, which transforms a proton into a neutron within the nucleus.

🔸 Proton-rich heavy nuclei return to the stability line by alpha decay.

🔸 Finally, very heavy nuclei fission, giving rise to light decay products.
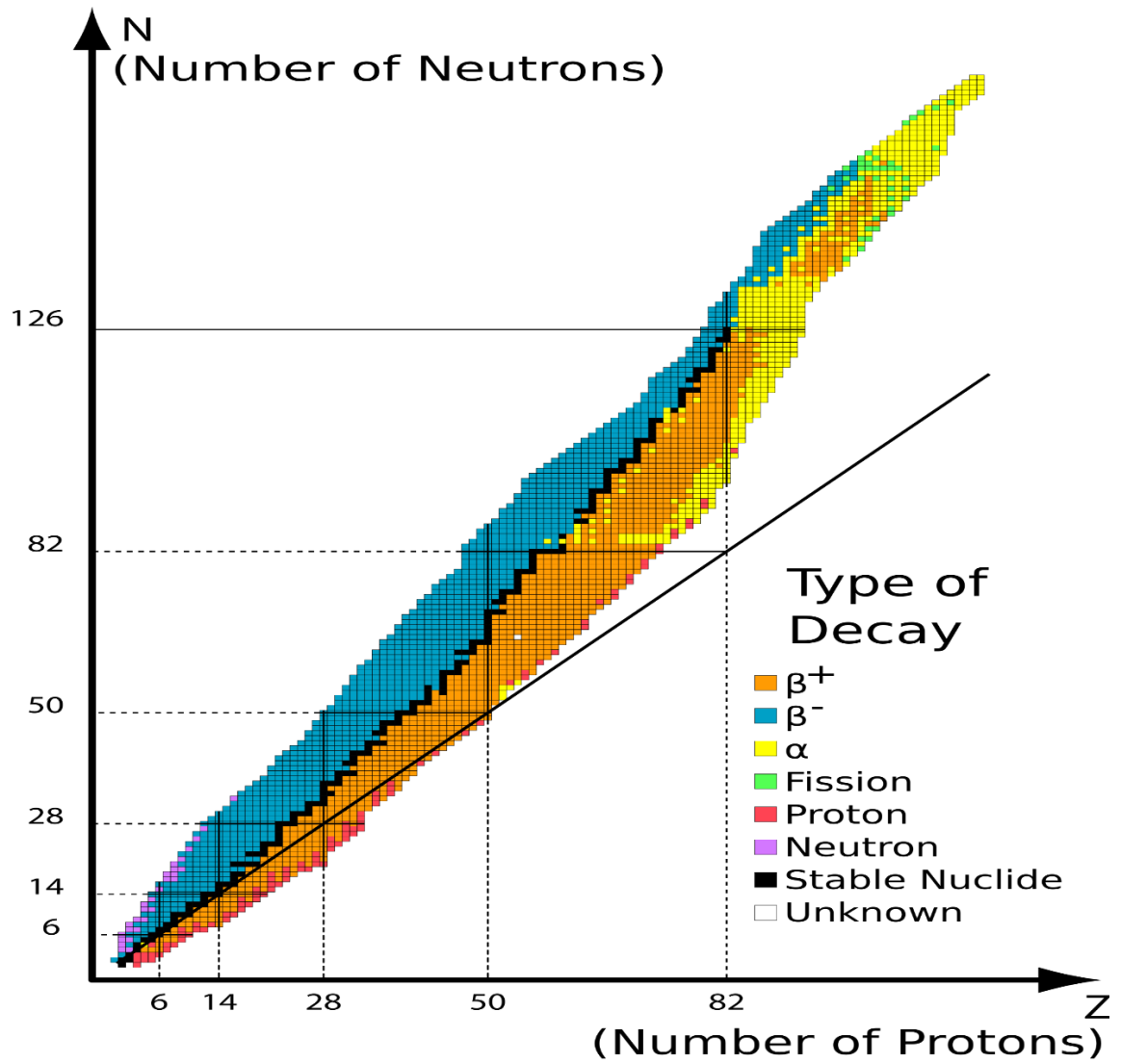
Chapter III:
Electronic structure of the atom

III-1- Wave-corpuscle duality

Classical physics distinguishes two kinds of fundamental entities:

Corpuscles, which are microscopic balls localized in space and possessing defined trajectories. The position and velocity of the corpuscle can be known along its trajectory.

Waves, on the other hand, are not localized. They do not carry matter, but information, momentum and energy.

Wave-corpuscle duality is, therefore, a principle according to which all physical objects can sometimes have wave properties and sometimes corpuscle properties.

III-1-1- Wave aspect of light

J. Maxwell defined light as a bundle of electromagnetic waves traveling at constant speed ($C = 3.10^8$ m/s) in a vacuum.

Light is characterized by its frequency or wavelength. Visible light is therefore only a tiny fraction of all electromagnetic waves.

But light is also made up of "grains of light", according to Albert Einstein, who argued that the energy of light is "granular". This "grain of energy" is called a photon. Each photon of radiation carries a quantum of energy characteristic of its frequency.

III-1-2- Corpuscular aspect of light: photoelectric effect

Electromagnetic radiation of frequency 'υ' can be thought of as a beam of indivisible particles known as photons. Each photon carries a quantum of energy 'E' :

$$E = h.\upsilon$$

Where: h is Planck's constant, $6.626.10^{-34}$ J.s.

As $\upsilon = \dfrac{C}{\lambda}$, (λ is the wavelength), the above relationship can also be written:

$$E = h\ \dfrac{C}{\lambda}$$

III-2- Interaction between light and matter

When a source of light energy strikes an object, it will reflect radiation at a certain wavelength, resulting in a specific color depending on the mechanisms of emission, reflection, absorption and transmission.

III-2-1- Emission spectrum of the hydrogen atom
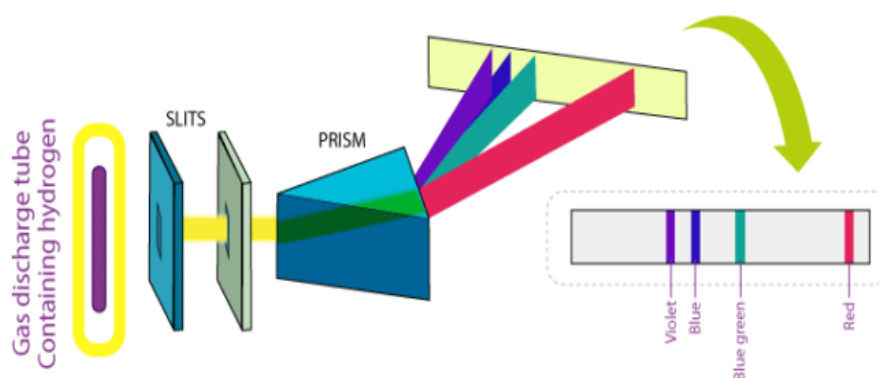
Experimental results:

❖ Spectral analysis of the emitted radiation shows the presence of a line spectrum.

❖ The spectrum of the hydrogen atom is the superposition of several series of lines, whose wavelengths lie between two limit values λmin and λmax.

❖ Within the same series, the lines become closer together as you move towards the shorter wavelengths.
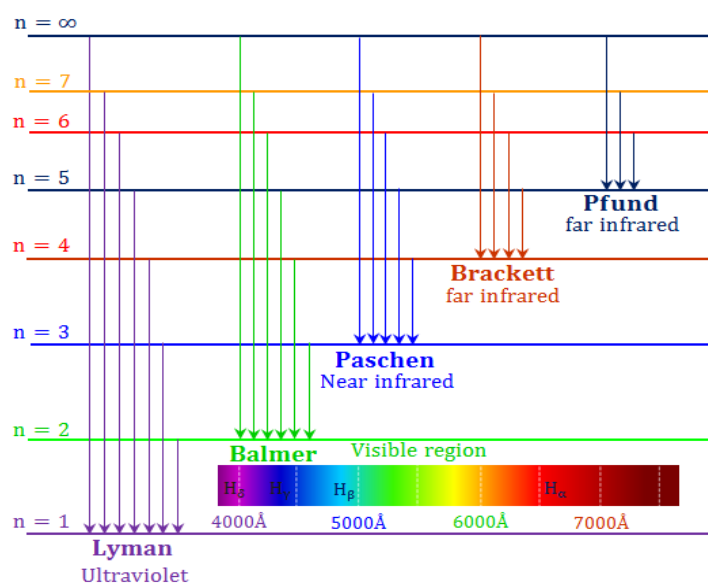
III-2-2- Empirical Balmer-Rydberg relationship

The empirical formula for calculating the wavelengths of the hydrogen atom spectrum is as follows:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$ **Balmer-Rydberg formula**

Where: R_H: Rydberg constant. Its experimental value is: **RH = 1.096 776.10^7 m^{-1}**

λ : Wavelength ;

n : : Natural number, such that n > 2

The seven visible lines observed make up the visible part of white light and form the Balmer series for which $n_1 = 2$ et $n_2 > 2$.

III-2-3- Notion of a series of lines

Ritz generalized Rydberg's empirical relation to find the wavelengths of all the lines in the different series observed according to the relation:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right)$$

With: n_1 and n_2 positive numbers ($n_2 > n_1$).

Hydrogen spectrum series, transitions and corresponding spectral range

Series	Transition	Spectral range
Lyman	$n_1 = 1$ and $n_2 \geq 2$	Ultraviolet
Balmer	$n_1 = 2$ and $n_2 \geq 3$	Visible
Paschen	$n_1 = 3$ and $n_2 \geq 4$	Infrared
Brackett	$n_1 = 4$ and $n_2 \geq 5$	Infrared
Pfund	$n_1 = 5$ and $n_2 \geq 6$	Infrared

III-3- Bohr's atomic model

III-3-1- Bohr's postulates

Bohr proposed three postulates to explain his theory:

✓ **First postulate:** There are stable (stationary) orbits of the electron, for which it does not radiate electromagnetic energy. These orbits correspond to defined energy levels.

✓ **Second postulate:** The electron can move from one orbit to another, i.e. from one energy level to another, by absorbing or emitting a quantum of energy.

$$E = E_i - E_f = h.\upsilon$$

With: E_i: energy corresponding to the starting orbit (initial energy) ;

E_f: energy corresponding to the arrival orbit (final energy);

υ = frequency of emitted or absorbed radiation.

✓ **Third postulate:** The electron's angular momentum 'L' is quantized as:

$$L = n \frac{h}{2\pi} = m_e . v_n . r_n$$

Where: n : principal quantum number, n = (1; 2; 3; ...) ;

me : electron mass ;

v_n : linear speed of the electron in its orbit ;

r_n : radius of the electron's orbit around the nucleus.

III-3-2- Radius of stationary orbits

Hydrogen consists of a positively-charged nucleus and a negatively-charged electron separated by a distance 'r'. The electron describes a circular trajectory with speed 'v', while the relatively heavy nucleus remains practically stationary.

According to Bohr's first postulate, the system is in equilibrium:

$$\vec{F_a} + \vec{F_c} = \vec{0} \text{ by projection: } F_a - F_c = 0 \text{ .....(1)}$$

With : F_a is the force of attraction; $F_a = \frac{k.e^2}{r^2}$;

Where: k : is a constant; $k = \frac{1}{4.\pi \, \mathcal{E}_0}$; $\mathcal{E}_0$: is the permittivity of vacuum;

F_c is the centrifugal force; $F_c = \frac{m_e . v^2}{r}$

$(1) \Rightarrow \frac{k.e^2}{r^2} - \frac{m_e . v^2}{r} = 0 \Rightarrow m_e . v^2 = \frac{k.e^2}{r}$ .....(2)

According to Bohr's postulates, it was found that:

$$L = n \frac{h}{2\pi} = m_e . v . r \Rightarrow v = n \frac{h}{2\pi . m_e . r} \text{ .....(3)}$$
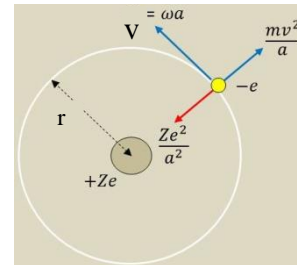
Replacing (3) with (2) gives us:

$$m_e \left[n \frac{h}{2\pi . m_e . r} \right]^2 = \frac{k.e^2}{r} \Rightarrow n^2 \frac{h^2}{4\pi^2 . m_e . r} = k.e^2 ;$$

From which we can extract 'r' : $r = n^2 \frac{n^2 . h^2}{4.k.\pi^2 . m_e . e^2}$

However, 'h', 'K', 'm_e' et 'e' are constants, so 'r' depends only on 'n'. The final relationship for 'r' will then be:

$$r_n = n^2 \frac{n^2 . h^2}{4.K.\pi^2 . m_e . e^2} \text{ ....(4)}$$

Knowing that: h = 6.626 .10^{34} J.s ; K = 9.10^9 (S.I) ; m$_e$ = 9,110.10^{-31}kg and e = 1,602.10^{-19} C.

For n = 1, first Bohr radius for the hydrogen atom:

$$r_1 = 0,53Å$$ (Å : Angstrom)

With: 1 Å = 10^{-10} m

III-3-3- Electron energy in a stationary orbit

In the hydrogen atom, the only electron located at a distance 'r' from a proton possesses energy, as it can provide work by being attracted to the nucleus. Physicists have shown that this energy, which is electrical potential energy, can be written as:

$$E_P = -k\frac{e^2}{r}$$

In the hydrogen atom, the electron moving at speed 'v' possesses energy, as it can, for example, displace another particle by colliding with it. Physicists have shown that this energy, which is kinetic energy, can be written as:

$$E_c = \frac{1}{2} m.v^2 = K. \frac{e^2}{r^2}$$

Where: $K. \frac{e^2}{r^2} = F_{coulomb}$

The total energy 'E_T' of the system considered is the sum of the potential energy 'E_P' and the kinetic energy 'E_C':

$$E_T = E_p + E_c = -k \frac{e^2}{r} + K. \frac{e^2}{2r} ==> E_T = -K. \frac{e^2}{2r} ;$$

Replacing 'r' in expression (4) gives:

$$E_T = -\frac{2.K^2.\pi^2.m_e.e^4}{n^2.h^2}$$

For : n = 1, $E_1 = -\frac{2.K^2.\pi^2.m_e.e^4}{h^2}$

$$E_1 = -21.76.10^{19} J = -13.6 \text{ eV}$$

With: 1eV = 1.6.10^{-19} J.

This value 'E_1' represents the fundamental state energy of the hydrogen atom.

So the relationship between the total energy and the fundamental state energy of hydrogen is::

$$E_T = \frac{E_1}{n^2}$$
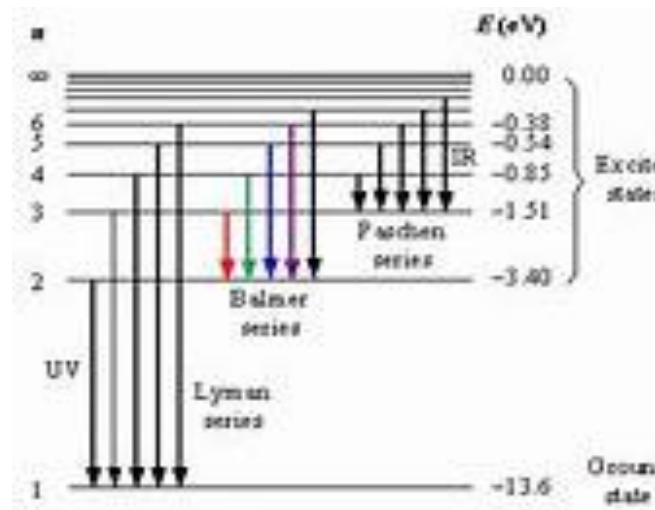
Conclusions :

- ♥ Layers with a high quantum number 'n' are the most energetic layers.
- ♥ As 'n' increases, the radius 'r_n' increases and the electron is less bound to the nucleus.
- ♥ At the limit, if n →∞ the electron has left the atom. The atom is then ionized.
- ♥ If 'n' increases, the energy levels get closer and closer together.
- ♥ The lowest energy level corresponds to n = 1, the atom's ground state.
- ♥ If n > 1, the atom is in an excited state.
- ♥ The ionization energy 'E_{ion}' of the hydrogen atom is the minimum energy required to pull the electron out of the fundamental state.

III-3-4- Relationship between wavenumber and energy levels

Planck's relation is used to calculate the energy carried by a photon. This relation is written:

$$E = h.\upsilon \quad .....(5)$$

Where: υ is the frequency (in hertz) of the electromagnetic wave associated with the photon under consideration. The frequency is equal to:

$$\upsilon = \frac{c}{\lambda} \quad .....(6)$$

But we have: $\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right).....(7)$;

Combining equations (7), (6) and (5), Planck's relation is then written:

$$E = h.C.\, R_H \left(\frac{1}{n_1{}^2} - \frac{1}{n_2{}^2} \right)$$

III-3-5- Application to hydrogenoids

An hydrogenoid is a monoatomic ion (a cation) with a single electron. Its structure is similar to that of the hydrogen atom, except for the charge on its nucleus 'Ze'. It is therefore an atom from which all but one electron has been stripped.

So, a hydrogen ion has 'n' protons and one electron. Ex: He^+ ; Li^{2+} ; Be^{3+}

Applying Bohr's postulates to hydrogenoids, we obtain the following reduced formulae:

+ **Radius:** $\boxed{r_n = \dfrac{n^2}{z}\, r_1}$ With: $r_1 = 0.53$ Å

+ **Total energy:** $\boxed{E_T = \dfrac{z^2}{n^2}\, E_1}$ With: $E_1 = -13.6$ eV

+ **Ritz formula:** $\boxed{\Delta E = Z^2.\, E_1}$ $\boxed{\Delta E = Z^2 \, h.C.\, R_H \left(\dfrac{1}{n_1{}^2} - \dfrac{1}{n_2{}^2} \right)}$

III-3-6- Inadequacy of Bohr's model

Bohr's model provides the first explanation for the existence of absorption and emission lines. It also justifies Balmer's experimental formula. Hertz's experiment confirms the model's theoretical results on the energy levels of the hydrogen atom.

However, Bohr's model does not, in the general case, explain the spectra of other atoms and molecules. It can be extended to hydrogenoid ions (n protons, one electron).

III-4- Hydrogen atom in wave mechanics

Four famous names are attached to the evolution of the atomic model:

❖ **J. J. Thomson:** the model assumes that electrons are immersed in a positively charged material.

❖ **Rutherford:** Matter is gathered in a very small nucleus charged with positive electricity, around which negative electrons gravitate.

❖ **Bohr:** The electron only radiates or absorbs energy when it changes orbit.

❖ **Schrödinger:** revolutionized the idea of an electron orbit, proposing a wave model in which the electron is described as a wave with an associated orbital, also known as a wave function.

III-4-1- Wave-corpuscular duality and De Broglie's relation

According to Einstein, the energy carried by a light wave does not flow continuously, but

moves in packets or quantums of energy called photons. These energy quantums are distinct from one another.

If 'w' is the energy of a photon, 'υ' its frequency of light radiation, 'w' and 'υ' are linked by the relationship:

$$w = h.\upsilon \ \ldots(1)$$

On the other hand, the energy 'w' and the celerity 'C' of light are linked by the relation:

$$w = m.C^2 \ \ldots(2)$$

Where: m is the mass of the photon.

Equating (1) and (2) gives: h.υ = m.C^2 $\Longrightarrow \upsilon = \frac{m.C^2}{h}$; since $\lambda = \frac{c}{\upsilon}$;

We obtain:

$$\boxed{\lambda = \frac{h}{m.c}}$$

This equation links the wave character 'λ' to the corpuscular character 'm'. The particle's energy 'E' is as follows:

$$\boxed{E = h.\upsilon}$$

From now on, this theory of wave-corpuscle duality is generalized to all particles, large or small, charged or not: an electron, a proton, a nucleus, an atom, a molecule, a satellite.

Subjected to the acceleration of a potential difference 'V', an electron possesses an energy:

$$Ep = 1/2 \ m.v^2 = e.V \Longrightarrow v = \sqrt{\frac{2.e.V}{m}} \ \ldots(8) \quad (V \text{ in Volt}).$$

The wavelength 'λ' of the associated wave is written

$$\lambda = \frac{h}{m.v} \quad \ldots(9)$$

Replacing (8) with (9) We get: $\boxed{\lambda = \frac{h}{\sqrt{2.m.e.V}}}$

III-4-2-Heisenberg's uncertainty principle

It's impossible to accurately determine the position and velocity of a particle like the electron simultaneously.

The average errors on position (Δx) and momentum (Δp), verify the following inequality relationship:

$$\Delta x.\Delta p \geq \frac{h}{2\pi} = \hbar \ \ldots 12$$

With: Δx is the uncertainty of position;

      Δp is the Uncertainty on the momentum ;

      $h = 6.63 \ 10^{-34}$ J.s; and $\hbar = 1.054.10^{-34}$ J.s.

But: $\Delta P = m.\Delta v$ ....(13). Combining (12) and (13) we obtain:

$$\Delta x.m.\Delta v \geq \frac{h}{2\pi} = \hbar \implies \boxed{\Delta x \geq \frac{\hbar}{m.\Delta v}} \text{ and } \boxed{\Delta v \geq \frac{\hbar}{m.\Delta x}}$$

This relationship means that if we can theoretically measure (x) with any desired precision ($\Delta x \rightarrow 0$), then Δv will become large since: $\Delta v \geq \dfrac{\hbar}{m.\Delta x}$

The position and velocity of a particle are called incompatible quantities: they cannot be measured simultaneously with the required precision.

Heisenberg's uncertainty principle has far-reaching consequences in wave mechanics: it is very difficult to know the exact trajectory of particles, since velocity and position cannot be known simultaneously.

Examples:

  \# Macroscopic object: M=1kg. If $\Delta x = 1m \implies \Delta V = 1.054.10^{-34}$ m/s. Excellent accuracy.

  \# Microscopic object. Electron: m $=10^{-30}$ kg. Si $\Delta v = 1$ m/s $\implies \Delta x = 10^{-4}$ m.

  Enormous inaccuracy compared with the size of an atom 10^{-10} m.

III-4-3- Wave function and Schrödinger equation

III-4-3-1- Atomic orbital model

Each electron in an atom is associated with a wave ψ (x, y, z, t). If the electron's state is stable, then the associated wave is stationary. This wave function is called the ˈelectronic orbital of the ˈatom.

The standing wave in the simple physical case of the vibrating string is as follows:
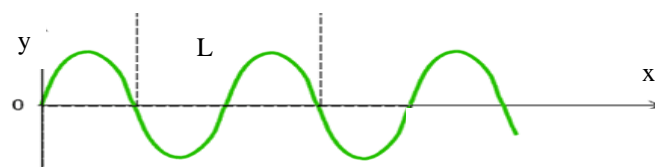
The wave propagation equation is: $y = A \sin \omega t \cdot \sin\left(\frac{2.\pi.x}{\lambda}\right)$

Where: A sin ω t is the amplitude function. The stability condition of the stationary system is:

$$\left.\begin{array}{l} x = 0 \\ \\ x = L \end{array}\right\} \Longrightarrow y = 0 \; ; \; or, \; L = n \; \frac{\lambda}{2}$$

An analogy can be drawn with the electron of the hydrogen atom orbiting the nucleus:
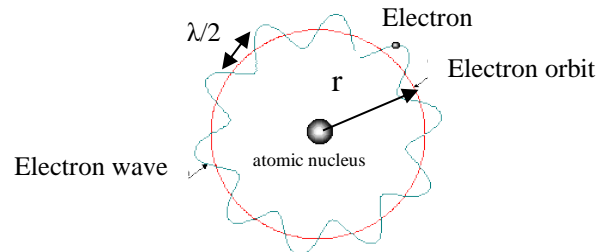
Assuming that the electron gravitates on a circle of radius (r). For the associated wave to be stationary, and by analogy with the vibrating string, we must have:

$$2\pi. \, r = n.\lambda \; ; \quad and \quad \lambda = \frac{h}{m.v}$$

So: $2\pi. \, r = n. \, \dfrac{h}{m.v} \Longrightarrow m.v.r = n. \, \dfrac{h}{2\pi} = n.\hbar$

$$\boxed{m.v.r = n.\hbar}$$

Generally speaking, scientists (Bohr, Einstein, Schrödinger, Heisenberg...) have developed the laws of wave mechanics. The laws of wave mechanics, which make it possible to recover all the experimental results concerning the mechanics of atoms.

III-4-3-2- Schrödinger equation

The laws of wave mechanics that allow us to determine the wave function 'ψ' have been determined and constitute the formalism of wave mechanics.

The fundamental equation to be satisfied by the wave function 'ψ' is the Schrödinger equation.

Consider the general equation of a one-dimensional wave function of constant amplitude:

$$\Psi \, (x,t) = A \sin \left(\omega \, t - \frac{2.\pi.x}{\lambda}\right) \; ;$$

Let's calculate : $\dfrac{\partial \Psi}{\partial x}$ et $\dfrac{\partial^2 \Psi}{\partial x^2}$;

$$\frac{\partial \Psi}{\partial x} = - \frac{2\pi}{\lambda} \; A \cos \left(\omega \, t - \frac{2.\pi.x}{\lambda}\right)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \ A \sin(\omega t - \frac{2.\pi.x}{\lambda}) = -\frac{4\pi^2}{\lambda^2} \Psi \implies \frac{\partial^2 \Psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \Psi = 0 \ \ldots.(8)$$

If Ψ is the wave function associated with a particle, then: $\lambda = \frac{h}{m.v}$;

Substituting donations into equation (8), we get:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{4\pi^2}{h^2} \ m^2. \ v^2. \ \Psi = 0 \ldots\ldots.(9)$$

However: $\frac{1}{2} m. \ v^2 = E_c = E_T - E_p \implies m.v^2 = 2 (E_T - E_p)$;

Equation (9) becomes:

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} \ (E_T - E_p). \ \Psi = 0$$

In general, in three dimensions of space, and by introducing the Laplacian operator:

$$\nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrödinger's equation will then be:

$$\Delta \Psi + \frac{8\pi^2 m}{h^2} \ (E_T - V). \ \Psi = 0$$

With: $V = E_{px} + E_{py} + E_{pz}$ (total potential energy).

We assume that the wave function associated with an electron must satisfy the Schrödinger equation. The solutions to this equation are stationary wave functions (i.e. orbits of the atom). These functions are written as:

$$\psi(x, y, z, t) = \psi(x, y, z) . \ e^{-2\pi.i.v_t}$$

The function $\psi(x, y, z)$ is a solution of the Schrödinger equation; $\psi(x, y, z)$ will then be an orbit of the atom, time not being involved in determining the atom's stationary states.

III-4-4- Solving the Schrödinger equation:

Consider a fixed proton (hydrogen atom) located at the origin of space coordinates, and an electron whose position is defined by these coordinates (x, y, z).

We have: $E_p = V = -k \ \frac{e^2}{r}$;

Schrödinger's equation is then written:

$$\Delta \Psi + \frac{8\pi^2 m}{h^2} \ (E_T + k \ \frac{e^2}{r}). \ \Psi = 0$$

34

An infinite number of solutions (Ψ, E) exist. The mathematical conditions for calculating orbitals introduce functions of three integers (n, l,m).

$$\Psi = \Psi \ (n, \ l, \ m);$$

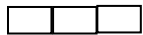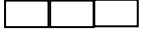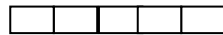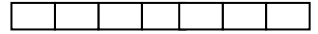### III-4-5- Quantic numbers and the notion of atomic orbital
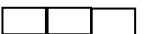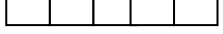
According to de Schrödinger, the solutions to his equation are standing wave functions (of the atom's orbits). These functions are written as:

$$\Psi = \Psi \ (n, \ l, \ m)$$

Such as :

- ⬇ 'n' is called the principal quantum number, it defines the electronic layer, it's a non-zero natural number. ($n \in N^*$)

- ⬇ 'l' is called the secondary (azimuthal) quantum number, it characterizes the sub-layer (or sub-level) occupied by the electron. $0 \leq l < n - 1$. ($l \in N^*$).

- ⬇ 'm' is called the magnetic quantum number, and defines the number of orientations in space that the electron can take when subjected to the action of a magnetic field. It characterizes the quantum bin occupied by the electron. $-l \leq m \leq +l$.

- ⬇ 's' (where ms) magnetic spin quantum number, linked to the electron's proper state, takes the values $+ 1/2$ or $- 1/2$.

Each 'Ψ' orbital, as a solution to the Schrödinger equation, is then represented by a triplet (n, l, m) and will be noted: Ψ(n, l, m,s).

Values of n	Values of l $0 \leq l < n-1$	Name of sublayer	Values of m $-l \leq m \leq +l$	Corresponding quantum cases
n=1	l= 0	1s	m =0	▭
n=2	l= 0	1s	m = 0	▭
	l= 1	2p	m = −1 ; 0 ; 1	▭▭▭
n=3	l= 0	3s	m = 0	▭
	l= 1	3p	m = −1 ; 0 ; 1	▭▭▭
	l= 2	3d	m =-2 ; -1 ; 0 ; 1 ;2	▭▭▭▭▭
n=4	l= 0	4s	m = 0	▭
	l= 1	4p	m = −1 ; 0 ; 1	▭▭▭
	l= 2	4d	m =-2 ; -1 ; 0 ; 1 ;2	▭▭▭▭▭
	l= 3	4f	m =-3; -2; -1; 0;1;2; 3	▭▭▭▭▭▭▭

III-5- Polyelectronic atoms in wave mechanics

All atoms in their stable state have more than one electron (Z protons and Z electrons), with the exception of the hydrogen atom. Each electron is subject to both the attraction of the +Ze nucleus and the repulsion of other electrons.

III-5-1- Electronic configuration of elements: Klechkowski's rule

Layers and sub-layers are filled in ascending order of the (n+l) pair. If two or more (n+l) pairs lead to the same value, they will be arranged in ascending order of 'n'.
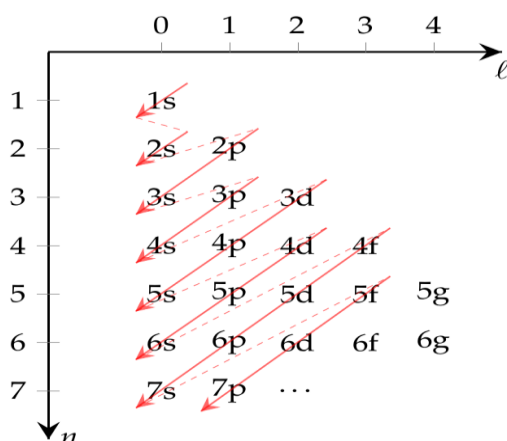
The filling order of the quantum sublayers is then:

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

III-5-2- Exception to Klechkowski's rule

There are exceptions to the Klechkowski orbital filling rule: some transition metals, lanthanides and actinides do not respect this order. In these cases, there is a transfer from their **'s'** sublayer (for transition metals) or **'f'** sublayer (for lanthanides and actinides) to their **'d'** sublayer, allowing the latter to be filled (10 electrons) or half-filled (5 electrons).

Example:

Cr : [Ar] $4s^2 3d^4$

As it happens, a half-full (nd^5) or full (nd^{10}) atomic 'd' orbital has a particular stability. This state can be achieved by "promoting" a single '4s' electron to the '3d' level, as is the case with:

Cr : [Ar] $4s^2 3d^4 \rightarrow$ Cr : [Ar] $4s^1 3d^5 \rightarrow$ Cr : [Ar] $3d^5 4s^1$

Cu : [Ar] $4s^2 3d^9 \rightarrow$ Cu : [Ar] $4s^1 3d^{10} \rightarrow$ [Ar] $3d^{10} 4s^1$

Sublayer 'd' is filled (10 electrons) at the expense of the sublayer 's'.

III-5-3- Atomic orbital filling rule

Establishing the electronic configuration of an atom or a poly-electronic ion in a given state consists in indicating the distribution, in this state, of the 'Z' electrons in the various atomic orbitals (1s 2s 2p,...), the number of electrons being noted as an exponent.

The filling of quantum bins or atomic orbitals must comply with the following four rules:
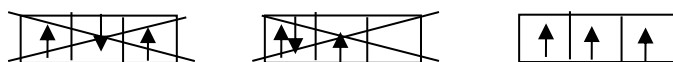
III-5-3-1- Pauli's exclusion principle

Pauli's principle is as follows: two electrons in the same atom cannot have identical quantum numbers (n, l, m, s).

Consequence:

Only a maximum of two electrons with opposite spin quantum numbers can be placed in the same quantum bin:
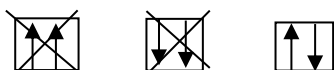
III-5-3-2- Hund's rule

In the fundamental state, when several degenerate atomic orbitals are free, electrons position themselves to occupy as many of them as possible. Electrons occupy these

degenerate orbitals with positive spin moments before moving to opposite spin positions. The fundamental state is given by a maximum of parallel spins. We therefore occupy a maximum number of orbitals before saturating them.

To sum up:

\#   If Pauli's exclusion principle is not respected, electronic configuration is impossible;

\#   If Pauli's principle is respected, as well as the filling order and Hund's rule, the configuration obtained is that of the electron in its ground state;

\#   If the filling order and/or Hund's rule are not respected, the configuration obtained is that of an excited state of the atom.

Example:

Chlorine has Z=17 protons and therefore 17 electrons, and has the following electronic configuration:

$_{17}Cl$: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^5$.

$$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^5$$
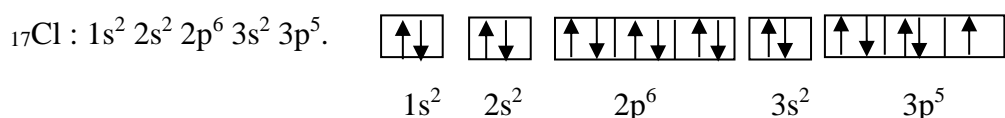
III-5-4- Screen effect: Slater approximation

The method consists in calculating the effective charge by considering that the numerous electrostatic interactions (attractions-repulsions) in an atom can be reduced to a small number of interactions that are simple to quantify.

Consider the attraction between the 'Z' protons in the nucleus and any 'E' electron in the atom. The attraction is disturbed by the electrons located between the nucleus and electron E. These electrons form a screen. These electrons form a screen. A screen constant is then defined, depending on the position of the atom's electrons relative to electron E. The charge 'Z' of the atom's nucleus then becomes an effective charge 'Z*' relative to the electron 'E'.

$$Z^* = Z - \sigma$$

Where: Z is the real nuclear charge;

       σ is the screen constant.

To calculate the effective charge, follow the steps below:

- o Write down the element's electronic configuration and order it;
- o Select the electron for which the effective charge is sought. All other electrons will make a partial contribution σi to the total screen constant σ. This contribution depends on:
  - ▪ The electron's orbital type (s, p, d or f);
- o The electron's electronic layer 'n'.
- o The value of σi is summarized in the following table:

Value of σi is summarized in the following table

	1s	2s 2p	3s 3p	3d	4s 4p	4d	4f	5s 5p	5d	5f	6s 6p
1s	0,3										
2s 2p	0,85	0,35									
3s 3p	1	0,85	0,35								
3d	1	1	1	0,35							
4s 4p	1	1	0,85	0,85	0,35						
4d	1	1	1	1	1	0,35					
4f	1	1	1	1	1	1	0,35				
5s 5p	1	1	1	1	0,85	0,85	0,85	0,35			
5d	1	1	1	1	1	1	1	1	0,35		
5f	1	1	1	1	1	1	1	1	1	0,35	
6s 6p	1	1	1	1	1	1	1	0,85	0,85	0,85	0,35

Chapter IV:

Periodic classification of the elements

IV-1- D. Mendeleyev's periodic classification

The classification used derives from that proposed by Dimitri Mendeleev (1869), based on analogies in the physical and chemical properties of certain groups of elements, such as: (Cl, Br, I), (S, Se, Te), (Li, Na, K), or (Ca, Sr, Ba). The 66 elements known at the time were arranged in order of increasing atomic mass in a table of rows and columns. Elements with similarities were placed in the same column. Today, elements are classified in order of atomic number.

IV-2- Modern periodic table

The current classification was last updated in 2016. The International Union of Pure and Applied Chemistry (IUPAC), the recognized authority on the rules and nomenclatures of chemistry, set the specifications for the periodic table.

The table contains 118 elements, of which 83 are primordial, older than the Earth itself. The last 24 elements, on the other hand, are synthetic: they do not exist naturally on Earth and are man-made. Other elements can also be found in the Universe as a result of supernova destruction, for example. The current periodic table has been reworked and is based on slightly different criteria from those of Mendeleev's table:

➢ Elements are no longer classified by atomic mass, but by ascending atomic number.
➢ Elements with the same number of electrons on their outer layer are placed in the same column (this last criterion is comparable to the one used by Mendeleev).
➢ The current classification has 7 rows called periods and 18 columns called families.
➢ Some periodic tables provide additional data for each element, such as electronegativity, electronic configuration, first ionization energy and oxidation states.

IV-3- Presentation of the periodic table

The periodic table therefore consists of:

❖ **Period:** A period corresponds to the elements placed on a horizontal line; it corresponds to a layer.
❖ **Column:** A column corresponds to elements placed on the same vertical line, whose highest-energy sub-layer has the same electronic configuration.

Consequences:

♦ Elements in the same column will have the same number of electrons in the last layer (outer layer);

♦ The number of the row to which an element belongs will reveal the number of its last layer, i.e. the principal quantum number n of its last layer.

❖ **Groups and sub-groups:** The columns of the periodic table are called groups. Groups are subdivided into 2 subgroups, A and B:

♦ An element belongs to subgroup A if its valence elements occupy only 's' and 'p' atomic orbitals (AO);

♦ An element belongs to subgroup B if its external structure includes a 'd' sublayer.

Group	I		II		III		IV		V		VI		VII		VIII	VIII$_A$
Sub-groupe	I$_A$	I$_B$	II$_A$	II$_B$	III$_A$	III$_B$	IV$_A$	IV$_B$	V$_A$	V$_B$	VI$_A$	VI$_B$	VII$_A$	VII$_B$	VIII$_B$	/
Column	1	11	2	12	13	3	14	4	15	5	16	6	17	7	8-9-10	18

❖ **Blocks :** The periodic table consists of 4 blocks (s, p, d and f).
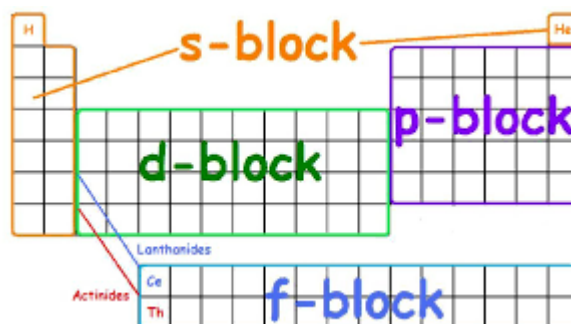
Example:

Find the period, group and subgroup of the following elements: Ni (Z=28), Zn (Z=30) and I (Z=53).

$_{28}$Ni : [Ar] $4s^2 3d^8$ we write: $_{28}$Ni : [Ar] $3d^8 4s^2$
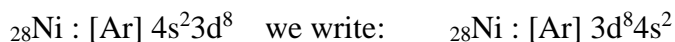
Nickel belongs to the 4th period; column 10; group VIII; sub-group B; block s.

$_{30}$Zn : [Ar] $4s^2 3d^{10}$ we write: $_{30}$Zn : [Ar] $3d^{10} 4s^2$

Zinc belongs to the 4th period; column 12; group II; sub-group B ; block d.

$_{53}$I : [Kr] $5s^2 4d^{10} 5p^5$;   we write: $_{53}$I : [Kr] $4d^{10} 5s^2 5p^5$
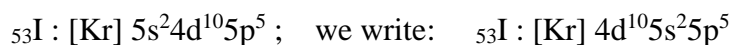
Iodine belongs to the 5th period, group VII, sub-group A ; block 17.

❖ **Families:** In the current classification, all elements in the same family have the same number of electrons on their outer layer, giving them similar chemical properties: they

41

react with the same type of compound, forming comparable molecules and ions. There are several main families:

- ✓ The alkali metal family, which corresponds to the first column, all the elements in this column have an outer layer with an electron. They all form cations by losing an electron. Alkali metals are shiny, soft and highly reactive. Because of their high reactivity.

- ✓ The alkaline-earth metal family, which corresponds to the second column, all have two electrons on their outer layer. They all form cations by losing two electrons.

- ✓ The lanthanide family: the name lanthanide comes from the element ̏lanthanide (first element in the family), (elements from Z=57 to Z=71).

- ✓ The actinide family: the name actinide comes from the element ̋actinium̏̏ (first element in the family), (elements from Z=89 to Z=103). These are heavy metals, and are all radioactive.

- ✓ The transition metal family: this family includes many elements with a particular electronic configuration. These elements come in a wide variety of colors. They are all metals that conduct electricity.

- ✓ The poor metal family: these are soft or brittle metals. They tend to form covalent bonds and have an amphoteric acid-base character.

- ✓ The metalloid family: these elements have special characteristics. They resemble metals, are brittle and do not conduct electricity.

- ✓ The non-metal family: these elements are excellent thermal and electrical insulators. Non-metals make up almost the entire constitution of living beings.

- ✓ The chalcogen family, corresponding to the sixteenth column.

- ✓ The halogen family, corresponding to the seventeenth column. Each of these elements is missing an electron, so that the last layer is.

- ✓ The rare gases family (also known as noble gases or inert gases) correspond to the last column. They all have a complete outer layer, making them very unreactive.

IV-4- Evolution and periodicity of the elements' physicochemical properties

IV-4-1- Atomic radius

For a given period, the atomic radius decreases from left to right. This is because the systematic increase in nuclear charge across the period contracts the electron orbitals. For an equal number of layers, the more electrons there are, the stronger the attraction of the nucleus.

For a given column, the atomic radius increases with Z. Electrons move further away from the nucleus when the principal quantum number of the layer to which they belong is greater.

IV-4-2- Ionic radius

Ions are not the same size as the atoms from which they derive, anions being larger and cations smaller, but they follow the same periodic trends.

This is the apparent radius of an atom that has lost or gained one or more electrons:

➕ The radius of a cation is always smaller than the radius of a neutral atom.

Examples: $r_i (Na^+) = 97$ pm $< r (Na) = 190$ pm   (r_i : ionic radius).

$r_i (Ca^{2+}) = 99$ pm $< r (Ca) = 197$ pm

The more charges the ion carries, the smaller the ionic radius.

Example: $r_i (Fe^{3+}) = 64$ pm $< r_i (Fe^{2+}) = 24$ pm $< r (Fe) = 126$ pm

➕ The radius of an anion is always greater than the radius of a neutral atom.

Example: $r_i (F^-) = 133$ pm $> rm (F) = 72$ pm

In a column, the radius of ions with the same charge increases from top to bottom.

IV-4-3- Ionization energy

It corresponds to the minimum energy (E_1) required to pull an electron out of an atom, in its gaseous state. It therefore corresponds to the departure of the electron least bound to the nucleus, i.e. the one occupying the highest energy AO. This is the or one of the valence electrons. There's a direct link between 'E_1' and valence orbital energy.

In the same row, ionization energy increases from left to right, and in the same column, it increases from bottom to top.

IV-4-4- Electronic affinity

Electronic affinity characterizes the opposite phenomenon of ionization, i.e. the ability of a neutral atom to capture an extra electron, according to the reaction:

$$A + e^- \longrightarrow A^- \quad\quad AE = E(A^-) - E(A) \;\ldots\ldots \text{ agreement 1}$$

With: AE electronic affinity.

In practice, electronic affinity is often defined in relation to the reverse reaction, by considering the ionization of the anion:

43

$$A^- \longrightarrow A + e- \quad AE = E(A) - E(A^-) \ldots. \text{ agreement 2}$$
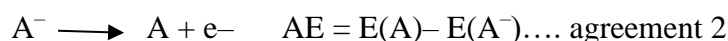
Unlike ionization energy, which is always positive, electron affinity can change sign. Using convention 2, if electron affinity is positive, then the anion is more stable than the neutral atom:

$$AE > 0 \text{ if } E(A) > E(A\text{-}).$$

The higher the electron affinity, the more electrons the atom tends to capture. The variation in electron affinity is broadly similar to that of ionization energy. Thus: electron affinity increases from left to right along the periods of the classification, and decreases along the columns.

IV-4-5- Electronegativity

The tendency of an atom to attract electrons to a molecule. Several electronegativity scales have been proposed to predict the type of bond that may unite 2 elements:

➢ Mulliken scale:

According to the Mulliken scale, the electronegativity of an element is calculated by the following relationship:

$$\chi_M = K \frac{A_e + E_I}{2}$$

With: $K = 0.317 eV^{-1}$;

Ae is the electron affinity ;

EI is ionization energy.

Example:

Express the Mulliken electronegativity 'χ' of atom : F : Z = 9 ; E = 17,4 and A = 3,4.

$$\chi_M = K \frac{A_e + E_I}{2} = 0.317. \frac{3.4 + 17.4}{2}$$

$$\chi_M (F) = 3,3$$

IV-5- Calculation of radii (atomic and ionic)

➢ Slater's method in general

Inter-electronic repulsion prohibits the use of Bohr's model for atoms other than hydrogenoids.

Various methods exist to overcome this drawback, including the one developed by J.S. Slater.

Slater's method "transforms" a polyelectronic atom into a hydrogenoid. To simulate a one-electron edifice, an effective nuclear charge perceived by each electron is calculated:

$$Z^* = Z - \sigma$$

IV-5-1-Atomic rays

\#   The expression for the atomic radius of a hydrogenoid is:

$$r = r_0 \, \frac{n^2}{Z} \quad ....(1)$$

From equation (1), it's clear that the atomic radius evolves within the same column, since the value of n increases by one unit as we move from one row to the next, while the value of 'Z*' hardly increases at all. As the 'n' term increases faster than 'Z*', the radius increases as we move down the same column.

Example:

r (Li) = 1.23 A° ; r (Na) = 1.54 A° ; r (K) = 2.03 A° ; r (Rb) = 2.16 A°

It's clear that: r (Rb) > r (K) > r (Na) > r (Li)

IV-5-2- Ionic radius

An atom seeks to stabilize itself by losing or gaining electrons. The result is an ion with the electronic structure of a rare gas.

Assuming the relationship in equation (1) remains valid for the resulting ion, 'n' and 'Z*' evolve as follows:

- ✓ 'n' decreases if electrons are removed from the valence shell, while 'Z*' also changes strongly. Since electrons have been removed, the shielding effect decreases and 'Z*' increases. This means: $\frac{n^2}{Z^*}$ decreases sharply, and the radius of the ion is much smaller than that of the neutral atom.
- ✓ 'n' increases if electrons are captured, so the shielding effect and 'Z*' decrease, but as 'n²' increases faster than 'Z*', the radius increases.

IV-5-3- Calculating ionization energy

The shielding effect "σ_j' on electron 'j' is the sum of the shielding effects "σ_{j-i}' exerted on electron 'j' by any other electron 'i', taking into account the situation of electron 'j'.

✛   For a hydrogenoid atom with atomic number 'Z', the energy is calculated by;

$$E_i = -13{,}6 \, \frac{Z^2}{n^2} \quad [eV]$$

➕ For a poly-electronic atom, each electron contributes an energy of:

$$E_i = -13,6 . \frac{Z^{*2}}{n^{*2}}$$

➕ The total energy of the atom is the sum of the contribution of each electron:

$$E = \sum E_i$$

Example :

1- Calculating the energy of the lithium atom (Li), Z = 3.

$_3$Li : $1s^2 \ 2s^1$
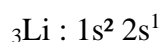
We use the table (previous chapter) representing the screen constants:

▪ The electron 1s has the effective charge: $Z_1^* = 3 - (2 . 0,85) = 1,3$

▪ Its energy is: $E_i = -13,6 . \frac{1.3^2}{2^2} = -5,75$ eV

• One of the '2s' electrons has an effective charge of: $Z_2^* = 3 - (1 . 0,30) = 2,7$

• Its energy is: $: E_2 = -13,6 . \frac{2.65^2}{1^2} = -99,14$ eV.

Total energy is therefore: $E = E_1 + 2 . E_2 = -2,65 - 2 . 99,14 = -200,94$ eV

2- Deducting the energy of first ionization :

During the reaction: Li ⟶ Li$^+$ + e$^-$;

First ionization energy : $E_{I-1} = -E_1 = 5,75$ eV.

Chapter V:

Chemical bonds

Introduction

Atoms are the building blocks of molecules. Atoms can join together to form molecules, in order to obtain the most stable electronic configuration.

In an atom, electrons close to the nucleus are much more stable (electrostatic stabilization) than electrons further away. It is therefore the outer electrons (peripheral or valence electrons) that are responsible for the chemical reactivity of atoms.

V-1- Covalent bonds in Lewis's theory

- ♣ In the Lewis representation, each atom is denoted by its atomic symbol.
- ♣ The Lewis representation is concerned only with the electrons of the outer layer.
- ♣ Valence electrons are represented by dots placed around the atoms. Lone electrons are called single electrons.
- ♣ Electrons can pair up with these single electrons to form electron doublets (electron pairs) in the form of a line.
- ♣ Single electrons try to pair up together so that the outer layer is as stable as possible, i.e. saturated with 8 electrons.
- ♣ The bond between two atoms, according to Lewis, is a pooling of two valence electrons. Once one or more electron pairs have been pooled, the atom acquires the configuration of the neighboring rare gas in ns2 np6 (Octet rule).

Example: Hydrogen molecule:

Each atom is made up of a proton (with a positive charge) around which an electron (with a negative charge) gravitates. There is a force of attraction between the proton and the electron belonging to the same atom. These same elements are also attracted by those of the neighboring atom.

$$H\bullet \ \bullet H$$

The two electrons are pooled and lose their belonging to one atom or the other. They form an electron pair. As a result, each 'H' atom is surrounded by two electrons and has reached the more stable configuration of Helium (the neighboring rare gas).

$$H - H$$

This pooling is called a covalent bond.

V-1-1- Valence layer

An atom's valence (or peripheral) layer is its last partially or completely filled electronic layer. It is characterized by the highest principal quantum number 'n'. It is the electrons in the valence layer, known as valence electrons, that are involved in chemical bonding. Notation from the electronic configuration of the rare gas preceding the atom directly highlights the valence electrons.

Example:

$^{17}Cl : 1s^2\ 2s^2\ 2p^6/3s^2\ 3p^5$; $^{17}Cl : [Ne]\ 3s^2\ 3p^5$.
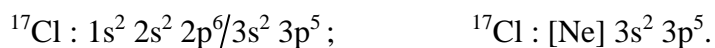
The last occupied layer is the layer with a principal quantum number equal to 3. The chlorine atom therefore has 7 valence electrons.

To facilitate the representation of chemical bonds, we use symbols that show only the valence electrons (Lewis symbols). These are identical for all elements in the same group of the periodic table.

V-1-2- Different types of bonds

V-1-2-1- Covalent bonds

A single covalent bond is one in which two single electrons are shared by two atoms. The pooled electrons belong to both atoms at the same time, corresponding to a gain of one electron for each atom. The covalent bond helps to hold the two atoms together, in a very strong way: the covalent bond is called a strong bond because it takes a lot of energy to break it. It is represented by a line.

If two atoms share a single covalent bond, it's called a single bond. If two atoms share two covalent bonds, they're called double bonds; if they share three covalent bonds, they're called triple bonds. Double bonds are stronger and more stable than single bonds. Triple bonds are even more stable.

Examples:

$HCl \longrightarrow$ H• •Cl: $\longrightarrow$ H — Cl

$N_2 \longrightarrow$:N: :N: $\longrightarrow$ N $\equiv$ N

$CH_4 \longrightarrow$ H ••C•• H $\longrightarrow$ H — C — H (with H above and below C)

$O_2 \longrightarrow$:O: :O: $\longrightarrow$ O = O

$CO_2 \longrightarrow$:O: :C: :O: $\longrightarrow$ O = C = O
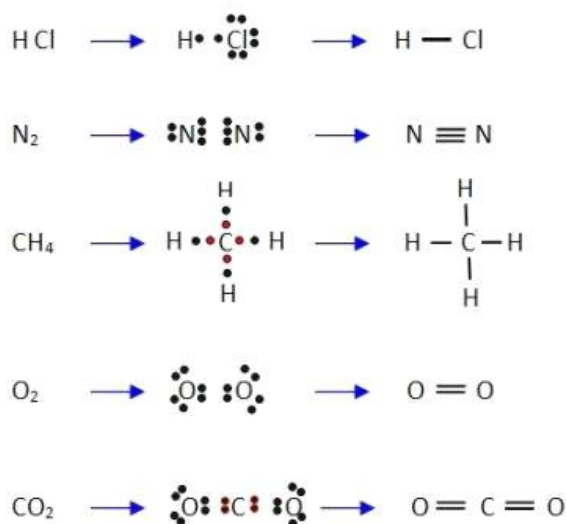
V-1-2-2- Dative bonding

A dative bond, (coordination covalent bond) is a description of the covalent bond between two atoms for which the two electrons shared in the bond come from the same atom. Dative bonds are evoked when a Lewis base (electron donor) provides a pair of electrons to a Lewis acid (electron acceptor) to give an addict. The process of forming a dative bond is called coordination. The electron donor acquires a positive charge, while the electron acceptor acquires the negative charge.

$$A \longleftarrow B \longrightarrow A - B$$
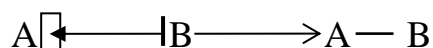
Examples :

  #   Hydronium ion H_3O^+

  #   Ammonium ion (NH_4):
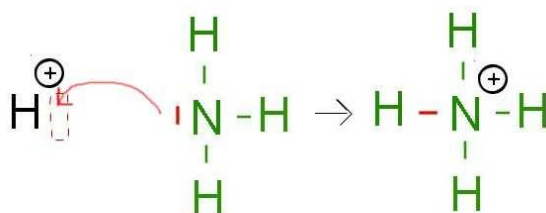
V-1-2-3- Ionic bonding

An ionic bond is a bond that can be formed by a pair of atoms with a large difference in electronegativity, typically between a non-metal and a metal. The metal donates one or more electrons to form a positively charged ion. The non-metal captures these electrons to form a negatively charged ion. The two ions formed often have a rare-gas electronic configuration. The bond results from the attraction between the cation derived from the metal and the anion derived from the non-metal.

Examples:

- Ionic bonding of sodium chloride (Na Cl) :

- Ionic bonding of magnesium dichloride (Mg Cl$_2$) :
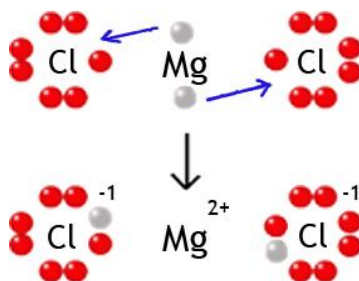
V-1-2-4- Polarized bonding

A single covalent bond between two atoms is said to be polarized if the two shared electrons are not equally distributed between the atoms.

One of the atoms in the bond exerts a stronger attraction on the shared pair of electrons, so the zone in which they move is closer to it: statistically, the electrons have a higher probability of being close to the more electronegative atom.

The influence of atoms on the bonding doublet is expressed in terms of electronegativity: the higher the electronegativity, the stronger the attraction. A difference in electronegativity between 0.4 and 1.7 is generally considered to be associated with a polarized bond.

Examples:

- Carbon - chlorine bond:

$$\chi = 3.16 \quad \overset{\delta^+}{C} - \overset{\delta^-}{Cl} \quad \chi = 3.16$$

- Dihydrogen sulfide:
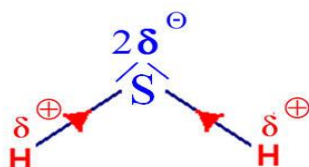
V-1-3- Lewis's diagram of molecules and molecular ions

* Duet and octet rule

Atoms tend to seek maximum stability and try to acquire a complete electronic layer;

Atoms tend to have the electronic structure of the neighboring noble gas.

To respect the duet or octet rule, an atom can gain or lose electrons by transforming itself into an ion, but it can also establish a covalent bond with another atom.

The Lewis representation shows the sequence of atoms, the covalent bonds between them and the non-bonding doublets.

The methods to be followed are:

- Dissociate all atoms;
- Give the electronic configuration of all separated atoms;
- Find out how many covalent bonds each atom must make;
- Sum up all external electrons;
- Calculate the number of doublets to be distributed over the molecule by dividing the number of external electrons by two;
- Divide the doublets in the molecule into binding doublets (covalent bonds) or non-binding doublets.

Examples:

Water molecule (H_2O):

$_1$H : $1s^1$

$1s^1$

H — $\overline{\underline{O}}$ — H

$_8$O: $1s^2\,2s^2\,2p^4$

Couche de valence $2s^2$ $2p^4$

* Aluminum tetra fluorine molecule (Al F$_3$) :

$_9$F : $1s^2\,2s^2\,2p^5$

$2s^2$ $2p^5$

$_{13}$Al : $1s^2\,2s^2\,2p^6\,3s^2\,3p^1$

$3s^2$ $3p^1$ $3s^0$ $3p^3$

$|\overline{F}|$

$|\overline{F}$ Al $\overline{F}|$
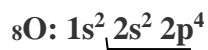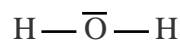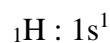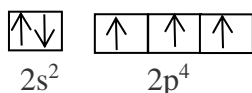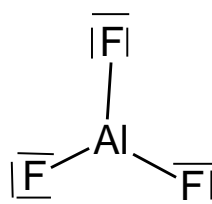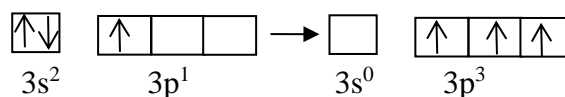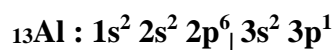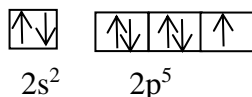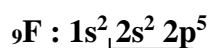
Examples:

❖ The chlorite ion ClO_2^-

$_{17}$Cl : $1s^2\,2s^2\,2p^6\,3s^2\,3p^5$ $|\overline{\underline{Cl}}\bullet$

$_8$O : $1s^2\,2s^2\,2p^4$ $\bullet\overline{\underline{O}}\bullet$

$|\overline{\underline{O}}\!\!-\!\!\overline{\underline{Cl}}\!=\!\overline{O}\rangle$
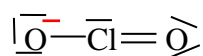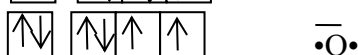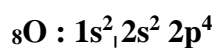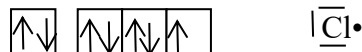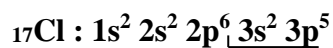
❖ The chlorate ion ClO_3^-

$|\overline{\underline{O}}$⁻

$\langle\overline{O}\!=\!Cl\!=\!\overline{O}\rangle$
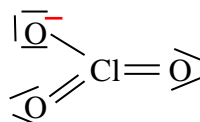
V-2- Polarized covalent bonding

A single covalent bond between two atoms is said to be polarized if the two shared electrons are not equally distributed between the atoms.

One of the atoms in the bond exerts a stronger attraction on the shared electron pair, so the zone in which they move is closer to it: statistically, the electrons have a higher probability of being close to the more electronegative atom.

In the most frequent case, the electronegativities are different and the result is a bond that is more or less ionic and more or less covalent - an intermediate situation.

The various possible ways of determining the polarization of a bond are:

♦ Calculating the difference in electronegativity between the two atoms ($0,4< |\Delta\chi| <1,7$) ;

♦ Verification of the presence of partial charges associated with the bonded atoms;

♦ Verification that the bond is associated with a non-zero dipole moment;

♦ Verification that the probability of the presence of shared electrons is greater near one of the atoms in the bond than near the other.

Formal charges: a formal charge 'q' carried by an atom in a molecule or ion (oxygenated, halogenated) is defined by :

$$q = v \text{ - e - d}$$

- Where: v is the number of electrons of the isolated atom ;

     e is the number of electrons in the atom participating in Lewis bonds;

     d is the number of electrons in the free doublets carried by the atom.

Note:

- In molecules of the same atoms (H_2, Cl_2, O_2...), the bonding doublet is shared between the two atoms of the bond ($\mu = 0$).

- In molecules of different atoms (HCl, H_2O...), the doublet is poorly shared, as one of the carbons is more electronegative than the other. The bond is said to be polar (it has a dipole moment).

Example: H — Cl ; $H^{\delta+} \longrightarrow Cl^{\delta-}$

V-2-1- Dipolar moment

In the case of two identical but opposite charges, respectively '+q' and '-q', separated by a distance 'd', the dipole moment is described by the vector:

$$\boxed{\mu = q \cdot d}$$

With :
$$\left.\begin{array}{l} +q = +\delta.e \\ -q = -\delta.e \end{array}\right\} \Longrightarrow \mu = |\delta|.e.d \qquad \boxed{\mu = |\delta|.e.d}$$

'e' s the electron's elementary charge, which is equal to $1{,}602.10^{-19}$ C.

* Dipole moment units

In the SI system, the unit of dipole moment is the coulomb x meter (C.m). The Debye (D) is also used, with:

$$\boxed{1D = 3.33 \times 10^{-30} \text{C.m}}$$

Note:

The dipole moment of a polyatomic molecule is the vector sum of the bond dipole moments, as shown below:
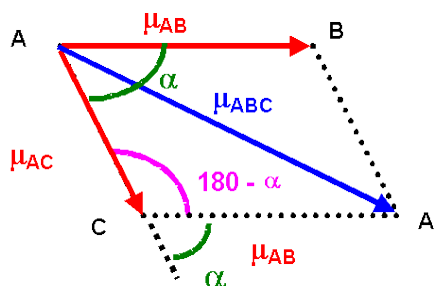
Example:

The dipole moment of the C-O bond is $\mu_{C\text{-}O} = 1{,}2$ D, $d_{C\text{-}O} = 143$ pm $= 143.10^{-12}$ m.

$$\mu_{C\text{-}O} = q.d = \delta.e.d \Leftrightarrow \delta = \mu_{C\text{-}O}e.d$$

$$\delta = 1{,}2 \cdot 3{,}336.10^{-30}.1{,}6.10^{-19}.143.10^{-12} = 0{,}174 \Longrightarrow \delta = 17{,}4\ \%$$

$$\overset{+17.4 \qquad -17.7}{C \rule[0.5ex]{2em}{1.5pt} O}$$
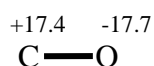
V-2-2- The partial ionic character of the bond

The ionic character of a bond is calculated according to the following relationship:

$$\boxed{\%\ \text{ionic} = 100\,\frac{\mu_{real}}{\mu_{theoretical}}}$$

Where: μ_{real} is the measured dipole moment;

$\mu_{theoretical}$ is that which the bond would have with +q and -q.

Note:

If the ionicity is greater than 50%, the bond is considered ionic and if it is less than 50%, it is considered covalent.

Example: Measuring the dipole moment of water:

The measured dipole moment of the water molecule is 1.84 D. The molecule has two polarized bonds separated by an angle α=105°.

So: $\mu_{H2O} = 2\,\mu_{OH}\,.\cos(105°/2) \implies \mu_{OH} = \dfrac{\mu_{H2O}}{2\cos\frac{105}{2}} \implies \mu_{OH} = 1.52$ D

V-3- Geometry of molecules

Canadian chemist R.J Gillespie developed the theory known as VSEPR:

Valence **S**hell **E**lectron **P**air **R**epulsion: Distribution of valence electron pairs around the central atom.

The molecule is symbolized by: A Xn Ep
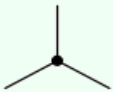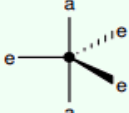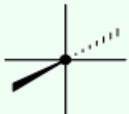
Where: A is the central atom,

X is the ligand (any atom bonded to A); n is the number of bonds;

E is the free electron doublet; p is the number of free electron doublets.

Knowing that the electron doublets in the valence layer repel each other, we can then predict the geometry of the molecule from a Lewis diagram.

The sum (n+ p), called the total number of doublets, provides information on the basic geometry of the molecule.

n+p	Electron Pair Arrangement		Molecular Shape		Examples
2		linear 180°	AX_2	linear	$BeCl_2$, CO_2
3		trigonal planar 120°	AX_3	trigonal planar	BCl_3, CH_3^+
			AEX_2	bent	$SnCl_2$, NO_2^-
4		tetrahedral 109.5°	AX_4	tetrahedral	CH_4, PO_4^{3-}
			AEX_3	pyramidal	NH_3, ClO_3^-
			AE_2X_2	bent	H_2O, SeF_2
5		trigonal bipyramidal 120° & 90°	AX_5	trig bipyramid	PF_5, $SeCl_5^+$
			AEX_4	"see saw"	SF_4, BrF_4^+
			AE_2X_3	T-shaped	ClF_3, XeO_3^{2-}
			AE_3X_2	linear	XeF_2, ICl_2^-
6		octahedral 90°	AX_6	octahedral	SF_6, PCl_6^-
			AEX_5	square pyramid	BrF_5, SF_5^-
			AE_2X_4	square planar	XeF_4, IF_4^-

(A = central atom, X = terminal atom, E = lone pair)

Example:

⬧ Compounds AXn :
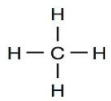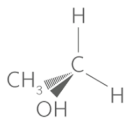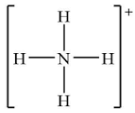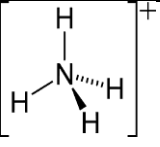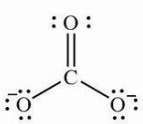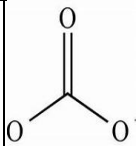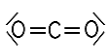
Consider the methanal molecule (CH_2O), shown opposite:

The central atom (A) is the carbon atom 'C'.

The bonded atoms 'X' are H, H and O. So n = 3.

The structure of methanal is therefore AX_3.

Example:

Compounds	External electron number	Lewis model	Geometry
CH_4 Methane	C: 4 external electrons H: 1 external electron $4 + (1).4 = 8$ e- 4 bonding doublet	H—C—H (with H above and below)	Tetrahedral structure molecule type: AX_4 109° angles
NH_4^+ Ammonium ion	N : 5 external electrons H : 1 external electron $5+(1).4-1 = 8$ e⁻ 4 bonding doublet	[H—N—H]⁺ (with H above and below)	Tetrahedral structure molecule type: AX_4 109° angles
CO_3^{--} Carbonate ion	C : 4 external electrons O : 6 external electrons $4 + (6).3 +2 = 24$ e⁻ 4 bonding doublets, 8 non-bonding doublets	:O: ‖ C / \ :Ö: :Ö:⁻	Tetrahedral structure molecule type: AX_3 120° angles
CO_2 Carbon dioxide	C : 4 external electrons O : 6 external electrons $4 + (6).2 = 16$ e⁻ 4 bonding doublets, 4 non-bonding doublets	⟨Ö=C=Ö⟩	Linear structure Molecule type: AX_2 180° angles

➕ Compounds AXn Ep

Consider the hydronium ion (H_3O^+):
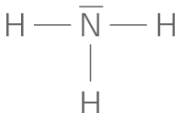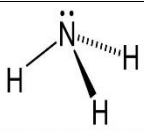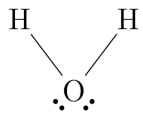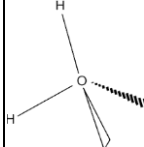
The central atom (A) is the oxygen atom O ;

The bonded atoms (X) are H, H and H. So n = 3 ;

There is a non-bonding doublet 'E' attached to the central atom. Therefore p = 1 ;

The structure of the hydronium ion H_3O^+ is therefore AX_3E.

Example:

Compounds	External electron number	Lewis model	Geometry
NH₃ Ammonia	N: 4 external electrons H: 1 external electron 5 + (1).3 = 8 e- 3 bonding doublet, 1 non- bonding doublets		Pyramidal structure with triangular base Molecule type: AX_3E_1
H₂O Water	H : 1 external electrons O : 6 external electrons (1).2+6 = 8 e⁻ 2 bonding doublets 2 non- bonding doublets		Bent structure Molecule type: AX_2E_2 104° angles

V-4- Chemical bonds in the quantum model:

As for isolated atoms, a molecular Schrödinger equation can be written for molecules. Solving this equation leads to molecular wave functions (or molecular orbitals) whose squares represent the probability of electron presence. This resolution is rigorously possible only in the simplest case, that of the molecular ion H_2^+. For more complex molecules, approximations are used.

V-4-1- Molecular orbital theory, LCAO method:

Principle of the LCAO method Linear Combination of Atomic Orbitals :

The Ψ solutions of the Schrödinger equation for an A-B molecule are linear combinations of the atomic orbitals corresponding to the valence electrons of the separated A and B atoms.

$$\Psi = a\,\Psi_A + b\,\Psi_B$$

The coefficients 'a' and 'b' must satisfy two conditions: the energy associated with the wave function must be minimal and the probability of finding the electron in space must be equal to 1.

This method will be applied to describe the H₂ dihydrogen molecule.

The atomic orbitals to be considered are the two 1sA and 1sB orbitals of hydrogen atoms A and B. The functions are denoted ΨA and ΨB

In the C.L.O.A method, the molecular orbital Ψ_{AB} is considered to be a linear combination of these two atomic orbitals Ψ_A and Ψ_B.

$$\Psi_{AB} = a\ \Psi_A + b\ \Psi_B$$

In reality, only the square of the wave function has any physical meaning (probability of presence).

$$\Psi_{AB}^2 = (a\ \Psi_A + b\ \Psi_B)^2 = a^2\ \Psi_A^2 + 2\ a.b\ \Psi_A\ \Psi_B + b^2\ \Psi_B^2$$

This expression contains a term where only atom A appears A $(a^2\ \Psi_A^2)$, a term where only atom B appears $(b^2\ \Psi_B^2)$ and a mixed term where both atoms A and B appear $(2\ a.b\ \Psi_A\ \Psi_B)$.

* The $a^2\ \Psi_A^2$ term corresponds to the probability of finding the electron very close to nucleus A.

* The term $b^2\ \Psi_B^2$ corresponds to the probability of finding the electron very close to nucleus B.

* The term $2\ a.b\ \Psi_A\ \Psi_B$ corresponds to the probability of finding the electron neither very close to nucleus A, nor very close to nucleus B, i.e. between the two atoms A and B, which corresponds to the formation of the chemical bond between these two atoms as in the Lewis model.

For reasons of symmetry, atoms A and B play the same role, so there's no reason for the electron to be closer to A than to B, or vice versa. The probability of finding the electron near A is therefore equal to the probability of finding it near B. $a^2\ \Psi_A^2 = b^2\ \Psi_B^2$ Furthermore, in this case, the Ψ_A and Ψ_B orbitals are totally identical and there is no need to distinguish between them, so we have:

$a^2 = b^2$ soit b = +a, /- a. There are therefore two solutions for Ψ_{AB} :

$\Psi_{AB} = a\ \Psi_A + a\ \Psi_B = a\ (\Psi_A + \Psi_B)$; or, $\Psi_{AB} = a\ \Psi_A - a\ \Psi_B = a\ (\Psi_A - \Psi_B)$.

These two expressions are simultaneously solutions of Schrödinger's equation. Two molecular orbitals are thus obtained from the two atomic orbitals.

These two molecular orbitals are different:

* The function $(\Psi_A + \Psi_B)$ is called bonding, as it corresponds to an increase in the probability of the electron's presence between atoms A and B, thus creating the bond.

V-4-1-1- Formation and nature of bonds

❖ **Axial overlap: sigma bond**

The 'σ' sigma bond is a covalent chemical bond created between two atoms by axial overlapping of orbitals. These can be 's' or hybridized 's' orbitals, but also p_z and dz^2 orbitals. The lobes of the two interacting orbitals point towards each other.

'σ' bonds are the strongest covalent bonds, as the axial overlap is greater than the lateral overlap, and only one 'σ' bond can exist between two atoms.
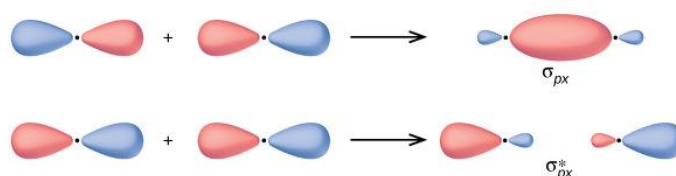
❖ **Axial overlap: pi bond**

The pi'π' bond is a covalent chemical bond created between two atoms by overlapping secondary quantum number ($l \geq 1$) orbitals (p, d... orbitals). The overlap is lateral, i.e. the two lobes of the two interacting orbitals are parallel. Moreover, there is no electron in the bonding axis.
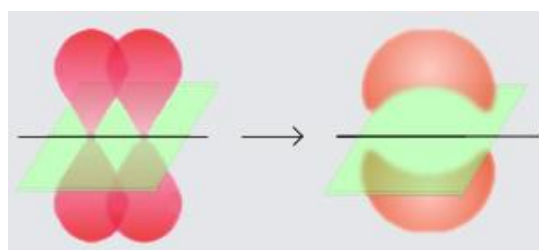
The π-bond is present in alkenes and alkynes in particular: its presence prevents free rotation around this bond, as it leads to molecular rigidity.

V-4-1-2- Aspect énergétique

Complete resolution of the Schrödinger equation leads to the energy values of the two molecular orbitals: the energy of the binding orbital is lower than that of the separate atoms, corresponding to stabilization. Conversely, the anti-bonding orbital has a higher energy, corresponding to destabilization.
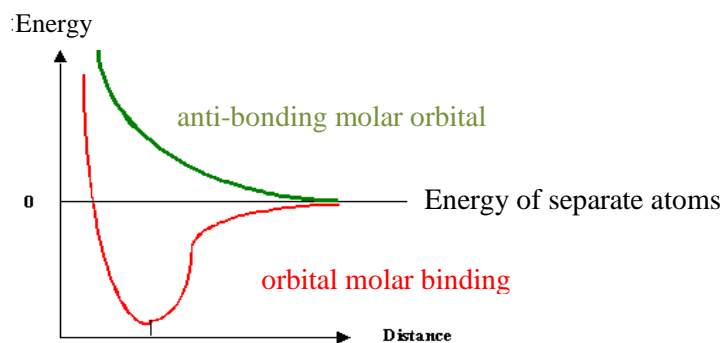
Ultimately, by overlapping, the two molecular orbitals of the same energy give rise to two molecular orbitals of different energies, one stabilized binding and the other destabilized antibonding. It can be shown and accepted that the destabilization of the anti-bonding orbital is greater than the stabilization of the bonding orbital. By convention, orbitals are designated by the letter 'σ' or 'π', and anti-bonding orbitals are superscripted with a star '*'.

Example: The case of hydrogen (H_2)

The atomic orbitals (O.A) to be considered are the '1s' orbitals.
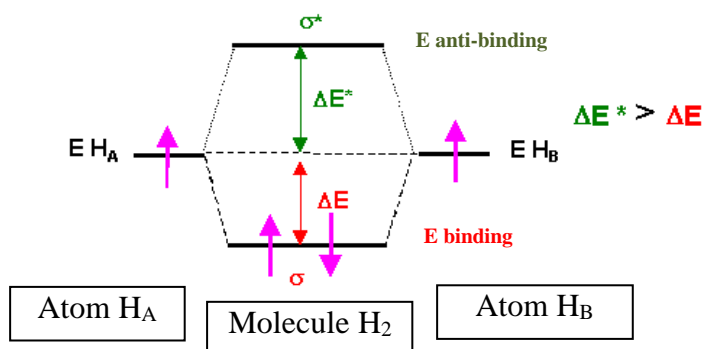
V-4-2- Generalization to homo and hetero-nuclear diatomic molecules

V-4-2-1- Energy diagram of molecules

a- Homo-nuclear diatomic molecules

*Filling molecular orbitals:

To achieve the correct bonding order (LO), electrons must be filled from the lowest to the highest energy levels, in accordance with the Pauli Principle and the Hund Principle.

Energy levels towards the highest, in accordance with Pauli's Principle and Hund's Principle.

Note:

* Electrons in non-bonding molecular orbitals (MOs) should not be counted;

* For an AB diatomic molecule, the least electronegative element is placed on the left;

* As the LO increases, the bond energy increases and the bond length decreases.

$$OL = 1/2 \ (n - n^*)$$

For the case of homo-nuclear diatomic molecules, the results obtained for H2 are generalizable.

Examples:

* **Bore molecule (B₂) :**

$_5B : 1s^2 \ 2s^2 \ 2p^1 \rightarrow$ 3 valence electrons; therefore B_2 has 6 valence electrons.

OL = 1/2 (n - n*) = 1/2 (4 - 2) = 1

The energy diagram for the B_2 molecule is similar to that for H_2

Electronic configuration:

$(2 \ \sigma_s)^2 \ (2 \ \sigma_s{}^*)^2 \ (2 \ \pi_x)^1 \ (2\pi_y)^1$
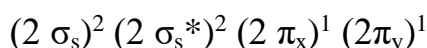
* The Oxygen molecule (O₂) :

$^8O : 1s^2 \ 2s^2 \ 2p^4 \rightarrow$ 6 valence electrons; therefore O_2 has 12 valence electrons.

OL = 1/2 (n - n*) = 1/2 (8 - 4) = 2

Electronic configuration:

$(2 \ \sigma_s)^2 \ (2 \ \sigma_s{}^*)^2 \ (2 \ \sigma_{pz})^2 (2 \ \pi_{x, \ y})^4 \ (2 \ \pi_x{}^*)^1 \ (2 \ \pi_y{}^*)^1$
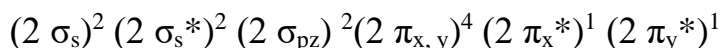
* **The case of Helium (He₂) :**

$_2He : 1s^2$; The diagram is identical to that obtained for H_2.

OL = 1/2 (2 - 2) = 0

The bond index is zero, meaning that no bond is formed between the two helium atoms. The molecule cannot therefore exist.
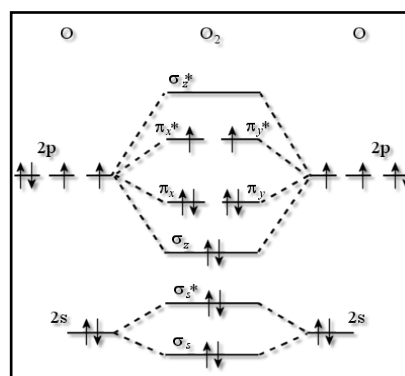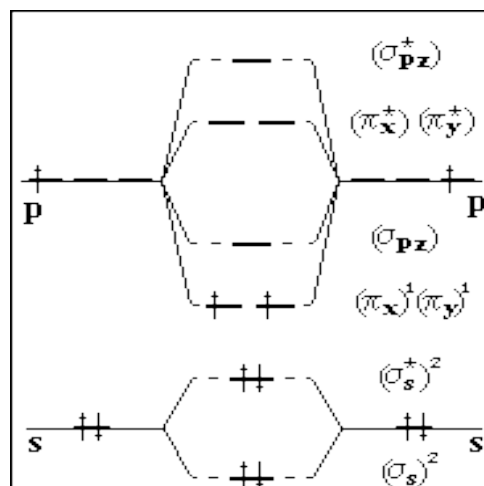
b- Heteronuclear diatomic molecules

A heteronuclear diatomic molecule is a molecule composed of two different atoms. For such a molecule, the contributions of the atomic orbitals will no longer be identical. The lowest-energy atomic orbital will have a greater contribution to the bonding molecular orbital, and the highest-energy atomic orbital will have a greater contribution to the anti-bonding molecular orbital.

Example:

* The hydrogen fluoride molecule (HF) :

In the case of this molecule, only the 1s level of 'H' and the 2p level of 'F', whose energies are close, participate in the formation of the bond. The atomic orbital of hydrogen can only co-axially overlap a single 2p orbital of the fluorine atom F, which is 2pz

V-4-2-2- Binding order

On an atomic scale, the bond order (or bond index) is the number of electron pairs linking two atoms. For example, in the case of dinitrogen (N≡N), the bond order is 3 because there are 3 bonds connecting the two atoms. In molecular orbital theory, bond order is defined as half the difference between the number of bonding electrons and the number of antibonding electrons.

Bond order = [(number of electrons in bonding molecular orbitals) - (number of electrons in antibonding molecular orbitals)] /2.

- The higher the bonding order, the more stable the molecule.
- If the bonding order is zero, the molecule cannot be formed.

V-4-2-3- Magnetic properties

Molecular symmetry influences the magnetism of the molecule. Magnetic susceptibility depends in particular on the number of unpaired electrons (single electrons).

A molecule containing only paired electrons (in doublets) is said to be diamagnetic (it orients itself in the opposite direction to the external magnetic field applied to it).

If there are unpaired electrons, the molecule is paramagnetic (oriented in the direction of the external magnetic field applied to it).

Example: F_2 is diamagnetic, while O_2 and NO are paramagnetic.

V-4-2-4- Molecule stability

In molecular geometry, bond length is the average distance between the nuclei of two

atoms linked by a chemical bond. This length is directly related to bond order: the greater the number of electrons involved in the formation of a bond, the shorter it will be. It is also inversely proportional to the energy of the bond: the stronger the bond, the shorter it is. In the case of a bond between two identical atoms, this length is twice the covalent radius of the atom in question.

- The molecule is increasingly stable as the energy of the bond increases;
- The molecule's stability increases with decreasing bond length.

V-4-3- Polyatomic molecules

The case of molecules with more than two atoms is more complex than that of diatomic molecules. The main additional difficulty is to bring molecular geometry into play. To overcome this difficulty, we turn to the notion of hybridization of atomic orbitals. A hybrid bond is one that is formed from other, different atomic orbitals. The shape of the molecule is characterized by the type of hybridization and therefore by its geometry (the angles of the central atom, and the equality of the bonds).

Chapter VI:

Radioactivity-nuclear reactions

Introduction

Radioactivity is the physical phenomenon whereby unstable atomic nuclei spontaneously decay into more stable atoms, simultaneously emitting particles of matter (electrons, helium nuclei, neutrons, etc.) and energy (photons and kinetic energy). There are two types of radioactivity:

VI-1- Natural radioactivity

Natural radioactivity is that which occurs naturally in nature.

When radioactive nuclei decay, high-energy ionizing radiation is emitted. Radioactive nuclei (whatever they may be) can evolve in only three types of radioactivity:

- ✓ Alpha (α) radioactivity, or the emission of alpha adiation;
- ✓ Beta (β) radioactivity, or emission of beta radiation;
- ✓ Gamma (γ) radioactivity, or emission of gamma radiation;

All three types can occur simultaneously or in cascade. Whatever the type of radiation considered, several conservation laws are satisfied:

- ◆ Conservation of charge: $Z_{before} = Z_{after}$;
- ◆ Conservation of nucleons: $A_{before} = A_{after}$;
- ◆ Conservation of energy: $E_{before} = E_{after}$.

VI-1-1- Alpha disintegration

Alpha radiation occurs when the decay of an unstable heavy nucleus (N+Z > 200) is accompanied by the emission of an alpha particle (or helium nucleus).
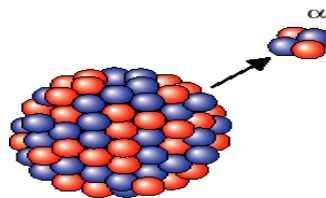
Assessment equation $^{A}_{Z}X \;\rightarrow\; ^{A-4}_{Z-2}Y \;+\; ^{4}_{2}\text{He} \;+ \text{(radiation } \gamma\text{)}$

Example: $^{238}_{92}U \;\rightarrow\; ^{234}_{90}Th \;+\; ^{4}_{2}\text{He}$

These reactions produce nuclides with a mass number equal to or very close to that of the target nuclide, and the nuclides formed are either stable or radioactive.

The 'α' particles are emitted with very high energies (between 4 and 8 MeV), specific to the emitting radionuclide.

VI-1-2- Beta minus disintegration (β^-)

Beta minus decay is a radioactivity characterized by the expulsion of an electron from a nucleus, β^- results from the transformation of a neutron into a proton and the release of a negative electron. It is a reaction that concerns neutron-rich atoms.

$$\substack{1\\0}n \rightarrow \substack{1\\1}P + \substack{0\\-1}e \quad \text{in general} \quad \substack{A\\Z}X \rightarrow \substack{A\\Z+1}Y + \substack{0\\-1}e$$

Example : $\quad \substack{14\\6}C \rightarrow \substack{14\\7}N + \substack{0\\-1}e$
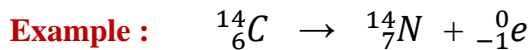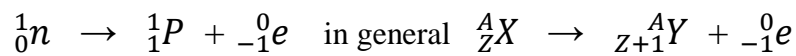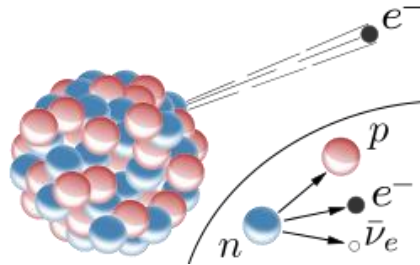
VI-1-3- Beta plus disintegration (β^+)

Radionuclides with too many protons (or too few neutrons) emit a positron ($\substack{0\\1}e$), so, beta decay plus, results from the transformation of a proton into a neutron and the release of a positive electron and photons.

$$\substack{1\\1}P \rightarrow \substack{1\\0}n + \substack{0\\-1}e \quad \text{in general} \quad \substack{A\\Z}X \rightarrow \substack{A\\Z-1}Y + \substack{0\\1}e$$
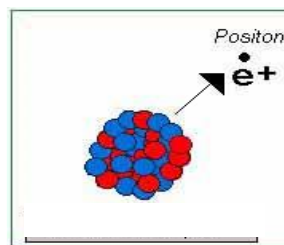
The particle denoted ($\substack{0\\1}e$), is a positron (or positron or anti-electron): with the same mass as the electron but the opposite charge.

Example: $\quad \substack{14\\8}O \rightarrow \substack{14\\7}N + \substack{0\\1}e$
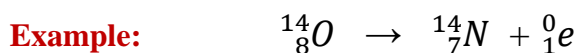
VI-1-4- Gamma disintegration

During alpha or beta radioactive decay, the unstable nucleus gives rise to a different nucleus. Very often, the decayed nucleus is in a momentarily unstable state, called an excited state (*). It has excess energy. The return of this excited nucleus to its stable ground state is achieved by the release of energy in the form of radiation of nuclear origin.

$$_{Z}^{A}X^* \rightarrow \qquad _{Z}^{A}X \quad + \quad \gamma$$

Excited nucleus   Stable nucleus   Radiation

Example: $_{28}^{60}Ni^* \rightarrow \ _{28}^{60}Ni \ + \ \gamma$
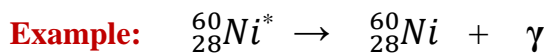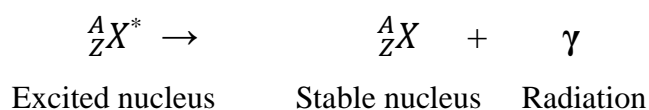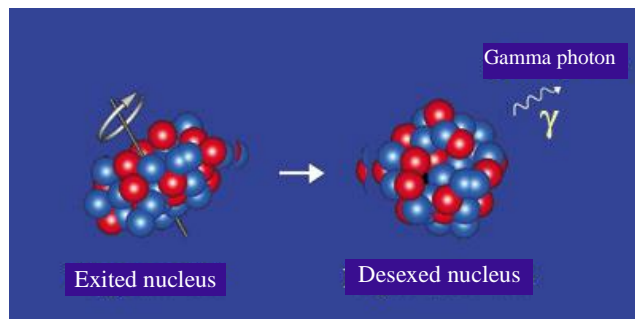
Note:

All disintegrations are accompanied by a release of energy: this energy is contained in the emitted radiation and transferred to the body that absorbs it (ionization of matter, destruction of chemical bonds, local heating, etc.).

VI-2- Artificial radioactivity and nuclear reactions

Artificial radioactivity is radioactivity induced by human activity using a particle gas pedal or nuclear reactor. It includes all the transmutation phenomena of radioisotopes created artificially by bombarding stable elements (aluminum, beryllium, iodine, etc.) with various particle beams (neutron, proton, α particle, deuteron).

VI-2-1- Transmutation

This is the modification of the number of nucleons in a nucleus. This can be done by bombarding the nucleus with a neutron or an alpha particle. The result is a new nucleus with a nucleon number close to that of the original nucleus.

$$_{7}^{14}N \ + \ _{2}^{4}He \rightarrow \ _{8}^{17}O + \ _{1}^{1}H$$
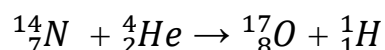
This reaction can be written in abbreviated notation: $_{7}^{14}N \ (\alpha, P) \ _{8}^{17}O$

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}H$$
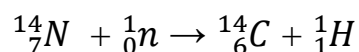
The notation is : $^{14}_{7}N$ (n , P) $^{14}_{6}C$

VI-2-2- Nuclear fission

Nuclear fission is the phenomenon whereby a heavy atomic nucleus is split into two lighter nuclides. This nuclear reaction is accompanied by the emission of neutrons and a significant release of energy.
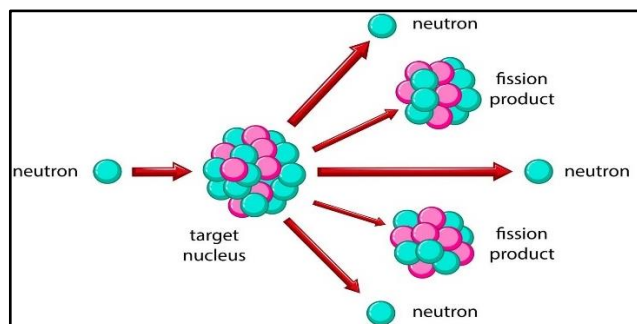
Example :

A ^{235}U nucleus is bombarded by a neutron, producing a ^{236}U nucleus in a highly excited (unstable) state. This nucleus undergoes fission, forming two fragments. The overall fission reaction is then:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{236}_{92}U \rightarrow ^{140}_{54}Xe + ^{94}_{38}Sr + 2^{1}_{0}n$$
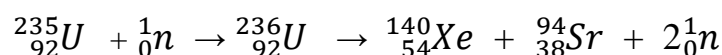
Note: Fission is a controlled chain reaction in nuclear reactors, not in an atomic bomb.

VI-2-3- Nuclear fusion

Nuclear fusion is the combination of two light nuclei, fusing into a heavier one. It occurs at extremely high temperatures, as the nuclei need sufficient energy to collide and fuse. This kind of nuclear reaction occurs in nature: at the heart of stars, for example, two hydrogen nuclei fuse to form a deuterium nucleus, then two deuterium nuclei fuse to form helium. Nuclear fusion releases enormous amounts of energy, greater than that of fission.
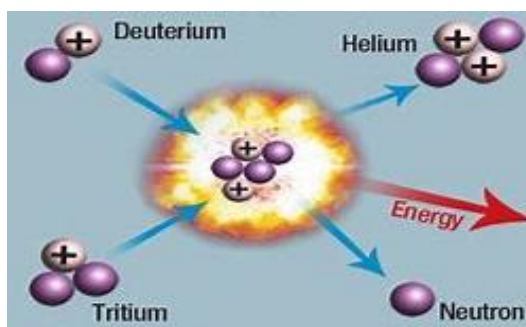
VI-3- Kinetics of radioactive decay

VI-3-1- Law of radioactive decay

The aim is to determine the statistical evolution, over time, of the number of radionuclides of the same type $_{Z}^{A}X$ contained in a sample.

Initial condition:

➕ At time $t = 0$, the sample contains N0 radionuclides;

➕ At time t, there are N radionuclides.

We can then write:

$$dN = - N \cdot \lambda \, dt \qquad .$$

Where: λ is the decay constant;

dN is the number of nuclei that decay over the time interval dt.

We therefore have the following differential equation: $\frac{dN}{N} = - \lambda \, dt$

To solve this differential equation, we determine the primitive to the left and right of the equality sign of the equality sign.

Where: λ is the decay constant.

We therefore have the following differential equation:

$$\frac{dN}{N} = - \lambda \, dt \implies \int_{N_0}^{N_t} \frac{dN}{N} = - \lambda \int_0^t dt$$

We obtain: $\ln N_t - \ln N_0 = - \lambda \, t \implies \ln \frac{N_t}{N_0} = - \lambda \, t \implies \frac{N_t}{N_0} = e^{-\lambda \, t}$

The final relationship is then:

$$\boxed{N_t = N_0 \, e^{-\lambda \, t}} \quad \dots (1)$$
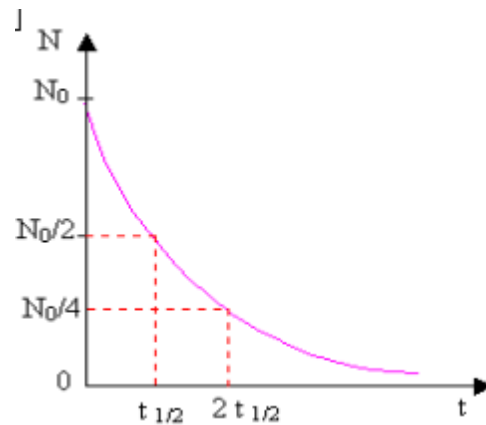
Equation (1) can be written in another form as a function of the mass of the radioactive element studied, since

In 1 mole of the element $\longrightarrow$ Avogadro number (N_A) of nuclei

In 'n' mol of the element $\longrightarrow$ N nuclei

$N = n \cdot N_A = \frac{m}{M} \; N_A$; from this relationship we can deduce that:

$N_t = \frac{m_t}{M} N_A$ and $N_0 = \frac{m_0}{M} \; N_A$; replacing these two relationships with eq (1),

we get :

$$m_t = m_0 \, e^{-\lambda \, t}$$

Where: n is the number of moles of the element;

m_t is the mass of the radioactive element at time t;

m_0 is the mass of the radioactive element at time t = 0.

VI-3-2- Radioactive constant

The radioactive constant 'λ' (or decay constant) is always greater than zero; is the constant characterizing the radioelement; its unit in S.I. is the inverse of the unit of time: s^{-1}, min^{-1}, h^{-1}, an^{-1}…).

$$\lambda = - \frac{1}{t} \; \ln \frac{N_0}{N_t}$$

VI-3-3- Radioactive activity

Radioactive activity 'A' is the number of radioactive nuclei decaying per second. It is also the number of particles emitted per unit of time.

$A = - \dfrac{dN}{dt}$; (The minus sign '$-$' denotes a decrease in the number of atoms as time goes by).

$A = -\dfrac{dN}{dt} = -\dfrac{d}{dt}(N_0\,e^{-\lambda t}) = \lambda.N_0\,e^{-\lambda t}$; $A_t = \lambda.N_t \implies A_0 = \lambda.N_0$

So : $\boxed{A_t = \lambda.N_0}$ and $\boxed{A_t = A_0\,e^{-\lambda t}}$

Unit of activity:

- ♥ Disintegration per second (d.p.s.) with: 1 d.p.s. = 1Bq (Bq is the becquerel),

- ♥ The curie (Ci); this corresponds to the activity of 1.0 gram of radium, and is worth **3,7.**10^{10} d.p.s.

VI-3-4-Radioactive period or half-life time

The radioactive period 'T' (half-life time, or ' $t_{1/2}$') of a radioelement is the time after which the number of nuclei 'N' is halved.

The half-life of radioactive nuclei can range from fractions of a second to billions of years. It is characteristic of a particular nuclide.

Examples:

$^{226}_{88}Ra(\alpha)$: T = 1590 years ; $^{238}_{92}U(\alpha)$: T = 4,5.10^9 years ;

$^{222}_{86}Rn(\alpha)$: T = 3,825 days ; $^{40}_{19}K(\alpha)$: T = 1,3.10^9 years ;

Neutron (unstable) : T = 702 seconds;   Proton (stable): T is infinite.

❖ Relationship between T and λ

At the half-life time, we have: $N_t = N_0/2$, so according to equ.1: $N_t = N_0\,e^{-\lambda t}$

We can write: $\dfrac{N_0}{2} = N_0 \implies \dfrac{1}{2} = e^{-\lambda t_{\frac{1}{2}}}$

We then obtain:

At half-life, we have: $N_t = N_0/2$, so according to equation.1 : $N_t = N_0\,e^{-\lambda t}$

We can write: $\dfrac{N_0}{2} = N_0\,e^{-\lambda t_{1/2}} \implies \dfrac{1}{2} = e^{-\lambda t_{1/2}}$

The result is: $\boxed{t_{1/2} = T = \dfrac{ln2}{\lambda}}$ and $\boxed{\lambda = \dfrac{ln2}{T}}$

VI-4- Application of radioactivity

VI-4-1- Tracers

Radiation can be used in a variety of ways:

As monitoring tools: once tracers (radioactive atoms) have been introduced into a medium, it is easy to detect the radiation they emit and track its fate (applications in medicine, science, the food chain, the environment, etc.);

Imaging: the attenuation of a beam as it passes through matter depends on the materials it passes through and their thickness (investigations in medicine, science, industry, etc.);

In treatment: the energy deposited by radiation in living matter can be significant and destroy organisms (treatment of tumors, destruction of bacteria, sterilization...).

VI-4-2- Nuclear arms

There are two types of bombs: A or atomic bombs, and H or hydrogen or thermonuclear bombs. Atomic bombs were the first nuclear weapons to be developed at the end of the Second World War. The core of an atomic bomb contains a sufficient quantity of fissile material for the development of an explosive chain reaction (uranium-235 or plutonium-239 at over 90%). The much more powerful H-bombs are based on the principle of nuclear fusion. Fusion reactions are triggered by the heat released by fissions.

Nuclear weapons release their energy in the form of blast energy, heat (fireball), visible light and ionizing radiation. A small bomb releases 50% of its energy by blast effect, 35% in the form of heat and the remaining 15% in the form of radiation.

VI-4-3- Energy source

Within the globe, fission radioactivity is the main source of heat. By heating magma, it drives volcanism and its greenhouse gas emissions. By liquefying the outer layer of the central core, it enables the movements that underpin the Earth's magnetism. This magnetic shield is essential to life on Earth, protecting it from deadly high-energy cosmic rays, particularly from the Sun.

In the Sun, the radioactive fusion of hydrogen and helium atoms heats its surface to 6,000°C. This enormous "black body" therefore radiates infrared, ultraviolet and a maximum of visible radiation. Received and filtered by the Earth's atmosphere, the Sun's radiation is essential to life. It is the basis of our climate.

VI-4-4- Dating ancient samples

VI-4-4-1- Dating in archaeology

Dating is a major issue in archaeology. It is a fundamental element in the study of an archaeological site: it enables us to locate the site within a given chronological period, to determine the duration of its occupation and the different phases of this occupation. Among dating methods, carbon-14 dating is by far the best known and most widely used in archaeology for over sixty years.

VI-4-4-2- Geological dating

Several radioactive elements can be used to date rocks. Take lead, for example. Lead isotopes 206, 207 and 208 come from the decay of uranium 238, 235 and thorium. Knowing the ratio of the number of lead atoms to the number of uranium nuclei, the date when the sample began to decay can be calculated. After a series of decays, each missing uranium nucleus gives rise to a lead nucleus.

VI-5- Dangers of radioactivity

Radioactivity, poorly controlled or used for non-peaceful purposes, can cause serious harm. For example, when alpha, beta and gamma particles pass through living matter, they cause ionization, or excitations of atoms that can lead to abnormal chemical reactions. A few hours or even years after exposure to radiation, secondary reactions can occur; fundamental macromolecules at cellular level (RNA, DNA) are affected, leading to the formation of cancers, and affecting the immune system. Morphological alterations are observed, including genetic effects; cells are destroyed or their division process altered. In the event of radioactive fallout, nuclides are absorbed by plants and find their way into the food chain.

As an indirect effect, radiation causes radiolysis of water (ionization of the water molecule), releasing free radicals, which are highly toxic chemical species. Fortunately, the body has repair capabilities. It can combat the destructive effects by eliminating the affected cells or rendering them inoperative. But if the doses received, however low, reach critical tissues, the damage becomes irreversible.

References

1- R. Ouahès et B. Dévallez, Chimie générale. Editions OPU - Alger, 1993.

2- S. Meziane. Chimie générale (structure de la matière). Edition BERTI- Alger, 2006.

3- Collection l'enseignement-chimique. Etude des liaisons chimiques (constituants de l'atome). Edition N°: 382, 1979.

4- Collection l'enseignement-chimique. Etude des liaisons chimiques (liaison chimique). Edition N° : 383, 1979.

5- Z. Sekkal. Atomes et liaisons chimiques. Editions OPU - Alger, 1986.

6- Sstudylibfr. Cours-Structure Atomique. studylibfr.com/doc/2516686

7- M. Fayard, Structure électronique atomes et molécules simples, Chimie physique, Edition HERMANN-Paris, 1969.

Appendix

Appendix 1: Physical constants and conversion factors

Name	Symbol	Value
Meter	M	
Nanometer	Nm	10^{-9} m
Angstrom	Å	10^{-10} m
Kilogram	Kg	
Atomic mass units	a.m.u. ou µ	$1,66 \ 10^{-24}$g
Liter	L	$1dm^3 = 1L$
Standard pressure	1 atm	101,3 kPa = 760. Torr = 760.mmHg
Standard temperature	C	32,0 °F = 0 °C = 273,15 K
Heat	Q	1 Cal = 4.184 J
Activation energy	E_a	kJ/mol
Specific heat of water (l)	C_p	4,18 J/g.°C
Specific heat of water (g)	C_p	2,02 J/g.°C
CONSTANTS		
Speed of light	C	$3,00 \times 10^{8}$ m/sec
Avogadro number	N_A	6.022×10^{23} particles
Universal gas constant	R	0,08206 L.atm/ mol.K 8,314 J / mol.K 2 cal / mol.K

Appendix 2: Periodic table of the elements

Appendix 3: Atomic element rays

Appendix 4: Electron affinity values (in eV)

H 0,75																	He
Li 0,62	Be											B 0,28	C 1,26	N	O 1,46	F 3,4	Ne
Na 0,55	Mg											Al 0,43	Si 1,39	P 0,75	S 2,08	Cl 3,61	Ar
K 0,5	Ca 0,02	Sc 0,19	Ti 0,08	V 0,53	Cr 0,68	Mn	Fe 0,15	Co 0,66	Ni 1,16	Cu 1,24	Zn	Ga 0,43	Ge 1,23	As 0,8	Se 2,02	Br 3,36	Kr
Rb 0,49	Sr 0,05	Y 0,31	Zr 0,43	Nb 0,89	Mo 0,75	Tc 0,55	Ru 1,05	Rh 1,14	Pd 0,56	Ag 1,3	Cd	In 0,38	Sn 1,11	Sb 1,05	Te 1,97	I 3,06	Xe
Cs 0,47	Ba 0,14	Lu 0,35	Hf 0,02	Ta 0,32	W 0,82	Re 0,15	Os 1,08	Ir 1,56	Pt 2,13	Au 2,31	Hg	Tl 0,38	Pb 0,36	Bi 0,94	Po 1,32	At 2,8	Rn
Fr 0,49	Ra 0,1	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	La 0,47	Ce 0,57	Pr 0,96	Nd 1,92	Pm	Sm	Eu 0,12	Gd	Tb 1,17	Dy 0	Ho	Er	Tm 1,03	Yb -0,02
**	Ac 0,35	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Appendix 5: Electronegativity values of elements (in eV)

H 2.1																	**He**
Li 1.0	**Be** 1.5											**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0	**Ne**
Na 0.9	**Mg** 1.2											**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0	**Ar**
K 0.8	**Ca** 1.0	**Sc** 1.3	**Ti** 1.5	**V** 1.6	**Cr** 1.6	**Mn** 1.5	**Fe** 1.8	**Co** 1.8	**Ni** 1.8	**Cu** 1.9	**Zn** 1.6	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8	**Kr** 3.0
Rb 0.8	**Sr** 1.0	**Y** 1.2	**Zr** 1.4	**Nb** 1.6	**Mo** 1.8	**Tc** 1.9	**Ru** 2.2	**Rh** 2.2	**Pd** 2.2	**Ag** 1.9	**Cd** 1.7	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5	**Xe** 2.6
Cs 0.7	**Ba** 0.9	**La** 1.1	**Hf** 1.3	**Ta** 1.5	**W** 1.7	**Re** 1.9	**Os** 2.2	**Ir** 2.2	**Pt** 2.2	**Au** 2.4	**Hg** 1.9	**Tl** 1.8	**Pb** 1.8	**Bi** 1.9	**Po** 2.0	**At** 2.2	**Rn** 2.4
Fr 0.7	**Ra** 0.7	**Ac** 1.1	**Unq**	**Unp**	**Unh**	**Uns**	**Uno**	**Une**									

Ce 1.1	**Pr** 1.1	**Nd** 1.1	**Pm** 1.1	**Sm** 1.1	**Eu** 1.1	**Gd** 1.1	**Tb** 1.1	**Dy** 1.1	**Ho** 1.1	**Er** 1.1	**Tm** 1.1	**Yb** 1.1	**Lu** 1.2
Th 1.3	**Pa** 1.5	**U** 1.7	**Np** 1.3	**Pu** 1.3	**Am** 1.3	**Cm** 1.3	**Bk** 1.3	**Cf** 1.3	**Es** 1.3	**Fm** 1.3	**Md** 1.3	**No** 1.3	**Lr**

Appendix 6: Description of a periodic table