الجمهورية الجزائرية الديمقراطية الشعبية
People's Democratic Republic of Algeria
وزارة التعليم العالي والبحث العلمي
Ministry of Higher Education and Scientific Research
جامعة محمد بوضياف – بالمسيلة
Mohamed BOUDIAF University – M'Sila

جامعة محمد بوضياف - المسيلة
Université Mohamed Boudiaf - M'sila
كلية التكنولوجيا
نيابة العمادة لما بعد التدرج والبحث العلمي
والعلاقات الخارجية

جامعة محمد بوضياف - المسيلة
Université Mohamed Boudiaf - M'sila
Faculty of Technology
Vice Deanship of Post-Graduation, Scientific Research and External Relations

رقم: 196/ ن.ع.ب.ع /ك.ت /2025

المسيلة في: 27 ماي 2025

مستخلص من محضر إجتماع المجلس العلمي لكلية التّكنولوجيا

رقم الدورة :25/03، المنعقد بتاريخ: 2025/05/27.

في يوم الثلاثاء السابع والعشرين من شهر ماي عام ألفين وخمسة وعشرين، وعلى الساعة الواحدة ونصف (13:30) بعد الزوال، إنعقد إجتماع للمجلس العلمي لكليّة التّكنولوجيا، في جلسة عادية بقاعة المناقشات بالكلية، ومن بين النقاط المطروحة للنقاش في جدول الأعمال:

المصادقة على تشكيل لجنة الخبراء للموافقة على المطبوعة البيداغوجية الجامعية

بعد الإطلاع على طلب الذي تقدمت به الأستاذة : **شتيوي سهيلة– أستاذ محاضر قسم أ** بالقاعدة المشتركة، بكلية التكنولوجيا بجامعة محمد بوضياف بالمسيلة للموافقة على المطبوعة البيداغوجية ، واستنادا للفصل الثاني للقانون الداخلي في مادتة الرابعة في فقرته الخاصة بسير المطبوعة والدروس على الخط، تمّ تقرير التّالي:

1– المصادقة على المطبوعة البيداغوجية ، المعنونة بـ:

Structure of Matter (Chemistry 1)
Common Base ST– Cycle License

2– تمّ تشكيل لجنة الخبراء المكونة من السّادة الآتية أسماؤهم:

- **غبولي محمد أمين**، أستاذ ، جامعة محمد بوضياف– المسيلة
- **جحيش مختار**، أستاذ، جامعة محمد بوضياف– المسيلة
- **شعباني صونية**، أستاذ، المدرسة العليا للطاقات المتجددة والبيئة والتنمية المستدامة – باتنة

وتمت الموافقة بالاجماع على هذه المطبوعة.

رئيس المجلس العلمي للكلية

المجلس العلمي

د. علي جريوي

الجمهـــورية الجزائـــــرية الديمقــــــراطية الشعــــــبية
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Faculty of Technology
Vice Deanship of Post-Graduation, Scientific Research and External Relations

كـلية التكنــولــوجيــا
نيابة العمادة لما بعد التدرج والبحث العلمي والعلاقات الخارجية

رقم:458/ ن.ع.ب.ع /ك.ت /2025

المسيلة في: 03 ديسمبر 2025

شهادة ادارية

المصادقة على تقارير خبرة للموافقة على مطبوعة بيداغوجية

بعد الإطلاع على تقارير لجنة الخبراء للموافقة على المطبوعة البيداغوجية للأستاذة : **شتيوي سهيلة – أستاذ محاضر قسم أ،** بالقاعدة المشتركة بكلية التكنولوجيا بجامعة محمد بوضياف بالمسيلة والتي كانت كلها ايجابية ، تمّ تقرير التّالي:

1-المصادقة على تقارير لجنة الخبراء للموافقة المطبوعة البيداغوجية والمعنونة بـــ:

Structure of Matter (Chemistry 1)

Common base ST (licence cycle)

2- حيث تمّ تشكيل هذه اللجنة بناء على اجتماع المجلس العلمي للكلية المنعقد بتاريخ **2025/05/27** المكونة من السّادة الآتية أسماؤهم:

-**غبولي محمد الأمين،** أستاذ ، جامعة محمد بوضياف- المسيلة

-**جحيش مختار،** أستاذ، جامعة محمد بوضياف- المسيلة

-**شعباني صونية،** أستاذ، المدرسة العليا للطاقات المتجددة والبيئة والتنمية المستدامة - باتنة

وتمت الموافقة بالاجماع على هذه المطبوعة.

رئيس المجلس العلمي للكلية

د. علي جريوي

People's Democratic Republic of Algeria
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وزارة التعليم العالي و البحث العلمي
Department of Science and Technology

Structure of Matter Course (Chemistry 1)
"1st Year License (LMD), ST core"

According to the 1st Year Common Core Program
Science and Technology
2024/2025

Presented by Dr. CHETIOUI Souheyla
Mohamed Boudiaf University -M'sila

EXECUTIVE SUMMARY

This *Structure of Matter* (Chemistry 1) course is for first-year students in the Science and Technology (ST), and Material Sciences (SM) fields. It is in line with the programme for the 1st year of the common core of the two areas.

It is intended to give a basic set of knowledge about the laws and concepts necessary for understanding the structure of matter.

The teaching of this subject allows the student to acquire basic formalisms in chemistry, especially within the subject describing the atom, the chemical elements and the periodic table with energy quantification.

The adopted plan proposes a gradual approach to general chemistry. This book is divided into six chapters.

- The first chapter of this course focuses on the fundamentals of general chemistry with a reminder of the states of matter, atoms, molecules and solutions.
- Chapter II is devoted to the classical conception of the atom and will deal with generalities about the structure of the atom and the various experiments that have highlighted its constituents, namely protons, neutrons, the nucleus and electrons.
- Chapter III deals with radioactivity and nuclear reactions.
- Chapter IV concerns the quantification of energy in the atomic model (wave-corporeal duality of light, hydrogen spectrum and classical models of the atom), and the study of the wave model of the atom.
- Chapter V is reserved for the periodic classification of the elements, the evolution and periodicity of the physico-chemical properties of the elements.
- The sixth VI and final chapter is reserved for chemical bonding: ionic bonding, covalent bonding, Lewis structure, VSEPR method and hybridization of atomic orbitals.

Sammary

Chapter I: Fundamentals

Chapter II: Main constituents of matter

Chapter III: Radioactivity – Nuclear reactions

Chapter IV: Electronic Structure of the Atom

    6. **Wave-body duality: Wave associated with the electron**
    7. **Atomic Orbit**

VII. Electronic configuration of a polyelectronic atom

    1. **Filling rules**
    2. **Stability Principle: Klechkowsky's Rule**
    3. **Pauli-Fermi principle**
    4. **hund's rule**
    5. **Establishment of the electronic configuration of an element**
    6. **Exceptions to the Rule**

VIII. Simplified electronic configurations

    1. **Valence electrons and core electrons**
    2. **Special case of "d" electrons**

Chapter V : The periodic table of the elements

I. Introduction

II. Periodic table of D. Mendeleev (1869)

III. periodic table

    1. **Periodic table description: Periodic table construction rules (groups and periods)**
    2. **Block structure of the elements of the periodic table**

IV. Main families of the periodic table

V. Positioning of the element in the periodic table

VI. Evolution and periodicity of the physico-chemical properties of the elements

Chapter VI: Chemical Bonds

I. Introduction

II. Covalent bonding in Lewis theory

III. octet rule

    1. **octet rule**
    2. **Formal charge**
    3. **Connection types concerned**
    4. **Bond polarity and dipole moment**
    5. **Partial ionic character (CI)**
    6. **Molecular Geometry**
    7. **Correspondence between hybridization and VSEPR**
    8. **Exercises**

Chapter I

Fundamentals

Chapter I: Fundamentals

I. Introduction

The term matter refers to everything that makes up the bodies that surround us, everything that has mass and volume.Matter consists of elementary particles: atoms.Chemists have highlighted a hundred elements that go into the composition of all material substances.

II. History of the Atom

Since antiquity, the problem of the nature (aspect) of matter has been posed, is it continuous or discontinuous ?

- 5th century BC. (Greece) Democritus imagines that matter consists of small indivisible and unbreakable particles, which he calls "atom".

- 4th century BC. (Greece) Aristotle claims that matter consists of 4 elements (fire, air, earth and water). This theory will prevail for almost 20 centuries!

- In 1805 John Dalthon (England) took up the idea of atoms, to explain proportions.

- J.J.THOMSON '1897 (Rayaume Uni) proves that certain rays consist of particles charged with negative electricity, which will be called "electrons". It measures the m/e ratio and gives the first model of the atom (the atom would be a charged "paste" + containing charged grains (electrons) -).

- In 1910, Rutherford formulated a new theory on the structure of the atom. According to him, the atom has a lacunar structure, a central spherical nucleus (dense and compact) with a diameter of the order of 10-14 m, formed of particles of (+) charges: the protons around the nucleus gravitate particles of (-) charges: electrons, and give the atom a diameter of the order of 10-10 m (planetary model). Later, the physicist J.Chadwick (1932) confirmed the existence of a third particle: the neutron of neutral charge.

- In 1913, Bohr proposed an atomic (layered) model to explain the hydrogen spectrum.

- In 1925 SCHRODINGER, HEISENBERG and DE BROGLIE invented (formulated) the theory of quantum mechanics. This theory establishes that electrons do not have a defined orbit, but makes it possible to determine their "probability of presence" around the nucleus.

III. Aspects of matter - Change of states

Matter exists in three forms: solid, liquid and gas. Cold and heat play a very important role in changing the physical state of matter.

a. **Solid state (s)**: are rigid bodies that retain a defined shape and volume. They are incompressible and can be liquefied by melting or evaporate as a gas.

b. **Liquid state (l)**: are compact but fluid enough to take the shape of the container that contains them and corresponding to their volume. They are practically incompressible. If two liquids mix together, they are said to be miscible. Liquids can dissolve solids up to a certain limit which is saturation.

c. **Gaseous state (g)**: occupy all the space made available to them. They are compressible and expand easily. Two gases placed in the same enclosure both occupy the entire available volume as if each of them were alone.

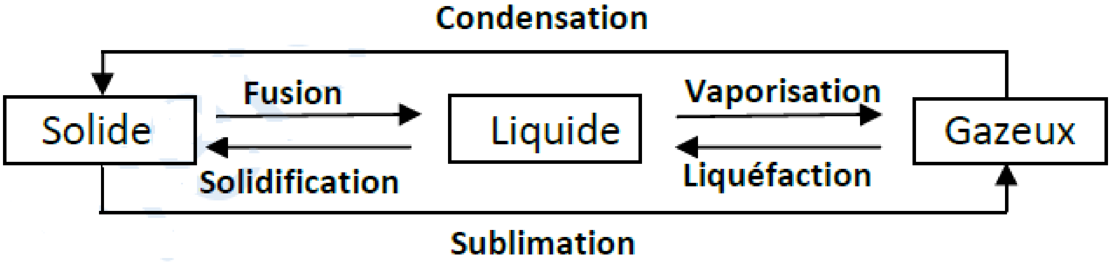
State changes are significant physical changes that occur at temperatures that are characteristic of the substance.

A physical change is a transformation that does not change the nature of a substance, it simply involves a change in its state, shape or physical dimensions.

The material is likely to change from one state to another under very specific temperature and pressure conditions.

The transition of matter from the solid state to the liquid state is by melting, from the liquid state to the gaseous state by vaporization and from the solid state to the gaseous state by sublimation.

These transformations are illustrated by the diagram below:



States of matter and its transformations at T and P = ctes

IV. Mixture and pure substances

The material is in the form of homogeneous or heterogeneous mixtures of pure substances. Immediate analysis makes it possible to separate the constituents of a mixture into pure substances. This separation is based on the differences in the physical properties of its constituents.

Homogeneous mixture

A homogeneous mixture consists of a single phase; the physicochemical properties are the same at every point of the mixture. In this case, separation techniques such as fractional distillation (difference in boiling temperature of liquids), precipitation (crystallization of a solid from a solution), etc., can be used.

Chemical analysis, in particular by mass spectrophotometry, makes it possible to identify the elements present in the compound and to determine their proportions.

Example

Air is a homogeneous mixture composed of 78% N_2 and 22% O_2. The two gases can be separated by liquefaction followed by fractional distillation.

2. Heterogeneous mixing

A heterogeneous mixture consists of two or more phases.

- If the mixture consists of several solids, the following are used: sieving (difference in particle size), levigation (difference in density, as in the case of the separation of gold and sand by washing with a stream of water that entrains the sand), dissolution, etc.
- If the mixture consists of solids and liquids, filtration or centrifugation is used.
- If the mixture consists of liquids, decantation is used, as in the case of the water-oil mixture. There are also several elemental analysis techniques that allow the separation of the constituents of a pure body composed into simple pure bodies.

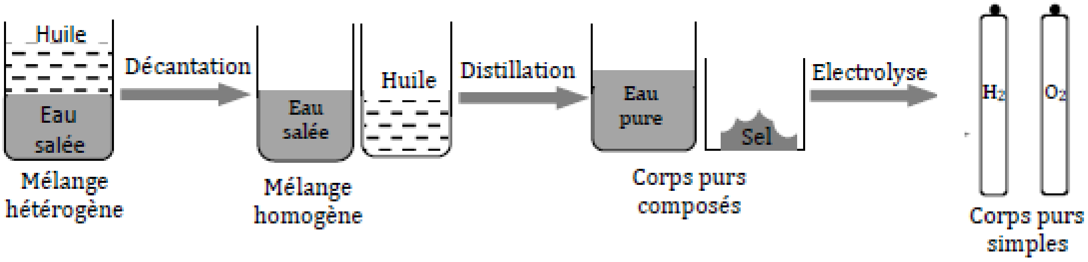
Example:

The most used processes in this case are of a chemical nature. Particular mention is made of:

- Thermolysis or pyrolysis which allows the decomposition of a substance by heat.
- Radiolysis, which consists of breaking down a substance by light radiation (UV, visible or IR).
- Electrolysis which allows the decomposition of a substance by electricity.

Example: Mixing salt water and oil

Salt water is a homogeneous mixture. By distillation, a physical process, the salt is separated from the pure water. By electrolysis, oxygen can be separated from hydrogen, which are the constituent elements of water.



A pure body is characterized by its physical (melting point, boiling point, density, refractive index, etc.) or chemical properties. There are two categories of pure bodies:

- Simple pure bodies consisting of a single type of element.

Example: O_2, O_3, H_2, Fe

- Pure composite bodies consisting of two or more types of elements.

Example: H_2O, $FeCl_2$, HCl, H_2SO_4

3. Solutions

A solution is a homogeneous mixture of two or more substances in varying proportions and without a chemical reaction. It consists of a dispersing medium called a solvent and one or more dissolved chemical species called solute(s). It can be in liquid or solid form The solvent is always in a much higher amount than the solute(s).

- **Solvent:** is any liquid substance that has the power to dissolve other substances without chemically modifying them and without modifying itself. If the solvent is water, the solution is said to be aqueous.
- **Solute:** is a solid, liquid or gas chemical species dissolved in a solvent. It is

characterized by different types of concentration.

4. Solution Properties

- **Density of a solution "ρ" :** This is the ratio of the mass of the solution and its volume

$$\rho = \frac{m\ \text{solution}}{V\ \text{solution}}\ \mathbf{(g/l)}$$

m solution = $m_{\text{solvent}} + m_{\text{solute}}$

$\mathbf{V_{solution}}$ = $V_{\text{solvent}} + V_{\text{solute}}$

- **Density of a solution "d":** This is the ratio of the density of the solution and its solvent.

$$d = \frac{\rho\ \text{solution}}{\rho\ \text{solvent}}$$

The relative density has no dimension.

If the solvent is water $\boldsymbol{\rho} = \mathbf{1\ g/ml}$

- **Molar fraction:** This is the ratio of the amount of material of compound "i" in moles contained in a solution divided by the sum of the amounts of material of all the constituents present in this solution.

$$x_i = \frac{\boldsymbol{ni}}{\sum \boldsymbol{ni}} \quad \text{with } \sum ni = n_T\ ,\ \sum xi = 1$$

- **Mass percentage (mass %):** This is the mass of the solute in grams contained in 100 g of solution.
- **Percentage by volume (% by volume):** This is the volume of the solute in cm^3 contained in 100 cm^3 of solution.

5. Different expressions of Nature

The concentration of a solution is the amount of compound dissolved in a certain volume of solvent.

- **Molar concentration "C_M":** This is the number of moles of solute per liter of solution.

$$\mathbf{C_M} = \frac{\text{n soluté}}{\text{V solvant}} = \mathbf{(mol/l)}$$

- **Mass concentration "C_m":** This is the mass of solute present per liter of solution.

$$C_m = \frac{\text{m soluté}}{\text{V Soulution}} = (g/l)$$

- **Molar concentration or molality "C $_{molal}$":** This is the number of moles of solute per kilogram of solvent.

$$C_{molale} = \frac{\text{n soluté}}{\text{m solvant}} = (mol/kg)$$

- **Normal concentration (normality) "C_N":** This is the number of gram equivalents ($\mathbf{n_{eq.g}}$) of solute contained in one liter of solution and the type of chemical reaction considered. In the case of acid-base reactions, the gram equivalent is the number of exchangeable protons whereas in oxidation-reduction reactions it is the number of electrons.

$$C_N = \frac{\text{neq.g}}{\text{VSolution}} = (eq.g/l) \text{ or } (N)$$

- **Gram-equivalent:** Is the amount of grams of a substance whose chemical action is equivalent to that of a gram-atom or a gram-ion.

  Example: A normal solution (**N**) therefore contains one gram equivalent of acid or base (**1** eq-g is the amount of acid or base likely to release or capture one mole of protonizable hydrogen): **HCl**, **HNO**, **KOH**, **NaOH**,...

6. Mixture separation methods

Sifting, Dissolution, Filtration, Decanting, Distillation, Crystallization......etc.

V. The laws of weights

The weight laws of chemistry, that is to say the laws relating to weighings and consequently to masses, were born from the macroscopic observation of matter.

1) Law of conservation of matter (Lavoisier 1774)

The total mass of the products formed is equal to the total mass of the reagents consumed (The mass balance study).

2) Law of defined proportions (Proust 1805)

When single bodies unite to form a defined compound body, the ratio between the masses of each reagent that have been consumed in the chemical reaction is constant.

3) Law of Multiple Proportions (Dalton 1808)

When two simple bodies can form several compounds, the masses of one of the constituents uniting with the same mass of the other are always in integer ratios.

VI. Basics and unity

Atom: 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. Atoms combine to form molecules.

- **1. Introduction**

The atom consists of elementary (subatomic) particles, it contains a nucleus at the center consisting of nucleons (**Z** positively charged protons, **A–Z** neutrons are neutral) and surrounded by **Z** negatively charged electrons. It is an electrically neutral entity. Electrical neutrality is due to the equal number of nuclear charges (protons) and electrons.

Z: Atomic number or number of charges. In a neutral atom, **Z** also represents the number of electrons. This number **Z** is very important because it characterizes a chemical element.

A: Mass number, the total number of nucleons (protons + neutrons), **A = Z+N**

Notation of a nuclide: $^{A}_{Z}\mathbf{X}$

- Nuclides with the same number of protons (same **Z**) correspond to the same element. They are the same number.

Example: Magnesium $^{24}_{12}Mg$, $^{25}_{12}Mg$, $^{26}_{12}Mg$

- **Isotopes** are nuclides that have the same **Z** (same number of protons) but different **A**'s (different number of neutrons).

$^{1}_{1}H$ (99.985%), $^{1}_{2}H$ (0.015%) and $^{1}_{3}H$ (traces) are isotopes.

- **Isobaric** nucleides are nuclides that have the same A (same number of nucleons) but different Z (number of different protons).

Example: Carbon $^{14}_{6}C$ and nitrogen $^{14}_{7}N$ are isobars.

- **Isotone nucleides** are nuclides that have the same **N** (same number of neutrons) but different **Z** (number of different protons).

Example: Carbon 12 $^{12}_{6}C$ and nitrogen 13 $^{13}_{7}N$

- **The molecule:** The molecule is the smallest chemical unit of an element or compound. It consists of identical (Cl_2) or different chemically bonded atoms (H_2O).
- **Supra-molecule**

A supramolecule is a structure with a well-defined geometry, assembled from several molecules linked together by weak bonds. Its properties are not those of its separate constituents (proteins, enzymes, etc.).

- **Molecule:** the molecule is a union of two or more atoms linked together by chemical bonds. It is the smallest part of a compound that has the same properties as the compound. It is characterized by its chemical formula.

  Example: Water molecule **H_2O**.

- **Mole:** The mole is the unit of measurement of the quantity of matter which is the quantity used by chemists to specify the quantity of elements or chemical compounds.
- **Avogadro number (N_A):** The Avogadro number of atoms or molecules corresponds to 1 mole of atoms or molecules **$N_A = 6.023 \times 10^{23}$**.
- 1 mole of particles (atoms, molecules, ions, etc.) is the amount of material that contains **$N_A = 6.023 \times 10^{23}$** particles.

- **Atomic mass unit (AMU):** The masses of the particles (**e**, **p**, **n**...) are not everything on our scale, so we use a mass unit different from kg but better adapted to the measured quantities, it is the AMU.

u.m.a is defined as being equal to one twelfth of the mass of a 12 C atom .

$$\textbf{1 u.m.a} = \frac{1}{12} \text{ x mass of a 12 C atom}$$

Mass of an atom of 12 C = 12 x 6.023 10^{23}

$$\textbf{1 uma} = \frac{1}{12} \times \frac{12}{6{,}023 \text{ x } 10^{23}} = 1.66 \text{ x } 10^{-24} \text{ g} = 1.66 \text{ x } 10^{-27} \text{ kg}$$

- **Atomic molar mass:** The molar mass of an element is the mass of one mole of atoms of that element or N_A of atoms.
- **Molecular Molecular Mass:** The molecular mass of a molecular compound is the mass of one mole of molecules of this compound or N_A molecules. It is equal to the sum of the atomic molar masses of the elements that make up the molecule.

Example: The molar mass of water **H_2O**:

$$\mathbf{M_{H2O} = 2\ M_H + M_O = 1 \times 2 + 16 = 18\ g/mol}$$

- **Number of moles (n)**: is the ratio between the mass of the compound and its molar mass :

$$n = \frac{m}{M} \ \textbf{(mol)}$$

- **Molar volume:** The molar volume (**V_M**) is the volume occupied by one mole of substance, it depends on the state of the substance.

$$\mathbf{V_M} = \frac{V}{n} \ \textbf{(l/mol)}$$

Chapter II

Main constituents of matter

Chapter II: Main constituents of matter

I. Introduction

Most of the scientific work that has proven the existence of the atom has been done over the past two centuries. Various experiments have proved that atoms are not the ultimate constituents of matter, and that they are themselves formed of several types of elementary particles.

II. Faraday's laws: relationship between matter and electricity :

If a sufficient potential difference is applied between two electrodes immersed in an electrolytic solution (HCl), the passage of an electric current is observed and simultaneously, a series of chemical reactions at the electrode-electrolyte contact surface (Figure II.1).

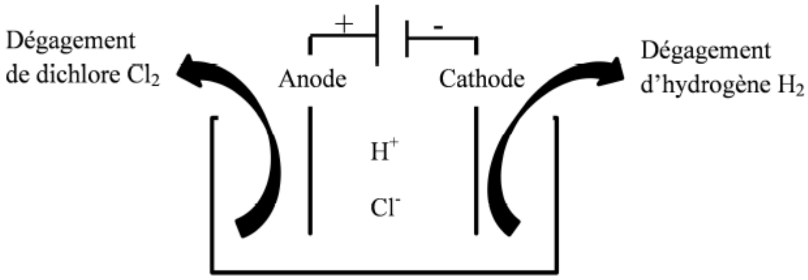


Figure 1. Simplified Schematic of Electrolysis of Hydrochloric Acid

At the electrodes, there is a release of gases in molecular form: a release of chlorine at the anode (+) and hydrogen at the cathode (-), this decomposition of hydrochloric acid is reflected globally by the equation:

$$2HCl \longrightarrow H_2 + Cl_2$$

In solution, it is known that HCl is dissociated into two ions H^+ and Cl^-. The fact that hydrogen appears at the negative electrode forces us to admit that the hydrogen ion is positively charged (Coulomb's law) and the chloride ion is negatively charged. Faraday's laws can be represented by the following form:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right)$$

M: the mass of the substance released at the electrode (g) and M its molar mass (g/mol)

Q: the total electric charge passed through the substance

F: Faraday's constant is 96485 C mol^{-1},

Z: the valence of the substance

M/z: corresponds to the equivalent of the total substance released.

III. Highlighting the constituents of the material

1. Atom

The notion of atom dates back to 400 BC, from the Greek atomos: indivisible, unbreakable. But the first experimental evidence for the existence of atoms was gathered in 1805 by Dalton.

2. Dalton atomic model

The first atomic theory is that of John Dalton, which was published in 1807. It proposes a fairly simple way of considering a chemical reaction: when molecules react with each other, their atoms separate from each other to recombine in the form of new molecules.

Dalton's law shows that the ratio of the masses that react does not vary continuously, which reflects the discontinuous nature of matter, chemical species engage in reactions only in discrete, extremely small and indestructible quantities, which Dalton designates as **atoms**.

Main items are:

- Matter is composed of small, spherical, indivisible, indestructible particles called atoms.
- The atoms of the same element are identical and the atoms of different elements are different in one or more respects (mass, size).
- A chemical compound is formed by the combination of two or more atoms. A given compound always contains the same relative numbers and types of atoms.
- In a chemical reaction, there is a change in the way atoms are bound to each other but the atoms themselves do not undergo any change, (no atoms are created or destroyed).

Although the foundations of Dalton's atomic theory are accurate, subsequent discoveries demonstrated that his model needed to be modified. In particular, Dalton's atom was in conflict with certain electrical phenomena known at the time when he enunciated his theory. It is known that there are two kinds of electrical charges in matter: positive charges (+) and negative charges (-) and that their effect cancels out. Charges of opposite signs attract while charges of the same signs repel. These observations coupled with the discovery of cathode rays and radioactivity led to the conclusion that the atom is not an indivisible and uniform sphere as Dalton had believed. On the contrary, the atom can be broken into particles even smaller than it: sub-atomic particles. These basic principles of atomic theory still remain the basis of chemistry today.

IV. Properties and characterization of the elementary constituents of the atom

The atom consists essentially of three elementary particles. It is an electrically neutral entity. It contains a given number of protons and neutrons also called nucleons (constituents of the nucleus), surrounded by electrons. Electrical neutrality is due to the equal number of nuclear charges (protons) and electrons. Until the end of the nineteenth century, atoms were considered, as in Dalton's system: stable, indivisible particles, in other words' elementary '. Towards the end of the nineteenth century, new experiments lead us to believe that the atom is in fact itself made up of particles that will be called sub-atomic. Several experiments have shown that the atom consists of several particles: protons, neutrons, electrons.

1. Electron

a-Experience of Crooks (1879) and characteristics of cathode radiation

This experiment is carried out in a discharge tube shown in the figure below. The pressure of the gas (air, helium, neon, etc.) in the tube is reduced to 10-6 atm. When a large potential difference (ddp) of about 1000 volts per cm is established between the two metal electrodes placed at the ends of a glass bulb containing gas. The gas remains dark but the glass of the bulb becomes fluorescent opposite the negative electrode (the cathode). Indeed, this observed fluorescence is due to the impact on the glass of invisible rays (radiation) from the cathode, hence its name cathode radiation, CROOKS considers that this radiation causes the glass to fluoresce. These cathode rays are deflected by an electric field towards the positive pole, which indicates that the particles constituting these rays are negatively charged.

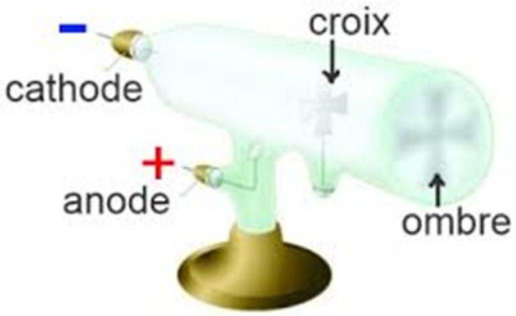


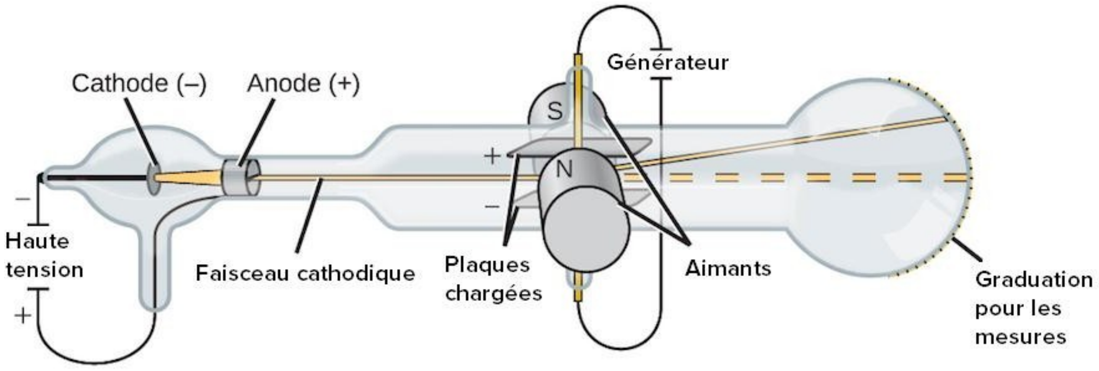
Figure 1: Crookes tube diagram

In 1891, Stoney gave the name of the electron to the particles constituting the cathode rays. This experiment shows that cathode radiation is actually a flow of particles capable by their impact of imparting motion to an object. These particles have a kinetic energy, thus consisting of particles with a mass.

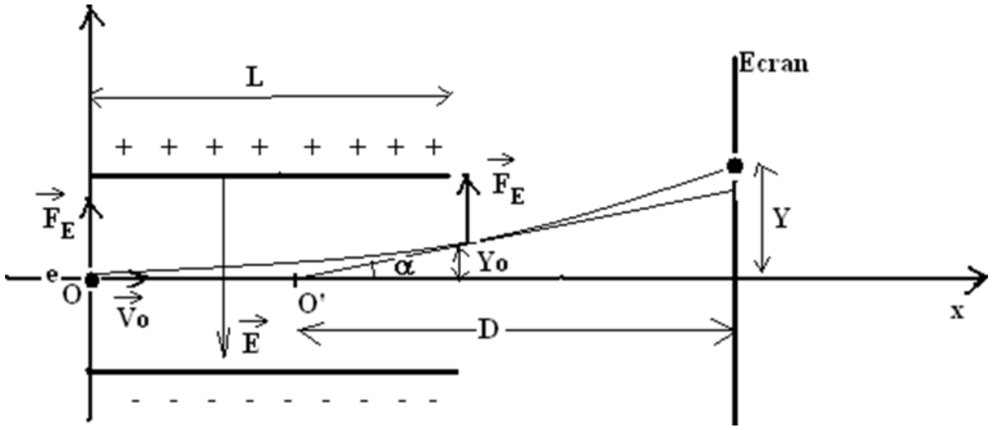
b- Experiment of J.J.Thomson (1895): Determination of the ratio |e|/m

A few years earlier, it had been discovered how to produce an electric discharge (an arc) by establishing an electric potential difference between two electrodes placed inside a partially evacuated tube. Such a device is called a discharge tube. J.J. Thomson undertakes a quantitative study of cathode rays he was able to determine the value of the charge/mass ratio of the particles from the cathode, the value of this ratio does not depend on the material of the cathode or the residual gas in the cathode ray tube.

|e /m| = 1.759.1011 Coulombs/Kg



J.J. Thomson's CRT diagram



Strength balance in J.J. Thomson's capacitor

c- Millikan's experience (1908):

Between 1906 and 1913 the American Robert Millikan carried out multiple experiments on oil droplets in order to determine the charge of the electron. Indeed, Millikan sprayed electrically charged (ionized) oil droplets between two plates and observed them using a microscope. His method consisted in immobilizing the droplets by increasing the electric field until the weight of the droplet was compensated by the electrostatic force. Millikan thus managed to obtain an approximate value of the elementary charge $|q_e| = {}^{1,591.10\ 19-}$ C, very close to the value accepted today which is qe $= -1,6021892.10^{-19}$ C. The mass of the electron is equal to: $m_e = 9,109.10^{-31}$Kg

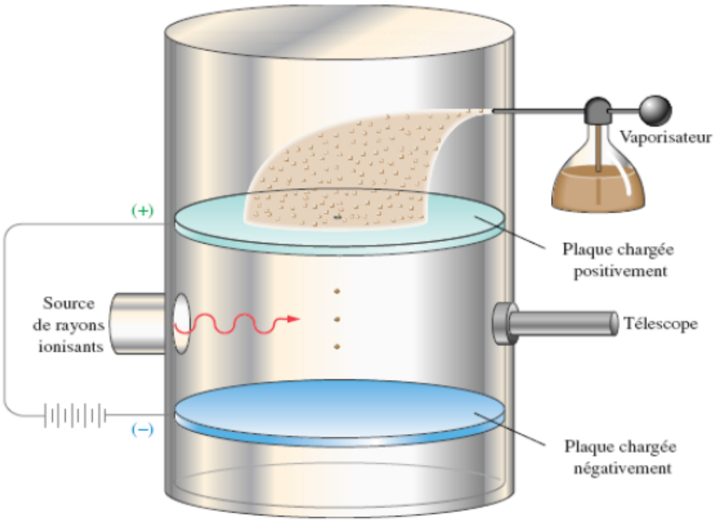


Figure 2: Millikan Experience

2. Discovery of the atomic nucleus:

a- Rutherford Experiment (1911-1919):

Ernest Rutherford wanted to check out Thomson's "raisin bread" model. To this end, he designed an experiment in which he bombarded a very thin sheet of gold with alpha particles (large positively charged particles) from the decay of a radioactive element such as radium. According to Rutherford, if Thomson's model was accurate, the heavy alpha particles had to pass through the metal foil with as much ease as a shell passes through tissue paper. But the results of his experiment were very surprising.

The experiment consists of bombarding a very thin sheet of metal (Gold) with radiation consisting of Helium (He^{2+}) nuclei

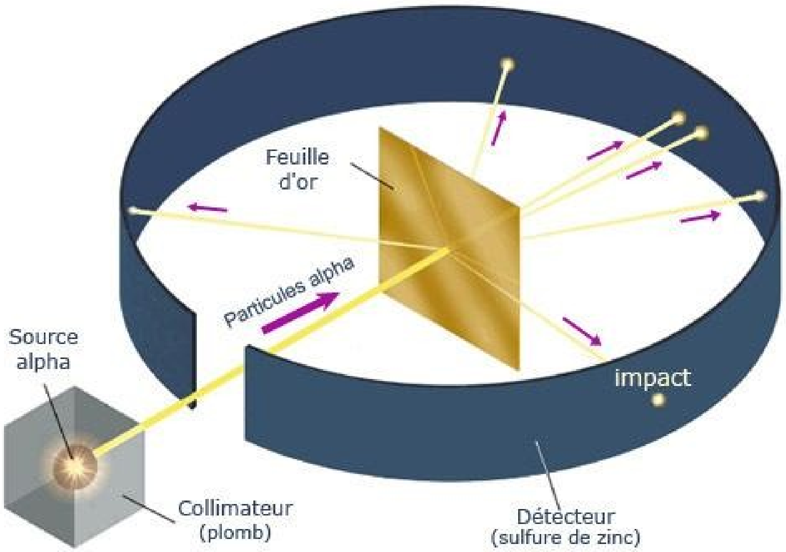


Figure 3: Rutherford Experimental Device

Bombarding very thin gold leaves with alpha particles, Hans Geiger and Ernest Marsden, then students of Rutherford, observed that a tiny fraction (1 in 8000) of these particles were deflected at a wide angle as if they were bouncing off a massive obstacle. Impacts were observed in the dark under a microscope on a glittering zinc sulfide screen. Rutherford concludes that the atom contained a massive core, of positive electrical charge, capable of repelling alpha.

The Rutherford experiment on particle-matter interaction, which led to the proposal of the planetary model of the atom, the Rutherford atom therefore consists of a dense and positively charged nucleus in which is concentrated practically all the mass of the atom, which is surrounded by electrons moving in a very large space compared to that occupied by the nucleus. He compared the atomic system to the planetary system where electrons nucleus and planets sun.

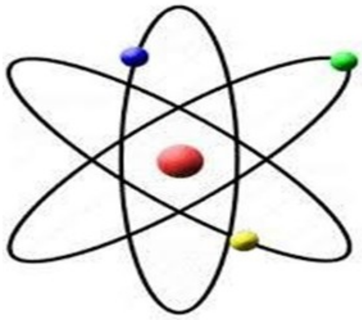


Figure 4: Rutherford Atomic Model

b-Goldstein experience

Goldstein designed a rarefied gas cathode ray tube, composed of a pierced metal cathode. He noticed that the emitted rays pass through the holes of the cathode and go in the opposite direction to the cathode rays. Goldstein therefore deduces that these rays are positively charged and calls them channel rays because they pass through holes as well as through channels. Particularity of these channel rays

- A magnetic field deflects them in the opposite direction to the cathode rays.
- Depending on the nature of the gas present in the tube, different q/m ratios are obtained
- This ratio is substantially greater than that between the mass and the charge of particles constituting the cathode ray
- Channel rays are significantly lighter than electrons

c- Demonstration of the proton: Rutherford experiment (1919)

By bombarding the nitrogen with **α particles,** Rutherford noticed the formation of oxygen and a new particle. After identification, the particle is positively charged, called a **proton**.

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}\ ({}^{1}_{1}\mathrm{p})$$

This reaction shows that the proton is a constituent of the nitrogen atom. Characterization studies show that the proton is a particle of elementary charge, **+e = +1.602 × 10^{-19} Coulomb**; and mass **mp = 1.67265 × 10^{-27} kg = 1.0073** a.u.

The mass of the proton is about 80–100 times greater than the sum of the rest masses of the quarks that make it up, while the gluons have zero rest mass.

The mass of the electron is negligible compared to that of the proton.

d- Neutron detection (Chadwick):

The neutron as its name suggests is neutral (no charge), however it has a mass and is attributed to the nucleus, discovered by Chadwick, by bombarding by α particles light elements such as beryllium, there appears a penetrating radiation consisting of electrically neutral particles, he called them **neutrons** and the formation of the carbon nucleus.

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

m_n = 1.67495 × $^{10-27}$ kg = 1.0087 uma

The mass of the neutron is 1839 times the mass of the electron.

The mass of the electron is negligible compared to that of the neutron.

3. Presentation and characteristics of the atom

The atom is described as a central nucleus around which move one or more electrons constituting the electronic procession. Since the mass of electrons is very low compared to that of nucleons, the mass of the nucleus is substantially equal to that of the atom.

The terms nuclear species, nuclide or nuclide are often used to designate an atomic nucleus. The nucleus is composed of two types of elementary particles: protons and neutrons are called nucleons.

Conventionally, a chemical element is represented by a chemical symbol written in one or two letters. The first letter is always an uppercase and the second letter, if it exists, is always a lowercase with a lower index **Z** and a higher index **A**.

Z is called atomic number or charge number, it designates the proton number. Each atom has **Z** protons (+**e** **Z**), so it characterizes a given atom. The atom is electrically neutral, **Z** also denotes the number of electrons revolving around the nucleus.

A is called the mass number, it denotes the total number of **nucleons (protons + neutrons)**. It is equal to the sum of the number of protons **Z** and the number of neutrons **N. A= Z+N. A** and **Z** are integers, they characterize an atom or its nucleus.

Set of atoms characterized by a defined number of protons (**Z**) in their nucleus. For a given element, the number of protons is fixed but the number of neutrons can vary. The element is then said to have isotopes.

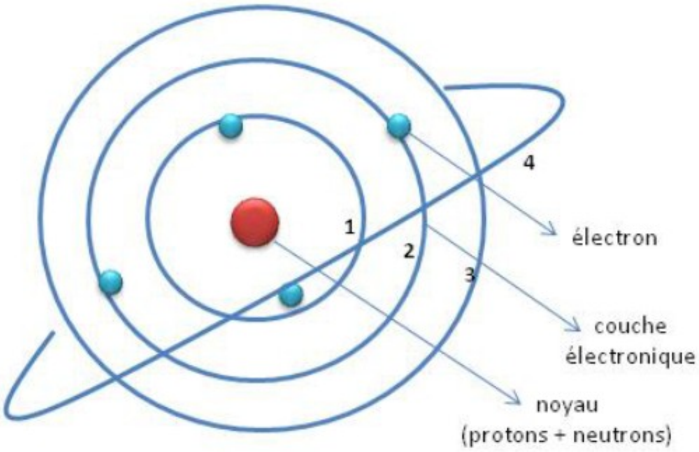


Figure 5: Rutherford Planetary Model

V. Isotopy and relative abundance of different isotopes

Isotope

Two atoms (or two nuclides) are called isotopes if they have the same charge number Z, but different by their mass number A. This results in a difference in the number of neutrons. An element can have one or more attributes. Some of these isotopes are found in nature; this is the case with hydrogen and uranium. They are called natural isotopes. Others are the result of human activity because they are produced by controlled nuclear reactions (nuclear reactors) or explosive reactions (nuclear bombs). They are called artificial isotopes.

isotopic composition

When an element has several isotopes, the percentage of the latter constitutes its isotopic composition.

Separation of isotopes

Some differences in physical or chemical properties between isotopes of the same element result from the mass differences of atomic nuclei and their consequences on the vibrational or rotational energies of molecules. These differences in properties can be used to separate isotopes. **Mass spectrometry** is a physical analysis technique for detecting and identifying molecules of interest by measuring their mass, and characterizing their chemical structure. Its principle lies in the gas phase separation of charged molecules (ions) according to their mass/charge ratio (*m/z*). It is used in virtually all scientific fields: physics, astrophysics, gas phase chemistry, organic chemistry, assays, biology, medicine...

The mass spectrometer developed by Bainbridge in 1933 makes it possible to measure the mass of ions of the same charge. The ions are selected by their speed and then differentiated by their mass, which makes it possible to separate the different isotopes of the same atom.

VI. Isotope separation and determination of atomic mass:

1)- Bainbridge spectrograph

To measure the mass of an atom in an isotope mixture, the method

more practical consists in measuring the ratio $\frac{q}{m}$ of an ionized atom (**q** being the charge of the ion and **m** its mass), using devices called "Mass Spectrographs", an example of which is that of Bainbridge. These mass spectrometers can separate isotopes from an element and measure their abundances.

The Bainbridge Spectrometer consists of four parts:

1- An ionization source.

2- Speed filter
3- An analyzer
4- A detector.

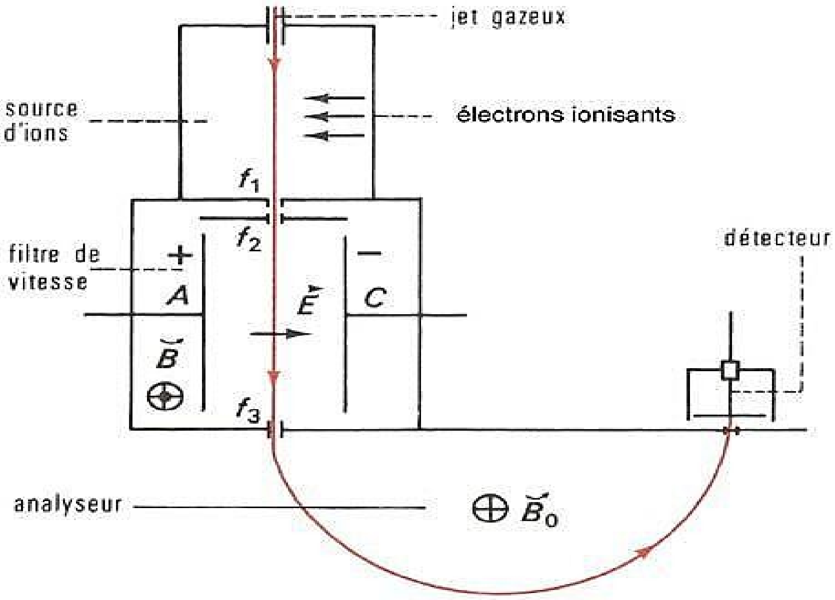


Figure 6: Principle of the Bainbridge Spectrometer

The principle of the Bainbridge mass spectrometer is presented here. The materials to be analyzed are introduced into an accelerator ionizer (not shown). The ions produced are introduced into the speed selector.

In this zone represented in yellow, the ions (mass m and charge +q) are subjected to uniform and perpendicular electric field E and magnetic field. The ions are subjected to the electrical force **Fe = q . E** and the magnetic force **Fm = q (V ^ Bo)**. The beam deflection is zero if these forces compensate each other.

The initial velocity V of the ions that can enter the analysis chamber is therefore equal to: **V = E / Bo (1)**.

The ions are then subjected to the action of a single magnetic field and describe in the analysis chamber (where a high vacuum prevails) a circular trajectory whose radius is given by the relationship: **R = m.V / q.B (2)**

If n is the number of nucleons (mass number) of the ion, its mass m is substantially equal to n 1.67. 10^{-27} kg.

Only charge ions q = +1.6.10 $^{-19}$ C are taken into account.

Modern spectrometers have advanced systems for ionization, deflection and detection but all are based on the same principle: the deflection of an ion by a magnetic field is a function of its mass.

$F_e = F_m \Leftrightarrow q\,E = q\,v\,B \Leftrightarrow v = E/B$........................(1)

$F_m = q\,v\,B_0$ ....(2)

$Fc = m\,v^2/R$ ....(3)

$F_m = F_c \Leftrightarrow q\,v\,B_0 = m\,v^2/R \Leftrightarrow q\,B_0\,R = m\,v$

$\Leftrightarrow m/q = R\,B_0/v$ ....(4)

$m/q = R\,B\,B_0/E$............(5)

$R = D/2$: $m/q = D\,B\,B_0/2E$............(6)

$m = M/N_A$: $M/q = N_A\,D\,B\,B_0/2E$............(7)

2)- Isotopic Abundance:

Isotopic abundance refers to the percentage by number of atoms of each of the isotopes present in the natural mixture. This abundance is equivalent to the molar fraction of each stable isotope.

3)- Relative atomic mass of an isotope (Mi):

Either an element X which has (i) isotopes of abundance: a1, a2, a3, a4 …ai, and atomic mass: m1, m2, m3, m4 …mi. The relative atomic mass of this element X is equal to the average of the relative atomic masses of its isotopes as a function of their abundances.

The average atomic mass of the element will be: $M\,(Xi) = \frac{\Sigma ai.mi}{100}$, with Σai = 100%.

Chapter III

Radioactivity – Nuclear reactions

Chapter III: Radioactivity – Nuclear reactions

I. Introduction

Radioactivity is ubiquitous in the universe and on Earth, with the fusion or disintegration of unstable atoms being common phenomena of matter. In the Earth, fission radioactivity is the main source of heat. By heating magma, it is the engine of volcanism and its greenhouse gas emissions. By liquefying the outer layer of the central core, it allows the movements at the base of terrestrial magnetism (Dynamo effect). This magnetic shield is essential to life on Earth as it protects it from deadly high-energy cosmic rays, especially solar.

In the Sun, the fusion radioactivity of hydrogen and helium atoms heats its surface to 6,000°C. This huge "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 for life (photosynthesis). It is the basis of the climate (winds and precipitation). Henri Becquerel discovered radioactivity in 1896, he had stored a uranium salt in a drawer on photo plates (a photographic plate) that were impressed as if it had been exposed to light. It shows that this ability to emit rays is an intrinsic property of the uranium element. He calls them uranic rays. The work undertaken by Pierre and Marie Curie, two years later, led to the discovery of two new radioactive elements: polonium and radium. Radioactivity is not specific to uranium, it is a property of atoms and therefore results from the instability of the atomic nuclei of certain natural elements.

II. Definition of radioactivity

Radioactivity is a natural physical phenomenon during which unstable atomic nuclei decay by releasing energy in the form of radiation (**α**, **β** or **γ**) to form more stable nuclei, it can result in the following decay equation:

$$\underset{\substack{\text{Noyau père}\\ \text{instable}}}{{}^{A}_{Z}X} \longrightarrow \underset{\substack{\text{Noyau fils}\\ \text{Excité}}}{{}^{A'}_{Z'}Y^{*}} + \underset{\text{Rayonnement}}{{}^{a}_{z}q}$$

The ratio between the number of protons and the number of neutrons is the main factor that will fix the stability or instability of a given nuclide. We can simply explain this fact, considering that the positively charged protons repel each other, the addition of neutrons stabilizes the nuclides by a "dilution" effect of the positive charges which, being further apart from each other, will tend to repel less. If the number of protons becomes too high (**Z > 84**) this effect of

"load dilution" becomes ineffective because Z is too high and there are no more stable cores. For A-Z / Z > 1.5, the element is usually radioactive.

During a nuclear reaction, there is conservation of the charge number Z and the mass number A. The phenomenon of radioactivity is a spontaneous nuclear transformation, it modifies the composition of the atomic nucleus and, consequently, the nature of the atom. The transformation from one nucleus to another nucleus is called radioactive transmutation. There are tow types of transmutation:

- Spontaneous: Natural radioactive decay (radioactivity manifested by natural nuclides)
- Provoked: Artificial Radioactivity

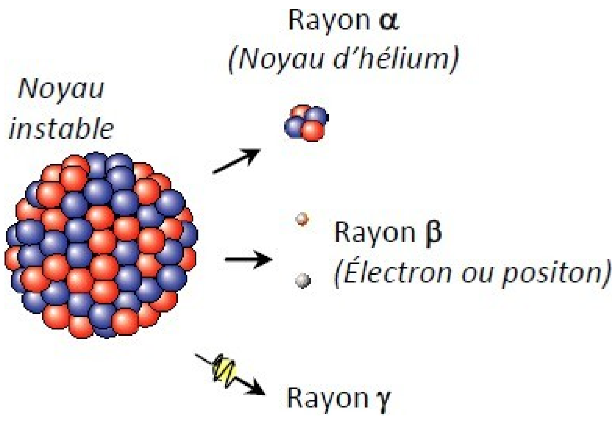
natural radioactivity

Natural radioactivity results from the instability of the nuclei of certain natural elements, it is a spontaneous decay of the nucleus giving a radioactive or stable nucleus and various radiations.

Some nuclides are unstable because their combination of protons and neutrons forms a fragile architecture, they have a certain probability of disintegrating, i.e. suddenly and spontaneously modifying their structure. This modification is accompanied by nuclear reactions that cannot be modified by any external intervention (temperature, pressure,etc.)

Types of radiation

There are three types of α, β and γ radiation.



3. Energy aspect

In radioactivity, there is conservation of the total number of nucleons and the overall charge. This in no way implies the conservation of mass; on the contrary, radioactive transmutations are always accompanied by a loss of mass Δm corresponding to the release of the amount of energy given by the Einstian relation:

$$E= \Delta m * c^2$$

Einstein relationship

In 1905, in elaborating the theory of special relativity, Einstein postulates that mass is one of the forms of energy: A system at rest, of mass m has a mass energy: $\mathbf{E = m.c^2}$ (Mass-energy equivalence relation), with E: mass energy in joules (J), m: mass in kilograms (kg), c: speed of light in vacuum ($c = 3.0.108\ m.s^{-1}$)

Consequence: If the system (at rest) exchanges energy with the external environment, (by radiation or by heat transfer for example), its energy variation ΔE and its mass variation Δm are linked by the relationship: $\mathbf{\Delta E = \Delta m\ .\ c^2}$

* If $\Delta m < 0$ then $\Delta E < 0$, the system transfers energy to the external environment and its mass decreases.

* If $\Delta m > 0$ then $\Delta E > 0$, the system receives energy from the external environment and its mass increases.

5. Mass fault and bonding energy

Atomic nuclei owe their cohesion to the **strong interaction force** between nucleons. It is a short-range force of attraction. It is far more important than repulsive electrical forces.

Mass defect: It is found that the sum of the masses of the A nucleons composing an atomic nucleus is always greater than the mass of the nucleus $^{A}_{Z}\mathbf{X}$

$$\Delta m = Zm_p + (A–Z)\ m_n – m_x > 0$$

To disperse all the nucleons of the nucleus, it is therefore necessary to provide the nucleus with the energy $\Delta m.c^2$. This energy represents **the bonding energy E_L of the nucleus**: $E_L = \Delta m.c^2$, E_L is also the energy that is released if an atomic nucleus is built from its components.

III. Types of radiation (radioactivity):

a) Stability curve: The nuclide stability curve (red curve on the N-Z diagram) indicates the approximate location of stable nuclides. In principle, stable nuclei (about 300) surround the curve closely while unstable nuclei (radioactive nuclei, radionuclides) (about 3000) move further away from it. As they disintegrate, the radioactive nuclei move closer to the stability curve through the emission of energetic radioactive radiation.

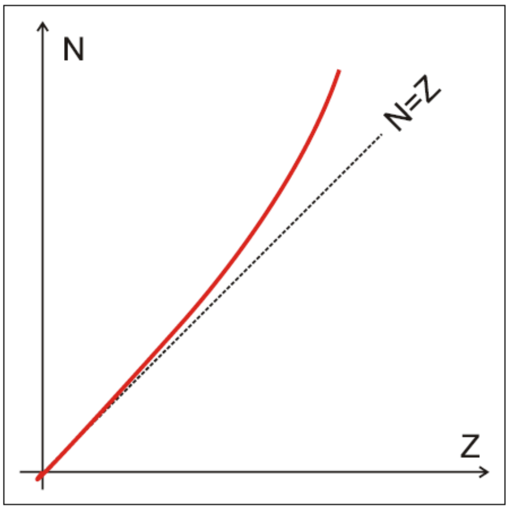


Figure -1- The nuclide stability curve

b) alpha decay

Some heavy radionuclides (N+Z > 200) emit alpha particles (or helium nuclei).

Balance sheet equation:

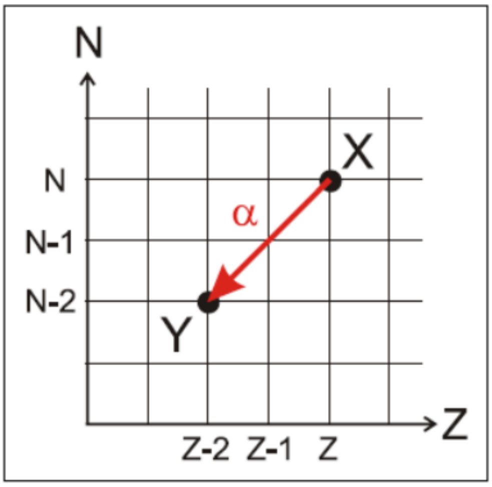
$$\boxed{{}^{A}_{Z}X \rightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}He}$$

The nuclide X is called "parent nucleus", the nuclide Y "child nucleus".

X and Y correspond to different chemical elements.

Example :

$${}^{226}_{88}Ra \rightarrow {}^{222}_{86}Rn + {}^{4}_{2}He$$



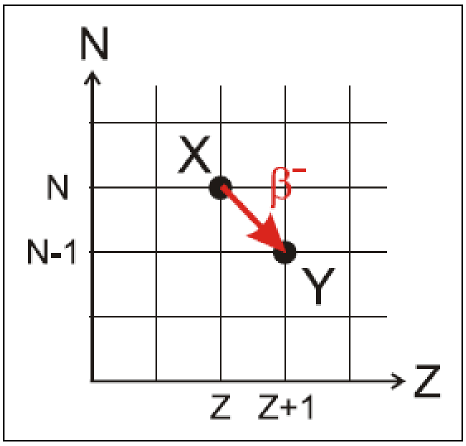
c) Disintegration β^-

Radionuclides with a surplus of neutrons (located to the left of the stability curve) emit an electron that comes from the decomposition of a neutron into a proton and an electronic antineutrino according to the equation:

Balance sheet equation:

$$^{1}_{0}n \rightarrow {}^{0}_{-1}e + {}^{1}_{1}p + \bar{\nu}_e$$

$$\boxed{^{A}_{Z}X \rightarrow {}^{A}_{Z+1}Y + {}^{0}_{-1}e + \bar{\nu}_e}$$



X and Y correspond to different chemical elements.

Example $^{90}_{38}Sr \rightarrow {}^{0}_{-1}e + {}^{90}_{39}Y + \bar{\nu}_e$

The antineutrino guarantees the conservation of the amount of movement and energy.

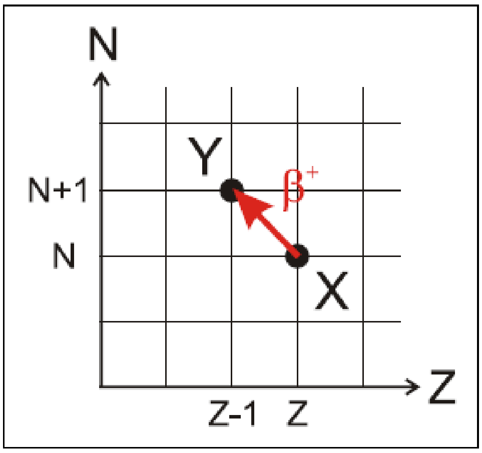
d) β^+ Disintegration

Radionuclides with too many protons (or too few neutrons, therefore located to the right of the stability curve) emit a positron that comes from decomposition of a proton into a positron, a neutron and a neutrino electronics:

Balance sheetequation:

$$^{1}_{1}p \rightarrow {}^{0}_{1}\bar{e} + {}^{1}_{0}n + \nu_e$$

$$\boxed{^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + {}^{0}_{1}\bar{e} + \nu_e}$$



X and Y correspond to different chemical elements.

The particle denoted 1e is a positron (or positron or antielectron) of the same mass as the electron but of opposite charge.

Example: ${}^{14}_{8}\mathrm{O} \rightarrow {}^{0}_{1}\overline{\mathrm{e}} + {}^{14}_{7}\mathrm{N} + \nu_{e}$

The neutrino ensures the conservation of momentum and energy.

e) Disintegration γ

After a radioactive transformation of the nucleus, the son nucleus is normally in an excited state (*) and de-excites by emitting one (or more) high-energy (gamma) photons.

$$\boxed{{}^{A}_{Z}\mathrm{Y}^{*} \rightarrow {}^{A}_{Z}\mathrm{Y} + \gamma}$$

IV. Radioactive families

When decay gives a radioactive nucleus, it decays giving in turn a nucleus that can be radioactive and so on. There is then a series of nuclides that appear one after the other and the whole constitutes a radioactive family.

There are three natural radioactive families:

1. Uranium 238 family in which **A = 4n+2** (n positive integer),
2. The actinium family in which **A = 4n+3** (n is an integer).
3. Thorium family in which **A = 4n** (n is an integer).

The final element of these three families is a stable isotope of Pb 206, 207 or 208.

- Artificial radioactive family: There is only one artificial radioactive family. The mass numbers **A** of the elements of this family are equal to **4n+1**. The final element is a stable isotope of ${}_{83}\mathrm{Bi}$.

Applications of radioactiviry :

- Energy: fission nuclear power plants, energy source (electricity production).
- Field of armaments: nuclear missiles, atomic bombs, etc.
- Medical: use of radioactive tracers for diagnostics, treatment of cancers, radioactive iodine is used in the scintigraphic examination of the thyroid, radiation of tumors, etc...
- Biology / geology: in vivo studies using radioactive markers, dating.
- Radioactive tracers for the control of many industrial manufacturing processes.

- Carbon-14 for dating ancient objects (up to about 40,000 years).

1. Radioactive decay kinetics: Law of radioactive decay

Each radioisotope has its own rate of decay.

Experience shows that the number of radioactive atoms $\frac{dN}{dt}$ that decay between **t** **t+dt** is proportional to the number of unstable atoms **N** present at the given time **t**.

The decay rate is given by the formula: $\frac{dN}{dt} = -\lambda N$

- λN: with the sign (-), it is the decrease in the number of radioactive nuclei.

$$\begin{array}{llcl} & \mathbf{A^*} & \longrightarrow & \mathbf{B\ (stable)} \\ \mathbf{t = 0} & \mathbf{N_0} & \longrightarrow & \mathbf{0} \\ \mathbf{t > 0} & \mathbf{N_t} & \longrightarrow & \mathbf{N_d\ (N_B)} \end{array}$$

The law of decay of the number of nuclei (atoms) of A as a function of time is obtained by integrating from this equation: **($\frac{dN}{dt}$= -λ dt)** between N_0 and N_t in the domain of **t (0, t)**, we obtain: $N_t = N_0\, e^{-\lambda t}$

where:

N_0 : initial number of radioactive nuclei (atoms) at **t=0**.

N_t : number of remaining nuclei (atoms) (not disintegrated) at a time t # 0.

N_d : number of disintegrated nuclei (atoms) and **($N_d = N_B = N_0 - N_t$)**.

N_B : number of nuclei (atoms) B formed at a time t, at t=0, $N_{B0}=0$.

λ: Radioactive constant or decay constant is characteristic of the nature of the radioactive nucleus.

λ is expressed in s^{-1}, h^{-1}, d^{-1} or an^{-1} depending on the unit of time.

We have: $N_B = N_d = N_0 - N_t$ if we replace $N_t = N_0\, e^{-\lambda t}$, we obtain:

$$N_B = N_d = N_0\,(1 - e^{-\lambda t})$$

2. Period T of the radioactive element or (half-life $t_{1/2}$):

This is the time it takes for half of the initially present radioactive nuclei $\frac{N_0}{2}$ to undergo decay. It is obtained by replacing in the previous equation t by **T** and **N_0** by $\frac{N_0}{2}$

$$\frac{N_0}{2} = N_0 e^{-\lambda T} \qquad N_{t1/2} = \frac{N_0}{2}$$

$$1/2 = e^{-\lambda T} \Rightarrow \ln\frac{1}{2} = -\lambda T$$

$$\ln 2 = \lambda T \qquad \Rightarrow \qquad T = \frac{\ln 2}{\lambda} \text{ ou } T = \frac{o{,}693}{\lambda}$$

- ➢ The period T does not depend on the initial number of nuclei.
- ➢ Temperature and pressure do not affect the value of T.
- ➢ The period characterizes a given nuclide.

a. Disintegration Speed or Activity (A):

The activity of a radioactive element is the number of decays that occur per unit of time.

$$A\frac{dN}{dt}$$

$$\mathbf{A = \lambda N}$$

b. Unit of activity: disintegration by second dps or Becquerel where **1 Bq = 1 dps**.

Other unit: **Curie**

The **Curie** is the activity of **1 g of radium 226**: **1 Ci = 3.7 x 10^{10} dps**

(Bq) $A_0 = \lambda N_0$: initial activity**,** this is the activity at time **t = 0**.

The law of disintegration can be given by the following relation:

We have**: $A_t = \lambda N_t$** with **$N_t = N_0 e^{-\lambda t}$ => $A_t = \lambda N_0 e^{-\lambda t}$ => $A_t = A_0 e^{-\lambda t}$**

Chapter III

Electronic Structure of the Atom

Chapter III: Electronic Structure of the Atom

I. Introduction

The theory of the electronic structure of atoms is based on the laws describing the movement of electrons. In order to combine the corpuscular nature (particle having a mass **m**) of the already known electron (Millikan and Thomson experiments) and the undulatory nature of the latter, several experiments have been carried out and several theories have been proposed.

II. Ripple Aspect of Light: Quantum Theory (Planck Hypothesis)

A black body is a body that can absorb and emit any radiation regardless of its wavelength and at any wavelength respectively. The study of this type of radiation allowed Planck in, to formulate the hypothesis that the radiant energy of the black body is not emitted in a continuous manner but in discontinuous quantities, that is to say in "packets" called **quanta** of energy (singular, quantum). it is said that the energy is **quantified.** According to Planck, each "packet" or **quantum** of energy is equivalent to $h\nu$ where **h** is a constant of proportionality and ν is the frequency of the emitted or absorbed radiation.

$$E = h\nu \quad (1)$$

E: energy of the radiation in joules.
h: constant of Planck = **6,626 x 10^{-34} J.s.**
ν: radiation frequency in s^{-1} or Hertz (Hz).

1. Corpuscular appearance of light: Photoelectric effect

The photoelectric effect was discovered in 1887 by Heinrich Hertz. Metals subjected to the action of a beam of light (very high frequency photons), give up electrons, the latter interact with the photons that bring them energy, this energy allows the electrons to move with a speed **v** which causes the passage of an electric current. This is the electric photo (light) effect (movement of electrons).

Einstein relied on quantum theory to explain this phenomenon. He assumed that electromagnetic energy exists in the form of small entities called **photons,** the energy of each photon being equal to the Planck quantum ($E=h\nu$). This energy **E** and the speed **c** of light are linked by Einstein's relation:

$$E = m c^2 \qquad (2)$$

By equalizing **(1)** and **(2)**:

$$h\upsilon = mc^2 \Rightarrow \upsilon = mc^2/h \quad \text{with: } \upsilon = c/\lambda$$

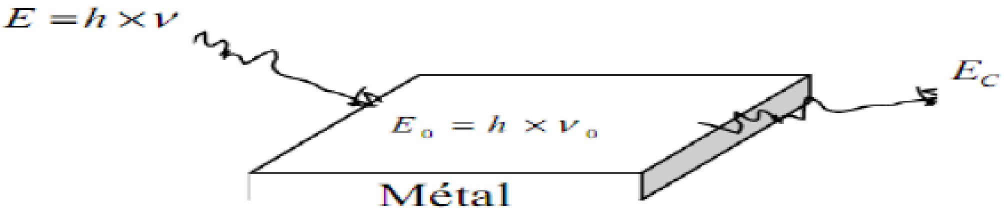
$$c/\lambda = mc^2/h$$

$$1/\lambda = mc/h$$

$$\lambda = h/mc \qquad (3)$$

Relationship **(3)**, which includes both mass and wavelength, reflects the double aspect, undulatory and corpuscular, of light.

Experiment: If a metal plate is illuminated with monochromatic light of frequency ν higher than the threshold frequency ν_0, the extra energy with respect to the characteristic energy of the metal $\mathbf{E_0 = h\nu_0}$ is dissipated in the form of kinetic energy taken by the electrons. $E_C = E - E_0 = h\nu - h\nu_0 = h(\nu - \nu_0)$



Note:

1- Only light of frequency $\nu \geq \nu_0$ determines electron emission;

2- If a photon of energy $(E = h\nu) \geq (E_0 = h\nu_0)$ is absorbed, the emitted electron will reach a maximum kinetic energy:

$$E_C = 1/2\, mv^2 = h(\nu - \nu_0)$$

2. Interaction between light and matter

- **Emission spectrum of the hydrogen atom**

This is the simplest atomic emission spectrum, it is obtained when hydrogen $\mathbf{H_2}$ is subjected under very low pressure (**≈1mmHg**) to an electric discharge created by a high voltage generator. This discharge dissociates the **H-H** bond in the hydrogen molecule and thus excites the hydrogen atoms, the excited atoms have energy that they release when they return to lower energy states by emitting electromagnetic radiation at different wavelengths. A prism makes it possible to analyze the light emitted, several groups of light lines on a dark background will be obtained on a photographic plate. The set of bright lines constitutes the emission spectrum of hydrogen.

Experience has shown that this emission spectrum has a large number of lines in the ultraviolet, visible and infrared. Each group of rays is called a series and bears the name of the scientist who discovered it. The first lines studied are in the visible range. They belong to the "**Balmer series**".

3. Spectrum of visible lines of the hydrogen atom:

- **Empirical Balmer-Rydberg relationship**

Analysis of the electromagnetic radiation emitted by the excited hydrogen atoms shows that it consists of four light lines, well separated red (R), blue (B), indigo (I), and violet (V) called respectively Hα, Hβ, Hγ and Hδ: this is the visible line spectrum of the hydrogen atom.

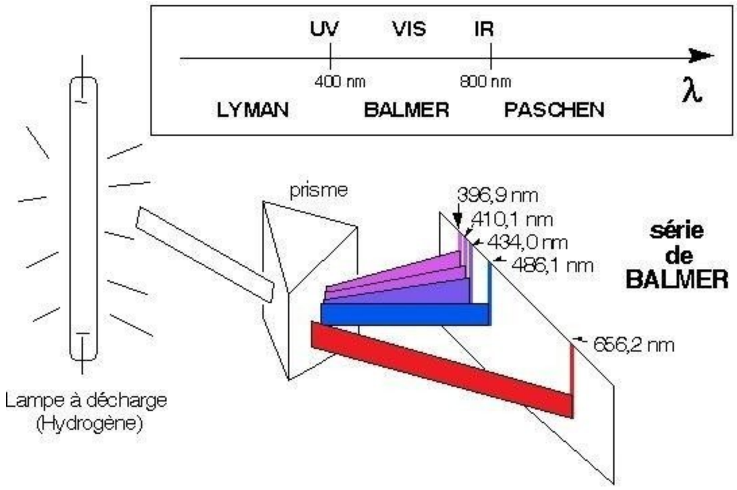


Figure 1. Emission spectra of hydrogen

Balmer suggested an experimental relationship to find the visible frequencies and calculate the wavelength of each line.

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

λ: wavelength in (cm, m, A°).

n: integer, **n_1** = 2 and **n_2** =3, 4, 5,......

R_H = 1.097 x 10^5 cm^{-1}: Rydberg constant for the experimentally determined hydrogen atom.

For **n** = 3, 4 , 5, 6 the frequencies of the four lines can be found.

III. Concept of a series of rays

Ritz generalized the Balmer-Rydberg formula to all lines of the hydrogen atomic emission spectrum. These lines are grouped into spectral series, located in various wavelength ranges, each series is distinguished by the name of the scientist it has discovered and corresponds to relaxation on an energy level. The first series, for example, called the **Lyman** series corresponds to the return of the excited electron to the ground state (n_1=1 and n' > n).

The spectrum of the hydrogen atom consists of monochromatic radiation of well-defined wavelengths **λ** . Experience has shown that the emission spectrum of the hydrogen atom has a large number of lines in the ultraviolet, visible and infrared. The first lines studied are in the visible range. They belong to the "**Balmer series**".

Série	**Transition**	**Domaine spectral**
Lyman	$n_1=1$, $n_2> 1$	Ultraviolet
Balmer	$n_1= 2$, $n_2> 2$	Visible
Paschen	$n_1=3$, $n_2> 3$	Infrarouge
Brackett	$n_1=4$, $n_2> 4$	Infrarouge
Pfund	$n_1= 5$, $n_2 > 5$	Infrarouge

IV. Interpretation of the hydrogen emission spectrum

Because of the high voltage, the H_2 electron is excited, it **absorbs** energy and then moves away from the nucleus, which makes it unstable, to regain its stability, it prefers to return to the nucleus, it must then **emit** energy in the form of light radiation (photon of frequency **υ**).

- **Light absorption:** When the hydrogen atom is not excited the electron is in a low energy orbit it is said to be in the ground state, similarly when this atom is subjected to a potential, it absorbs energy which results in

an electronic transition from the fundamental level to a higher energy level (higher level) is said to be in an excited state.

- **Light emission:** The electron of the excited atom is in an unstable state, it returns to its most stable energy level (the lower level) it is the ground state by emitting radiation. The hydrogen line spectrum shows that only certain energy levels are allowed.

V. Bohr Atomic Model: Hydrogen Atom

The first approach to quantifying the electronic properties of an atom is due to Niels Bohr. He studied the hydrogen atom and developed a structural theory of the atom, which combined Rutherford's planetary model, Planck's quantum theory, and the spectral studies that helped him establish and explain his suggestions, primarily the "spectral emission study of the hydrogen atom." It shall be based on the following principles:

The electron according to the Bohr model orbits around the nucleus in stationary circular orbits. For the orbit to be stable, it is necessary that:

$$\overrightarrow{|\mathbf{F}_{\boldsymbol{cent}}|} = \overrightarrow{|\mathrm{F}_{\boldsymbol{att}}|} \Longrightarrow \frac{m_e v^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \Longrightarrow m_e v^2 = \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$\boldsymbol{\varepsilon_0}$ is the permittivity of vacuum

The total energy of the system is equal to the sum of thekinetic energy and the potential energy

$$E_P = \int_{\infty}^{r} F_a \, dr \Longrightarrow E_P = -\frac{Ze^2}{4\pi\varepsilon_0 r} \text{ et } E_c = \frac{m_e v^2}{2} \text{ or } m_e v^2 = \frac{Ze^2}{4\pi\varepsilon_0 r} \Longrightarrow E_c = -\frac{Ze^2}{8\pi\varepsilon_0 r}$$

1. Bohr's assumptions

a. First Postulate: The electron moves in circular orbits around the nucleus, but only in fixed ray orbits. A simple expression relates the radius of these orbits, *r*, to multiples of integers, *n*.

$$r = n^2 . a_0 . 1/Z$$

In this expression, a_0 is the radius of the electron's orbit when *n* is 1 and corresponds experimentally to 52.9 pm. Various electron orbits of the hydrogen atom are partly illustrated in the following figure:

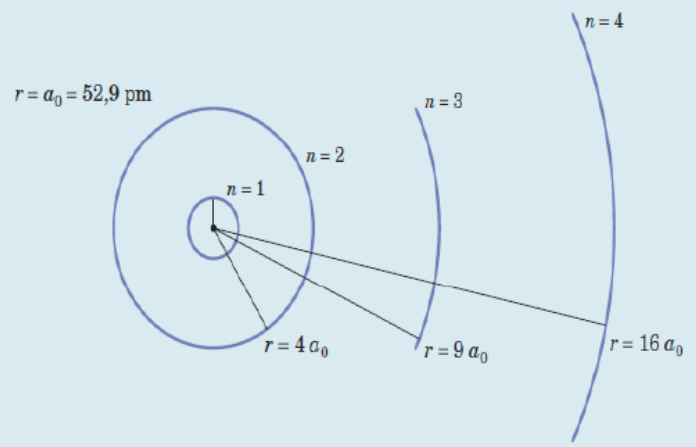


Figure 2: Representation of the partial circular orbits of the hydrogen atom.

b. Postulate 2:

The amount of angular motion of an electron on an orbit, *m.v.r*, is quantified. It is an integer multiple, n, of h/2π.

m.v.r = n/2where h is Planck's constant; m is the mass of the electron and n is the quantum number

According to this quantification condition, the electron has a determined amount of energy for each orbit and no intermediate energy is possible. Thus, each orbit is considered a **stationary state**.

The lowest energy orbit corresponds to the **ground state** of the electron ($n = 1$) and all others describe **excited states**.

Stationary state: state describing a fixed position of the electron with respect to the nucleus.

Ground state: The lowest energy state of an atom's electrons.

Excited state: energy state of the electrons of an atom, higher.

By introducing Planck's constant into this postulate, Bohr has distinguished himself from classical physics; this postulate represents an element of quantum theory that will be integrated into the development of this theory.

c. Third Postulate:

The electron emits no energy as long as it remains in a stationary orbit. When the electron shifts from a higher energy level, $_2$, to a lower level,1, radiation is emitted and its energy content is determined by Planck's equation.

$$En_2 - En_1 = h\nu = h.c/\lambda$$

h is Planck's constant, **h** = **6,623 10^{-34} j.s**

Absorbed radiation will be such that : $En_2 - En_1 > 0$.

The radiation emitted will be such that : $En_1 - En_2 < 0$.

Photon absorption or emission corresponds to a change in the electron's orbit.

The energy of the absorbed (or emitted) photon is equal to the energy difference between the two levels

$|En_2 - En_1| = \Delta E = h\nu = h\ c/\lambda$

Radius of stationary orbits

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

$$\overrightarrow{F_a} + \overrightarrow{F_c} = \vec{0} \quad \left\|\overrightarrow{F_a}\right\| = \left\|\overrightarrow{F_c}\right\| \quad \text{Avec } \left\|\overrightarrow{F_c}\right\| = \frac{m_e v^2}{r} \text{ et } \left\|\overrightarrow{F_a}\right\| = \frac{Ke^2}{r^2}$$

$$\text{Or } \left\|\overrightarrow{F_a}\right\| = \left\|\overrightarrow{F_c}\right\| \quad \Rightarrow \frac{m_e v^2}{r} = \frac{Ke^2}{r^2} \Rightarrow m_e v^2 = \frac{Ke^2}{r} \qquad (1)$$

According to Bohr's second postulate describing the quantification of orbital angular momentum, we have:

$$m_e v r = n\frac{h}{2\pi} \Rightarrow m_e{}^2 v^2 r^2 = n^2\frac{h^2}{4\pi^2} \Rightarrow m_e v^2 = n^2\frac{h^2}{4m_e \pi^2 r^2} \qquad 2$$

The combination of equation (1) with (2) leads to the expression of the radius of the orbit:

$$\boxed{r = n^2\frac{h^2}{4Km_e \pi^2 e^2}}$$

Since 4and eare constant then r depends only on the positive number called the main quantum number, i.e.:

$$\boxed{r_n = n^2\frac{h^2}{4Km_e \pi^2 e^2}}$$

For n = 1, $r_n = r_1 = 0{,}529$ Å. The first ray of Bohr’s atom. $r_n = n^2 . r_1$

2. Energy of the electron on a stationary orbit

The total energy of the system E_T is equal to the sum of the kinetic energy and the potential energy

$$E_P = -\frac{K\ e^2}{r} \quad \text{et} \quad E_c = \frac{m_e v^2}{2}$$

According to equation (1) we have:

$$m_e v^2 = \frac{Ke^2}{r} \Rightarrow \frac{m_e v^2}{2} = \frac{Ke^2}{2r}$$

$$E_T = -\frac{K\ e^2}{r} + \frac{Ke^2}{2r} = -\frac{Ke^2}{2r} \qquad \Rightarrow \boxed{E_T = -\frac{Ke^2}{2r}}$$

By replacing the equation of r in the total energy equation:

$$E_T = -\frac{Ke^2}{2r}$$

The total energy as a function of n will be:

$$E_T = -\frac{Ke^2 4\pi^2 K m_e e^2}{2h^2}\frac{1}{n^2} = -\frac{2K^2\pi^2 m_e e^4}{h^2}\frac{1}{n^2}$$

$$\boxed{E_T = -\frac{2K^2\pi^2 m_e e^4}{h^2}\frac{1}{n^2}}$$

For n = 1,

$E_n = E_1 = -\frac{2K^2\pi^2 m_e e^4}{h^2}$ = **- 21.76 10^{-19} J = - 13.6 ev** (this is the energy of the ground state of the hydrogen atom).

The states corresponding to a higher n are excited states of an electron having received an excess of energy. $E_n = E_1\frac{1}{n^2}$

The energy of the electron is quantified and depends only on a number n, which is an integer and is called a quantum number.

The excitation energy of the hydrogen atom is the energy needed to move the electron from orbit n1 to an orbit $_{n2}$.

The ionization energy of the hydrogen atom is The energy required to move the electron from the orbit n = 1 to n = ∞.

3. Frequency of radiation emitted

According to Bohr's third postulate: During the transition of the electron from an energy state **In_1** to a higher energy state In_2: There is absorption of **$\Delta E = E_2 - E_1 = h.\upsilon$**, On the other hand, the return from **n_2 (In_2)** to **n_1 (In_1)** is accompanied by an emission of the same amount of energy in opposite sign such that: **ΔE emitted = $In_1 - In_2 = h\upsilon$**

The return of the electron from an energy state in $_2$ to a lower energy state in $_1$ is accompanied by an emission of a photon such that:

$$h\nu = E_{n_2} - E_{n_1} = \frac{2K^2\pi^2 e^4\ m_e}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Hence the frequency of the radiation emitted:

$$\nu = \frac{c}{\lambda} = \frac{2K^2\pi^2e^4\ m_e}{h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The wave number 1/{\ displaystyle 1} will then be written:

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{2K^2\pi^2e^4\ m_e}{h^3\ c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The wavelengths emitted or absorbed by the hydrogen atom are given by the Ritz-Rydberg formula:

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

Where **n1** and **n2** are positive integers such that $\mathbf{n_2 > n_1}$

With $\mathbf{R_H}$ (Rydberg constant) equal to: $$R_H = \frac{2K^2\pi^2e^4\ m_e}{h^3\ c}$$

VI. Applications for the spectrum of lines of the hydrogen atom

On the basis of the equation: - **6**, it is possible to calculate the energy of the various states in which the hydrogen atom may be found. $\mathbf{E_\infty - E_1 = 13.6}$ **eV** corresponds to the energy that must be supplied to the atom to remove the electron: this is the ionization energy of the hydrogen atom ($\mathbf{E_I = 13.6}$ **eV**).

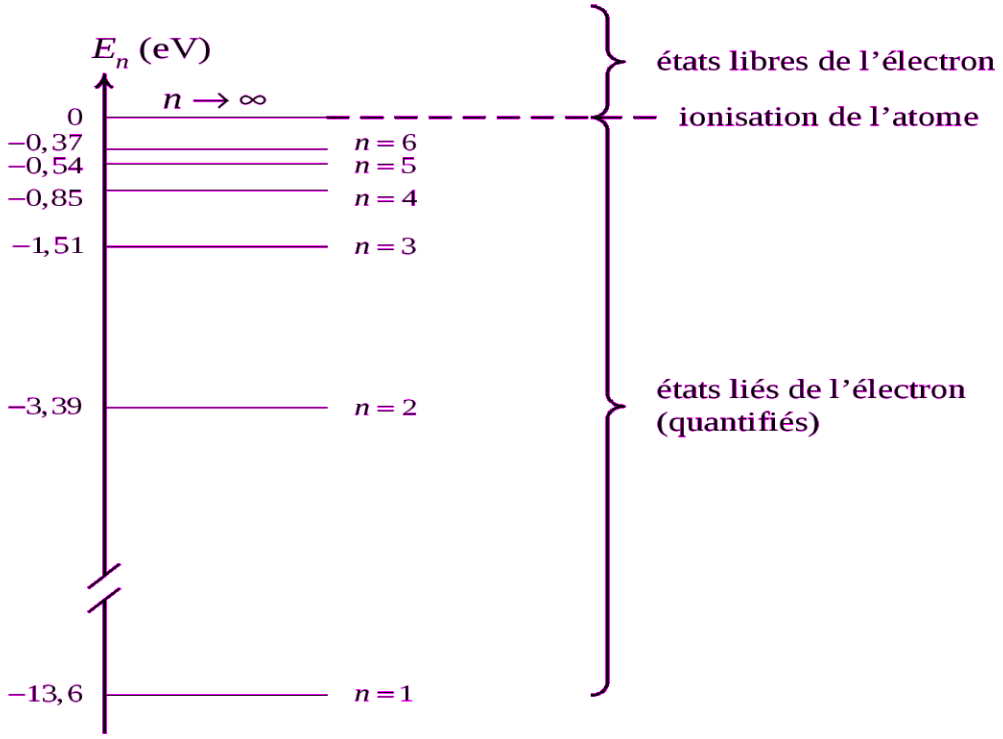


Figure 3: Energy diagram of the hydrogen atom

Bohr's theory satisfactorily interprets the optical spectrum of the hydrogen atom and allows the calculation of the Rydberg constant. However, its application to atoms of more than one electron reveals difficulties.

1. Application of Bohr's theory on hydrogenoids

a. Definition of a hydrogenoid

It is an atom that has lost all its electrons except one, which makes it similar to a hydrogen from the point of view number of electrons so we can apply Bohr's theory on this hydrogenoid.

Examples of hydrogenoids**:** $_2\mathbf{He}^+$, $_3\mathbf{Li}^{2+}$, $_4\mathbf{Be}^{+3}$

The $_2\mathbf{He}$ helium atom has two electrons, while the $_2\mathbf{He}^+$ ion has 1 electron.

The lithium atom $_3\mathbf{Li}$ has three electrons, while the ion $_3\mathbf{Li}^{++}$ has 1 electron.

The beryllium atom $_4\mathbf{Be}$ has four electrons, while the ion $_4\mathbf{Be}^{+3}$ has 1 electron.

$\mathbf{E_1' = E_1 Z^2}$ with $\mathbf{E_1}$ the energy of the ground state of the hydrogen atom.

For the calculation of the **rn, En,** and **Vn**, a reasoning similar to that of the hydrogen atom is made by considering a nucleus whose charge is **Ze (Z ≥ 2).**

$$\mathbf{r_n = \frac{n^2}{Z} r_{1H} \quad : \quad r_{1H} = 0{,}53\ A^\circ}$$

$$\mathbf{E_n = \frac{Z^2}{n^2} E_{1H} \quad : \quad E_{1H} = -13{,}6\ eV}$$

- Radius of the first orbit :

-Bonding energy of the nucleus electron of the hydrogenoid in its ground state (n=1):

E1: Energy of the ground state of the hydrogen atom.

In addition to his remarkable success in interpreting the emission spectrum of the hydrogen atom, Bohr confirmed Planck's theory on the quantification of energy and he paved the way for the study of the electronic structure of the atom but his theory remains insufficient.

of the Bohr Model

-Does not explain the emission spectrum of the hydrogen atom which becomes more complex in the presence of a magnetic field.

-It failed to interpret the emission spectra of poly or multielectronic atoms.

-It did not take into consideration the presence of several layers.

-IS only valid for hydrogen and hydrogenoids, not for polyelectronic atoms, because it does not take into account the influence of a given electron on its neighbors.

-Does not allow to describe the chemical bond (in particular the covalent bond).

2. Application of the Bohr model to polyelectronic atoms

In a polyelectronic atom, the electron responsible for emitting the optical spectrum of lines is separated from the nucleus by deep electrons. The given electron is then attracted both by the nucleus and repelled by the other electrons. The real attraction exerted on it is less than that exerted by the nucleus alone. There is a shielding effect on the part of the deep electrons with respect to the optical electron which decreases the nucleus-electron attraction called **constant of the shielding effect σ.**

The effective atomic number seen by the electron i is: $\mathbf{Z^* = Z - \sigma}$

Z*: often called **effective load.**

Z: **actual core load.**

σ : screen constant, it represents the repulsion caused by the presence of the electrons located between the nucleus and the electron studied.

Z* is all the smaller as there are electrons between the nucleus and the electron i.

To calculate the force of attraction between this electron and the nucleus, the energy En of this electron and the wave number, this screen effect must be taken into consideration**.**

The electrostatic force for a polyelectronic atom is then written:

$$F_e = \frac{k(Z-\sigma)e^2}{{r_n}^2}$$

$$r_n = n^2 \frac{r_1}{(z-\sigma)}$$

r_1: radius of the 1st orbit of the hydrogen atom **(r_1= 0.53 A°).**

$$E_n = \frac{E_1(z-\sigma)^2}{n^2}$$

E_1 : energy of the 1st orbit of the hydrogen atom **($E_1 = -$ 13, eV)**

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H(Z-\sigma)^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R_H Z^{*2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

This formula is analogous to Moseley's law.

Analysis of the emission lines of the X-ray spectrum of a number of elements allowed Moseley to establish an empirical law linking the frequency of the emitted radiation **ν** and the atomic number **Z.**

$$\sqrt{\nu}=\mathbf{a}(\mathbf{Z}-\boldsymbol{\sigma})$$

a and ≈ are constants.

The spectral lines are grouped by series (series **K**, **L**, **M**, etc.) and each series has several lines ($_{\text{lines}}$, for the **K** series for example)

•: line for which n_1 =1 and n_2 = 2

•: line for which n_1 =1 and n_2 = 3

3. Application of Bohr theory to hydrogen spectra (success of Bohr theory):

Radiation can be studied by passing it through a prism. The sun's radiation can be broken down into a succession of radiation of various hues ranging from red to purple.

- The solar radiation spectrum The solar spectrum is a continuous spectrum.

The spectrum of the emission of Hydrogen is a discontinuous spectrum (Spectrum of lines), consisting of very fine lines of various hues, separated by vast dark spaces. The success of Bohr's theory lies in the fact that it can explain the discontinuous spectrum of Hydrogen.

4. Orbits and Energy Levels of the Hydrogen Atom:

The orbit n=1 corresponds to the state of the most stable electron (ground state). The absorption of light by the atom causes the electron to jump into a higher orbit. Several series of lines can be distinguished.

A series of lines corresponds to the set of all the lines that return the electon to a given level of n fixed. Each series of stingrays has been named after its discoverer:

n= 1: LYMAN series (ultraviolet); n= 2: BALMER series (visible); n= 3: PASCHEN series (infrared); n= 4: BRACKETT series (near infrared) and n= 5: PFUND series (far infrared).

Bohr's theory proved to be very limited with regard to systems comprising more than one electron, i.e. the polyelectronic atom. Hence the need for a new theory called the quantum theory of the atom.

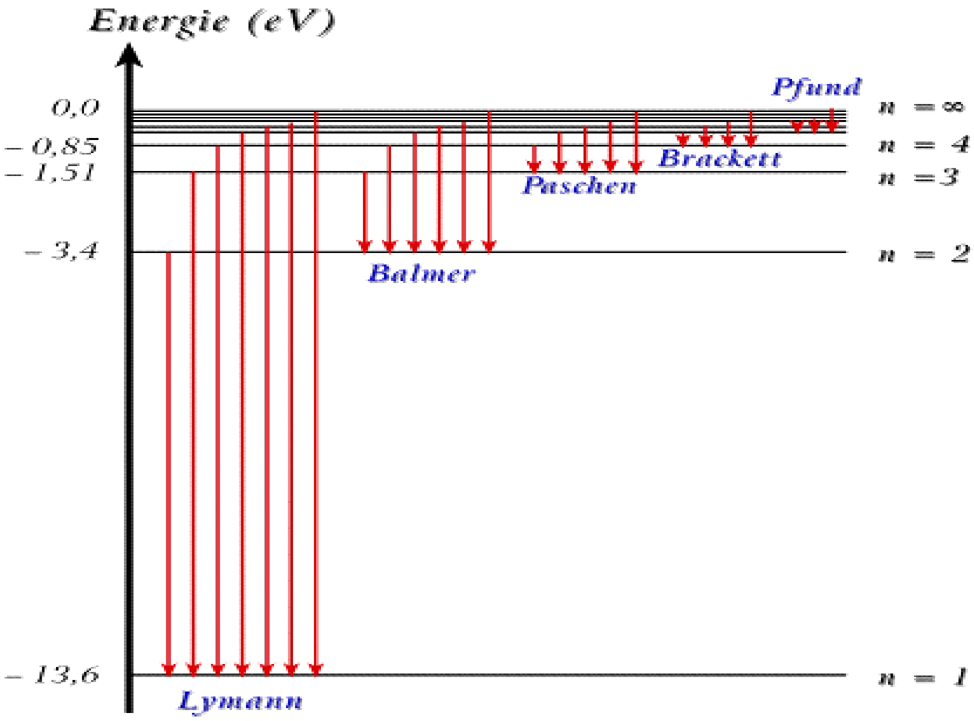


Figure 4: Representation of the spectrum of electronic levels of hydrogen

5. Hydrogen atom in wave mechanics

Introduction: Hydrogen atom in wave mechanics

Bohr's theory provides the first atomic model in which an accurate location of the electron, on a determined orbit, is admitted. The nucleus containing protons and neutrons, around which electrons orbit in different orbits.

The atomic models developed in classical mechanics (Rutherford, Bohr) or wave mechanics (De Broglie, Heisenberg, Schrodinger) make it possible to represent the simplest atom, that of hydrogen and its behaviour.

However, as early as 1930 Bohr's theory had to give way to a new theory based on modern ideas based on the wave properties of matter. it became clear that the movement of electrons was not limited to well-defined orbits but rather a complex movement better described by associating wave properties with the calculation of probability. The notion of the precise location of the electron has been replaced by a statistical notion of the probability of the presence of the electron. The mathematical processing is based on the Schrodinger equation, the resolution of which corresponds to the function **Ψ**, called the wave function. **$[\Psi]^2$** gives the probability of the presence of the electron in a certain volume of space, characterized by its x, y, z coordinates.

6. Corpuscle-wave duality: Wave associated with the electron:

The Broglie relation

Planck and Einstein had already shown the undulatory and corpuscular nature of light (dualitic aspect). Louis De Broglie in 1925 showed that any moving material particle (corpuscle), of mass **m**, moving at the speed **v** can be associated with a pilot wave of wavelength **λ** such that: between the frequency **ν** of the associated wave and the energy **E** of the particle, there exists the relationship **E = hν**

In De Broglie's model, the electron is described by a standing wave such as:

$$2\pi r = n\lambda = \frac{nh}{mv}$$

This means that: the total length of the orbit is equal to an integer number of wavelengths of the de Broglie wave.

2. Heisenberg uncertainty principle

It is not possible to know simultaneously and accurately the position x and the momentum p of a particle. This now excludes at the atomic scale the notion of trajectory or orbit of the electron. Heisenberg postulated that a simultaneous measurement of the position and velocity of a particle could only be made within the limit where the uncertainties Δx and **ΔP** verify the relationship:

$$\Delta x . \Delta P \geq \frac{h}{2\pi}$$

P: momentum **(p=mv)**.

h: Planck's constant = **$6.625x10^{-34}$ J.s**

7. Atomic Orbit

wave function

Since the position and velocity of a particle cannot be known at the same time, it is difficult to accurately predict its trajectory.

In wave mechanics, an electron located at a point of coordinate (x, y, z) at the instant t, is described by a function Ψ (x, y, z, t) called wave function which has no physical meaning and which is a function of the coordinates of the electron**.** If the electron is in a stationary state of energy, then the wave associated with it is stationary (constant t).

b. Likelihood of presence:

Wave mechanics provides a less accurate representation of the hydrogen atom than does Bohr's planetary model, with its well-defined orbits. We are no longer talking about the exact position of the electron, but about the probability that the electron is in a given region of the atom.

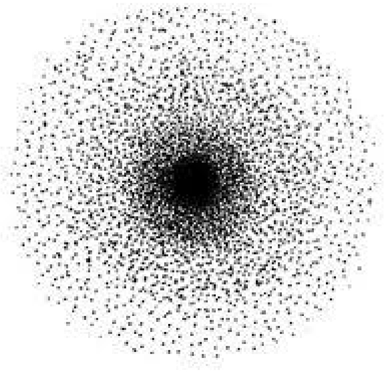


Figure 5: Possible electron positions: electron cloud

c. Schrödinger's equation:

De Broglie's wave had no equation. Schrödinger, starting from the waves of Louis De Broglie, proposes a wave equation to describe a particle and in particular an electron.

$$\hat{H}\Psi = E\Psi$$

$\hat{H}$: Hamiltonian operator.

E : total energy of the electron (sum of kinetic and potential energies).

$\Psi(x,y,z)$ is the wave function associated with the electron, representing the state of the latter.

It is a solution of the Schrödinger equation. The solutions of this equation indicate that the electron can only take a limited number of energy values that are the same as those predicted by Bohr's theory. Solving the Schrödinger equation provides one or more wave functions, or orbits, associated with each of the permitted energy levels. Allowed orbitals are characterized by quantum numbers.

d. Quantum Numbers

The Schrödinger equation admits for its solution solutions that introduce the notion of quantum numbers. In fact, it takes four to describe a given electron completely and unequivocally.

In the quantum model, electrons are not characterized bytheir trajectories but by their energies. The state of an electron is defined by four quantum numbers.

- **principal quantum number**

It is a non-zero natural integer designated by the number: 1, 2, 3, 4 (layers k, L, M, N…..). It corresponds to the number of the layer to which the electron belongs, it defines the size of the orbital and the energy associated with it.

- **Secondary or azimuthal quantum number l**

It defines the general shape of the atomic orbital and can take integer values from **0** to **n-1**.

$$\mathbf{0 \leq l \leq n- 1}$$

refers to the layer to which a letter is assigned.

l	**0**	**1**	**2**	**4**
Sublayers	**s**	**p**	**d**	**f**

The electrons of a given layer **n** are distributed over sub-layers of energies $E_{n,l}$ fixed by the data of the doublet (**n**, **l**) alone.

If **n = 1**; **l = 0**: orbital **s.**

If **n = 2**; **l = 0**: orbital **s**

l = 1: **p** orbital

- **Magnetic quantum number m**

It gives the number of orbitals (quantum boxes) in the sub-layer and defines the orientation in space of the orbital or areas of probability of presence. The values of m are integer and limited by the values of l:

$$\mathbf{-l \leq m \leq +l}$$

Each sub-layer **(n, l)** contains **(2l+1)** quantum or atomic orbital cells defined by the possible triplets **(n, l, m)**.

To symbolize the different shapes of the orbital, we use a quantum box represented by a rectangle ▢

l = 0: orbital **s; m = 0**

l = 1: **p orbital; m = -1 , 0, +1**

A triplet **(n, l, m)** defines a quantum square.

- **Quantum spin number s or m_s**

It was introduced by the English physicist Dirac in order to treat the behavior of the electron in quantum mechanics. It tells us about the proper movement of the electron in the presence of an external magnetic field $\vec{B}$.

The electron rotates on itself like a spinning top, which generates a magnetic moment called spin. Two values are acceptable:

$s=+\frac{1}{2}$ **et** $s=-\frac{1}{2}$

If the spin is directed upwards: $\uparrow s=+\frac{1}{2}$

If the spin is directed downwards: $\downarrow m_s=-\frac{1}{2}$

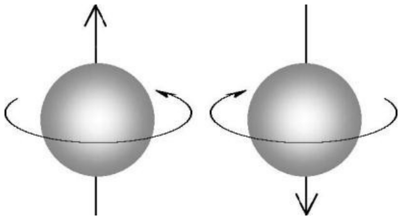
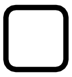


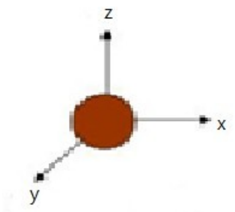
Figure 6: Representation of electron spin

For a layer **n**, the number of quantum cells is $\mathbf{n^2}$ and the maximum number of electrons that can be distributed over all the sub-layers of the layer is $\mathbf{2n^2}$. A quantum cell can only contain a maximum of **2** electrons of opposite spins.

e. Forms of atomic orbitals

Orbital s: is of spherical geometry centred on the nucleus and can accommodate a maximum of 2 electrons. This orbital is represented by a rectangular box.

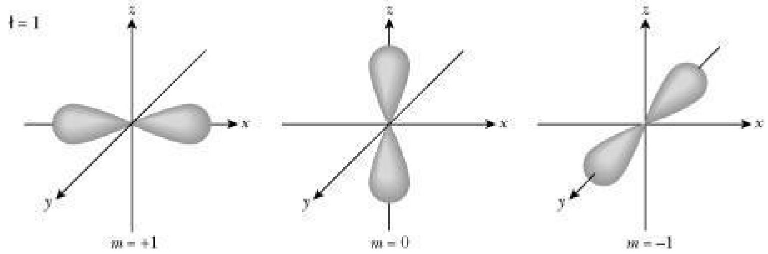




Atomic Orbital Geometry ns

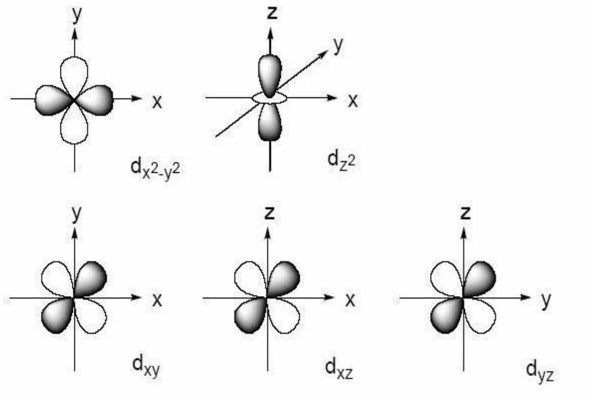
Orbital p: consisting of 2 adjoining lobes: e**l** e has two lobes on the x-axis **(m= -1, P_x)**, two lobes on the y-axis **(m=0, P_y)**, two lobes on the z-axis **(m=1, P_z)**. (the 3 orbitals **p (p_x, p_y and p_z)** can accommodate a maximum of 6 electrons).

P$_x$ P$_y$ P$_z$



Atomic Orbital Geometry np

Orbital d: el e has 4 lobes in the form of a flower, there are five shapes 5 possible geometries (the 5 **d** orbitals can accommodate a maximum of 10 electrons).



Atomic Orbital Geometry nd

VII. Electronic configuration of a polyelectronic atom

1. Filling rules

The electronic configuration of an atom is the **Z-electron** distribution of the atom in a ground state on atomic orbitals.

2. Principle of stability: Klechkowsky rule

The ground state of the atom represents the minimum energy level, therefore the most stable state of the electron. The electrons will start by occupying the lowest energy levels at the limit of the vacant places.

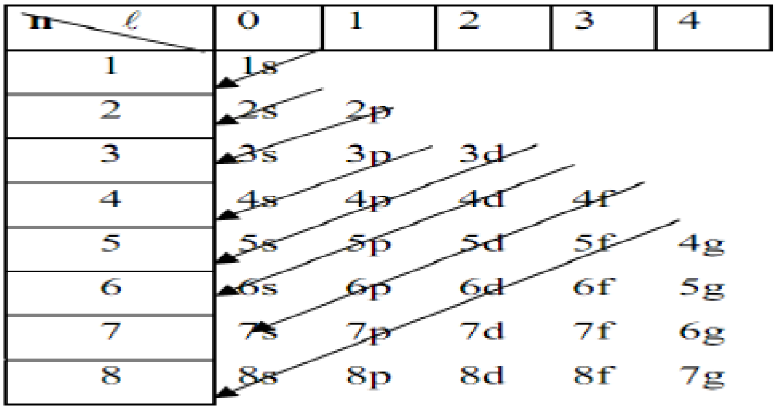
The filling of layers and underlayers is given by Klechkowsky's rule. It is done in ascending order **(n + l)**.

If **n+l** is the same, the sublayer with the smallest **n** will be filled first.

Examples: **4p** and **3p**, **(n+l) = 4** for both sublayers, **n** the smaller is that of **3p** so **3p** filling comes before **4s**.

- The various layers and sublayers are written in a table, each row corresponding to a value of **n**.

- The filling is done along the diagonals.



Schematic representation of Klechkowsky's rule

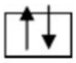
The filling order of the quantum sub-layers is then:

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

Pauli-Fermi principle

Before attempting to correlate the electronic structures, we need to learn how to distribute the electrons on the different orbitals.

It is Pauli who first states the basic principle, according to which this distribution takes place: two electrons of the same atom cannot have their four identical quantum numbers **n, l, m** and **s**. Consequence:

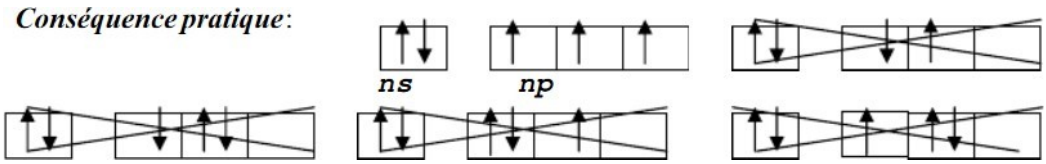


For example: if **n**, **l,** and **m** are the same, we have **s = + 1/2** for one and **s = - 1/2** for the other.

4. hund's rule

In the ground state, in an underlayer comprising several quantum cells of the same energy, the electrons occupy the maximum number of quantum cells before pairing, the spins of the unpaired electrons being parallel. This rule can be interpreted as follows: two electrons carrying identical charges repel each other and therefore do not tend to end up in the same region of space. As a result, two electrons end up in separate orbitals as long as there are orbitals corresponding to the same energy level.

Practical consequence:



4. Establishment of the electronic configuration of an element

The electronic configuration of atoms or ions is obtained by applying Klechkowsky's rule and taking into account Pauli's exclusion principle and Hund's rule.

Example**:** Either to establish the electronic configuration of the element of **Z = 53**.

$$\mathbf{1\,s^2,\ 2\,s^2,\ 2\,p^6,\ 3s^2,\ 3\,p^6,\ 4\,s^2,\ 3\,d^{10},\ 4p^6,\ 5\,s^2,\ 4\,d^{10},\ 5\,p^5}$$

It is necessary to return the various layers and sublayers to their natural order by increasing values of **n**.

$$\mathbf{1\,s^2,\ 2\,s^2,\ 2\,p^6,\ 3s^2,\ 3p^6,\ 3\,d^{10},\ 4\,s^2,\ 4p^6,\ 4\,d^{10},\ 5\,s^2,\ 5\,p^5}$$

Simplified writing:

K2, L8, M18, N18, O7.

The electronic configuration of the outer layer or valence layer of rare gases is written: $\mathbf{ns^2\ (n\text{-}1)d^6\ np^6}$ except $\mathbf{{}_2He\ 1s^2}$, completely filled which gives them great stability.

6. Klechkowsky Rule Exceptions

From level **n=4**, the filling of atomic orbitals does not strictly comply with the Klechkowsky rule. Numerous irregularities appear in the filling of sub-layers **d** and **f**.

A sub-layer “d” has a state of maximum stability if it is either half filled or completely filled. It can be considered that an electron of the underlayer "jumps" on the underlayer d to complete it at 5 or 10 electrons. This rule applies particularly to configurations of the type $\mathbf{d^9\ s^2}$ (Cu, Ag and Au) and $\mathbf{d^4\ s^2}$ (Cr, Mo) which will be transformed into $\mathbf{(n\text{-}1)d^{10}\ ns^1}$ and $\mathbf{(n\text{-}1)d^5\ ns^1}$ respectively.

VIII. Simplified electronic configurations

We adopted a simplified writing of electronic configurations highlighting the valence layer.

For this, we will use particular atoms called rare gases (or noble or inert), these rare gases have the particularity of being chemically very stable.

1. Valence electrons and core electrons

Writing the electronic configuration of an atom in the ground state reveals two types of electrons.

a. Valence electrons: are the outermost electrons of an atom that are located at the highest level those of the highest energy orbitals, these electrons belong to the valence layer. It is with these electrons that the largest value of the main quantum number is associated. They are the furthest from the nucleus of the atom, so less bound than the others. They are therefore involved in the establishment of chemical bonds.

From a purely chemical point of view, the last layer occupied is essential because it is it that will fix in priority the chemical properties of the atom.

b. Lower layer electrons: are called inner electrons or core electrons, and their main quantum number is lower than that of the outer layer. They do not participate in the formation of chemical bonds because the energies of electrostatic interaction with the nucleus of the atom are too high for them to leave the interaction of the nucleus.

Examples:

Ca (**Z= 20**): Electronic configuration $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2}$

The two electrons of the **4s** layer are valence electrons while the remaining 18 electrons are internal electrons or core electrons.

C (**Z=6**): Electronic configuration $\mathbf{1s^2\ 2s^2\ 2p^2}$

Only the four electrons of the **n=2 layer (2s 2p)** participate in the chemical reactions: they are **valence** electrons.

2. Special case of "d" electrons

If the **nd** sublayer is not completely filled with **10 electrons**, these electrons belong to the valence layer and therefore participate in the creation of chemical bonds.

Example:

Fe (**Z=26**): its electronic configuration is written: $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6}$

The electrons $\mathbf{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6}$ are **core** electrons sincethey are located on the deep or internal layers, while the electrons $\mathbf{4s^2\ 3d^6}$ are **valence** electrons. They participate in chemical reactions.

The **3d** electrons are part of the **valence** layer, the iron atom then has 8 **valence** electrons and 18 **core** electrons.

d. Case of ions

- **Anions** ($\mathbf{X^{n-}}$)

An electron for each negative charge was added to the electronic structure of the neutral atom.

Examples:

$\mathbf{Cl\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5}$

$\mathbf{Cl^-\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6}$

$\mathbf{{}_8O\ \ 1s^2\ 2s^2\ 2p^4}$

$\mathbf{{}_8O^{2-}\ 1s^2\ 2s^2\ 2p^6}$

- **Cations** ($\mathbf{X^{n+}}$)

An electron for each positive charge is subtracted from the last layer of the electronic structure of the neutral atom.

Example:

$\mathbf{{}_{11}Na\ 1s^2\ 2s^2\ 2p^6\ 3s^1}$

$\mathbf{{}_{11}Na^+\ 1s^2\ 2s^2\ 2p^6\ 3s^0}$

$\mathbf{{}_{25}Mn\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5}$

$\mathbf{{}_{25}Mn^{2+}\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5}$

Chapter V

The periodic table of the elements

Chapter V : The periodic table of the elements

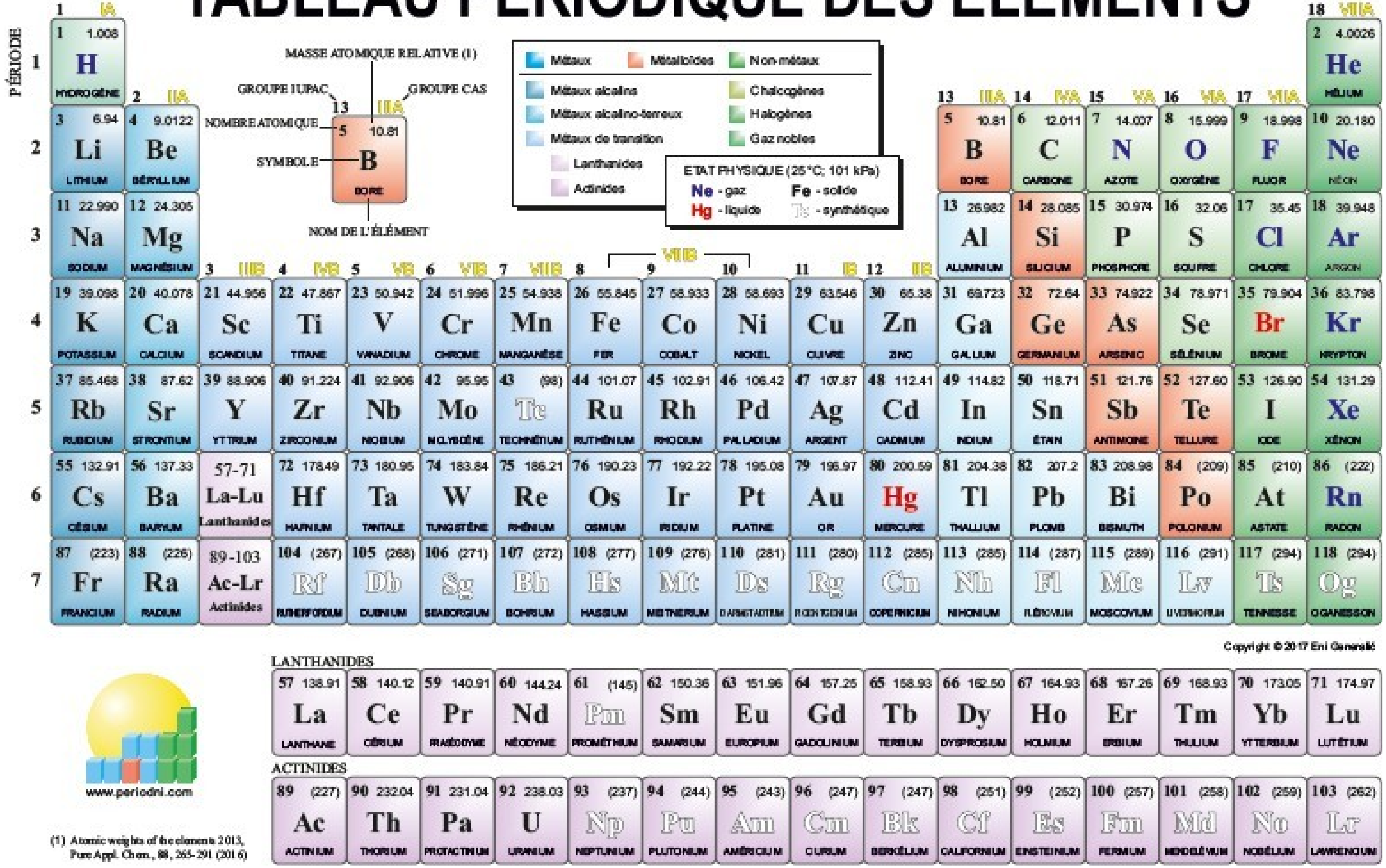
I. Introduction

The periodic table of the elements or simply periodic table of the elements (also called Mendeleev table), represents all the chemical elements, ordered by increasing atomic number, and organized according to their electronic configuration, which underlies their chemical properties.

His invention is generally attributed to the Russian chemist Dmitry Mendeleev, who in 1869 built a table different from the one we use today but similar in principle, whose great interest was to propose a systematic classification of the chemical elements known at the time in order to emphasize the periodicity of their chemical properties, to identify the elements that remained to be discovered, and even to be able to predict the properties of these elements then unknown.

The periodic table has undergone many readjustments since then until taking the form we know it today, and has become a universal reference to which all types of physical and chemical behaviors of the elements can be related. As of February 2010, its standard shape had 118 elements, ranging from $_{1}\mathbf{H}$ to $_{118}\mathbf{Lr}$

TABLEAU PÉRIODIQUE DES ÉLÉMENTS



MASSE ATOMIQUE RELATIVE (1)
GROUPE IUPAC
GROUPE CAS
NOMBRE ATOMIQUE
SYMBOLE
NOM DE L'ÉLÉMENT
13 IIIA 5 10.81 B BORE

- Métaux
- Métalloïdes
- Non-métaux
- Métaux alcalins
- Métaux alcalino-terreux
- Métaux de transition
- Lanthanides
- Actinides
- Chalcogènes
- Halogènes
- Gaz nobles

ETAT PHYSIQUE (25 °C; 101 kPa)
Ne - gaz
Fe - solide
Hg - liquide
Ts - synthétique

GROUPE

PÉRIODE	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.008 H HYDROGÈNE																	2 4.0026 He HÉLIUM
2	3 6.94 Li LITHIUM	4 9.0122 Be BÉRYLLIUM											5 10.81 B BORE	6 12.011 C CARBONE	7 14.007 N AZOTE	8 15.999 O OXYGÈNE	9 18.998 F FLUOR	10 20.180 Ne NÉON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNÉSIUM											13 26.982 Al ALUMINIUM	14 28.085 Si SILICIUM	15 30.974 P PHOSPHORE	16 32.06 S SOUFRE	17 35.45 Cl CHLORE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANE	23 50.942 V VANADIUM	24 51.996 Cr CHROME	25 54.938 Mn MANGANÈSE	26 55.845 Fe FER	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu CUIVRE	30 65.38 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.971 Se SÉLÉNIUM	35 79.904 Br BROME	36 83.798 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.95 Mo MOLYBDÈNE	43 (98) Tc TECHNÉTIUM	44 101.07 Ru RUTHÉNIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag ARGENT	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn ÉTAIN	51 121.76 Sb ANTIMOINE	52 127.60 Te TELLURE	53 126.90 I IODE	54 131.29 Xe XÉNON
6	55 132.91 Cs CÉSIUM	56 137.33 Ba BARYUM	57-71 La-Lu Lanthanides	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALE	74 183.84 W TUNGSTÈNE	75 186.21 Re RHÉNIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINE	79 196.97 Au OR	80 200.59 Hg MERCURE	81 204.38 Tl THALLIUM	82 207.2 Pb PLOMB	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinides	104 (267) Rf RUTHERFORDIUM	105 (268) Db DUBNIUM	106 (271) Sg SEABORGIUM	107 (272) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (276) Mt MEITNERIUM	110 (281) Ds DARMSTADTIUM	111 (280) Rg ROENTGENIUM	112 (285) Cn COPERNICIUM	113 (285) Nh NIHONIUM	114 (287) Fl FLÉROVIUM	115 (289) Mc MOSCOVIUM	116 (291) Lv LIVERMORIUM	117 (294) Ts TENNESSE	118 (294) Og OGANESSON

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LANTHANIDES

57 138.91 La LANTHANE	58 140.12 Ce CÉRIUM	59 140.91 Pr PRASÉODYME	60 144.24 Nd NÉODYME	61 (145) Pm PROMÉTHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.05 Yb YTTERBIUM	71 174.97 Lu LUTÉTIUM

ACTINIDES

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMÉRICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKÉLIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDÉLÉVIUM	102 (259) No NOBÉLIUM	103 (262) Lr LAWRENCIUM

www.periodni.com

(1) Atomic weights of the elements 2013, Pure Appl. Chem., 88, 265-291 (2016)

II. Periodic table of D. Mendeleev (1869)

Mendeleev develops the classification closest to the current periodic table, in addition to the classification of chemical elements by increasing atomic mass, he puts in the same columns the elements with similar physico-chemical properties. Mendeleev's table contained 7 columns (also called **groups**) and 12 rows (called **periods**). This table contained empty boxes because all the elements had not yet been discovered, 63 elements were known at the time.

III. Modern Periodic Table

The current periodic table classifies the elements by increasing atomic number Z. It differs little from the classification according to the increasing order of atomic masses, which is why it is sometimes called Mendeleev's table. Whereas in reality an element is defined by its atomic number Z and not by its atomic mass, which can vary as a result of the existence of isotopes.

This table should have 32 columns and 7 rows, but to reduce the size of the table we represent two series of elements of Z = 58 to 71 and Z = 90 to 118 below the main table which has 18 columns (groups) and 7 rows (periods).

1. Description of the periodic table: Rules for the construction of the periodic table (groups and periods)

The periodic table is a consequence of electronic configurations. The periodic table is based on the formation of groups consisting of elements with similar chemical properties.

Elements whose valence layer is characterized by the same value of **n** (layers **K**, **L**, **M**, **N**, etc.) are grouped in the same line (**period**), and elements whose electronic configuration of the valence layer is similar are grouped by column (**family or group**). Elements of the same family have the same number of valence electrons.

a. Periods

A horizontal line in the periodic table constitutes a period. Periods Are Cool

number of 7 and different lengths. The period number corresponds to the main quantum number **n** of the outer layer.

b. Groups

The periodic table consists of 18 columns divided into 9 groups (**I** to **VII** and **0**) with subgroups (**A** and **B**).

Subgroup A: contains elements whose outer sublayer is **ns or np.**

Subgroup B: contains the elements whose outer layer contains the sublayer **d**

Group number corresponds to the number of electrons of the outer layer (**ns**, **np**) for subgroups **A** ($\mathbf{I_A}$ up to $\mathbf{VIII_A}$), the group corresponding to the noble gases that should constitute group $\mathbf{VIII_A}$ is denoted group **0**. Indeed, the outer layer of these elements ($\mathbf{ns^2\ np^6}$) is saturated, which gives them great stability, they are characterized by the degree **0**, which explains the absence of chemical reactivity (inert gases).

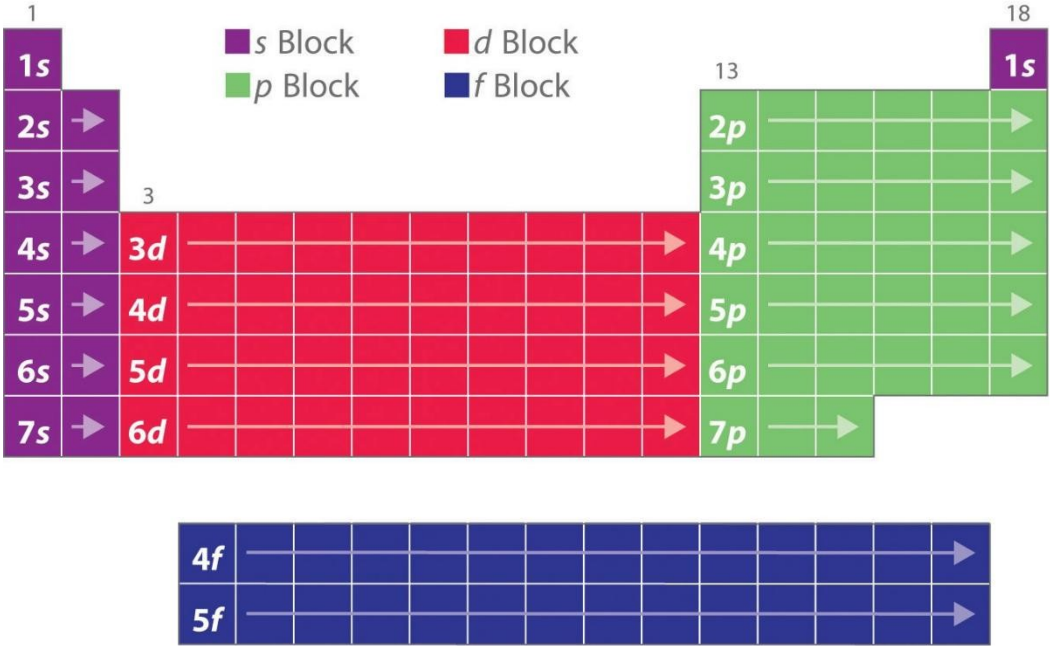
For subgroups **B**, the group number corresponds to the number of electrons in the outer layer (**ns** + (i − **i) d**), unless the total is **8**, **9** or **10** (then group $\mathbf{VIII_B}$ is denoted group **III**) or if the total is **11** or **12** (then $\mathbf{I_B}$ or $\mathbf{II_B}$).

Indices **I**, **II**, **III**,…… indicate the number of electrons on the outer layer.

Group	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII Triad**	**VIII Rare gases**
S/Group	**A / B**	**A / B**	**A / B**	**A / B**	**A / B**	**A / B**	**A / B**	**B**	**A**
Column	**1 / 11**	**2/12**	**13.3**	**14/4**	**15.5**	**16. 6**	**17/7**	**8, 9, 10**	**18**

2. Block structure of the elements of the periodic table

The periodic table is divided into 4 **blocks (s, p, d and f)** corresponding to the type of the last valence sub-layer occupied. The number of columns of each block corresponds to the maximum number of electrons that can be placed in each sub-layer: **2 / 6 / 10 / 14**, for the sub-levels **s / p / d / f** respectively.



Subgroup A: Represented by two blocks **s** and **p**.

Subgroup B: Family located between $\mathbf{II_A}$ and $\mathbf{III_A}$, represented by block **d**.

Block s: It is placed to the left of the periodic table and consists of columns **1** and **2** which contain the elements whose electronic configuration involves the electrons $\mathbf{ns^1}$ and $\mathbf{ns^2}$. The number of valence electrons indicates the number of the column.

Block p: It is placed to the right of the periodic table and consists of six columns of **13** to **18** and corresponds to the progressive filling of the **np** sub-layer, the $\mathbf{(n-1)\ d}$ and **ns** sub-layers being saturated with $\mathbf{(n-1)\ d^{10}}$ and $\mathbf{ns^2}$. The number of valence electrons plus **10** indicates the number of the column.

Block d: It is placed between block **s** and block **p** consists of 10 columns from 3 to 12 involving the progressive filling of sub-layer $\mathbf{(n-1)d}$, sub-layer **ns** being saturated with $\mathbf{ns^2}$. Note that the column number indicates the number of electrons **s** and **d**.

Block f: This block, presented in two lines, is placed at the bottom of the main table. The elements of this block, which are **14** in number per line, correspond to the filling of the sub-layers **f**.

IV. Main families of the periodic table

- Family of alkali metals (column **1**, group $_{\mathbf{IA}}$): electronic configuration of the valence layer of type $\mathbf{ns^1}$, it comprises Li, Na, K, Rb, Cs and Fr. Alkali metals are metals that have only one valence electron. They all form cations by losing an electron (Li^+, Na^+, K^+ etc.).

- Alkaline earth family (column **2**, group $\mathbf{II_A}$) with an external electronic structure $\mathbf{ns^2}$ (Be, Mg, Ca, Sr, Ba and Ra). They have two valence electrons. They all form cations by losing two electrons (Be^{2+}, Mg^{2+}, Ca^{2+} etc...).

- Family of halogens (column **17**, group $\mathbf{VII_A}$) of external electronic structure $\mathbf{ns^2\ np^5}$ they have **7** valence electrons. It includes fluorine, chlorine, bromine, iodine and astatine, they are non-metals and form the ions F^-, Cl^-, Br^-, I^- and At^-.

Family of noble gases (noble or inert) (column **18**, group $\mathbf{VIII_A}$ or **0**), this family includes helium, neon, argon, krypton, xenon and radon, they all have a complete outer layer **ns np** except $_2\mathbf{He}\ \mathbf{1s^2}$. Rare gases exist in atomic form (not associated in molecules) and they are chemically very stable.

- Family of 1st category transition elements (columns from **3** to **12**, groups), their configuration ends on a sub-layer **d**.

- Elements of the triads, constitute groups **VIII** or **III** (columns 8, 9 and 10).

There are three types of triads: Iron Triad (Fe, Co, Ni), Palladium Triad (Ru, Rh, Pd) and Platinum Triad (Os, Ir, Pt).

- Rare earth family (block **f**), these are 2 nd category transition elements, corresponding to the filling of the sub-layer **f**. Indeed, the orbitals that correspond to the filling of the **4f** orbital follow the lanthanum (La) from which their name is called the **lanthanides**, those that correspond to the filling of the **5f** orbital follow the actinium (Ac) from which their name is called the **actinides**.

In the periodic table there are some filling "anomalies", ensuring a higher level of stability for the elements concerned. The **Z** elements
= 29, 47 and 79 should be in $\mathbf{ns^2\ d^9}$. They are actually in $\mathbf{ns^1\ d^{10}}$. Elements
Z = 24 and 42 should be $\mathbf{ns^2\ d^4}$. They are actually $\mathbf{ns^1\ d^5}$.

V. Positioning of the element in the periodic table

The positioning of the element is done from the configuration of the outer layer.

-Period: number of the outer layer.

- Group: the number of valence electrons.

- Subgroup A: Electrons of valence **ns or ns** and **np.**

- subgroup B: Electrons of valence **ns** and **(n-1)d**.

For elements belonging to subgroup **B** (block **d**), the valence layer will be of the form $\mathbf{ns^x}$ $\mathbf{(n\text{-}1)d^y}$. The sum **(x+y)** of the electrons will tell us about the group of the element:

- When **3 (x+y) 7**, the corresponding elements will belong to the groups

$\mathbf{III_B}$, $\mathbf{IV_B}$, $\mathbf{V_B}$, $\mathbf{VI_B}$ and $\mathbf{VII_B}$.

- When **8 (x+y) 10**, the corresponding items will belong to the group

$\mathbf{VIII_B}$ or **III**.

- When **(x+y) > 10** :

$\mathbf{(n\text{-}1)\ d^{10}\ n\ s^1}$, the elements will belong to subgroup $\mathbf{I_B}$ **(n-1)**
$\mathbf{d^{10}\ n\ s^2}$,the elements will belong to subgroup $\mathbf{II_B}$

Examples:

$_{37}$**Rb**: $_{36}$[Kr] $\mathbf{5s^1}$: 1 valence electron, Rb therefore belongs to group **I** and subgroup **A**.

$_{33}$**As** $_{18}$[Ar]$3d^{10}$$\mathbf{4s^2 4p^3}$: 5 **valence** electrons, As therefore belongs to group **V** and subgroup **A**.

VI. Evolution and periodicity of the physico-chemical properties of the elements

a. Atomic Radius r_a

There are several definitions of atomic radius. Its value can be obtained by experimental measurements or calculated from theoretical models.

The notion of atomic radius is very arbitrary. Indeed, the radius can only be defined if the atom is engaged in a molecule, it depends on the nature of the bonds.

- The atomic (or covalent) radius corresponds to half the distance between two atomic nuclei of a homonuclear diatomic molecule.
- The radius of an atom corresponds to the average distance between the nucleus and the electron of the outer layer.

When moving from left to right on the same line (period) of the periodic table, electrons are added to the same layer. As the effective nuclear charge increases, the electrons are attracted more and more, the atoms thus become more and more compact and as a result the atomic radius decreases.

Over a period: if **Z** increases then $\mathbf{r_a}$ decreases

$$\text{If } \mathbf{Z} \nearrow \Rightarrow \mathbf{F_{att}} \nearrow \Rightarrow \mathbf{r_a} \searrow$$

Going down a column from top to bottom, the number of peripheral electrons increases because the number of layers increases and consequently the atomic radius increases.

On a column: if **Z** increases then $\mathbf{r_a}$ increases

Z ↗ the **n** ↗ ⇒ volume therefore electronic cloud increases and $\mathbf{r_a}$ ↗

b. Ion beam $\mathbf{r_i}$

The cation (positive ion) resulting from the loss of electrons from the atom. It has fewer electrons compared to its respective element. The loss of an electron is accompanied by a decrease in the shielding effect, the nucleus attracts the remaining electrons more intensely than in the corresponding element. A cation has a radius $\mathbf{r_i}^+$ smaller than the atom from which it originates (**r cation r atom**).

The anion (negative ion) resulting from the gain of electrons from the atom. It has extra electrons compared to its respective element. The gain of an electron leads to an increase in the shielding effect and therefore a decrease in the attraction of peripheral electrons by the nucleus. The intensity of the repulsive forces between the electrons increases. An anion is therefore larger than the atom from which it originates (**r anion r atom**).

- For ions with the same electronic (isoelectronic) configuration, Example:

($\mathbf{Cl^-}$, $\mathbf{K^+}$, $\mathbf{Ca^{2+}}$, ...) if Z increases $\mathbf{r_i}$ decreases.

At equal charges, the ionic radius varies in the same direction as the atomic radius:

If **Z** increases then r_i decreases.

c. Ionization Energy (EI)

This is the energy that must be supplied **(EI > 0)** to an atom (or an ion) to remove an electron in its ground state and in the gaseous state. This term refers only to the formation of cations.

In the same period **EI** varies in the opposite direction of the atomic radius.

From top to bottom in the same column, the number of layers increases, the valence electrons are further and further away from the nucleus, the nucleus/electron attraction decreases, the external electron to be expelled is easier to tear off. The first ionization energy decreases from top to bottom in a group.

d. ionizing energy

- The first ionization energy (**EI_1**) corresponds to the energy to be supplied to an isolated gaseous atom to remove the first electron located on the outer layer.

$$\mathbf{X(g) + EI_1 \rightarrow X^+(g) + e^-}$$

- Second ionization energy (**EI_2**): this is the energy needed to tear a second electron from the atom in the gaseous state.

$$\mathbf{X^+(g) + EI_2 \rightarrow X^{++}(g) + e^-}$$

As the electrons are torn off, the element becomes more and more positively charged, so it attracts more and more of its electrons. The repulsion between the electrons decreases after each ionization and the attractive force of the nucleus is greater and greater which makes extraction more and more difficult.

For a given element, there is therefore an increase in ionization energies with the degree of ionization: **$EI_1 < EI_2 < EI_3$...**

This can be explained that the first electron to be removed is that of the outermost layer, so the farther from the nucleus, the closer to the latter the more difficult the ionization.

e. Electronic Affinity (EA)

This is the opposite phenomenon of ionization. The electronic affinity of an atom **X** is the energy released when this gaseous atom captures an electron.

$$\mathbf{A\ (g) + e^- \rightarrow A^-\ (g) + AE}$$

In an **AE** period increases when **Z** increases In an
AE group decreases when **Z** increases

f. Electronegativity χ (E.N)

It is the power to attract an electron by an element. An element that easily loses one or more electrons is said to be electropositive.

Electronegativity is a dimensionless quantity that reflects the ability of an element to attract electrons in a bond doublet, an attractor element is said to be electronegative and has a high value of χ. A donor element is electropositive and the value of χ is low.

The electronegativity varies in the same direction as the ionization energy i.e.: From left to right in the same period **Z** increases then EN **increases.** from top to bottom in the same group **Z** increases then **EN** decreases.

Chapter VI

Chemical Bonds

Chapter VI: Chemical Bonds

I. Introduction

Atoms tend to acquire the most stable electronic structure which is that of the nearest noble gas in the periodic table. To acquire this electronic structure, atoms can either gain or lose electrons to form ions or form chemical bonds by pooling one or more pairs of electrons, which are called bond doublets, represented by a dash between the two atoms.

The model of the atom we studied represents the isolated atom. However, apart from rare gases, very few bodies are formed of isolated atoms. In most of the bodies around us, atoms are bound to each other to form molecules whose energy is lower than that of the atoms that make them up. The molecule is the result of an assembly of atoms (2 or more), linked together by chemical bonds.

II. Covalent bonding in Lewis theory

- **Valence-Valence Electrons - Valence Layer**

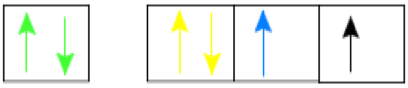
The valence of a chemical element is the number of chemical bonds it can form. This notion is directly related to the electronic configuration of the valence electrons of the chemical element in question, these are the electrons of the outer layer called valence layer or peripheral layer. It is equal to the number of unpaired electrons (singles).

The existence in this layer of electron doublets, single electrons or empty atomic orbitals (empty boxes) determines the chemical properties of a given element.

Example:

- Hydrogen: $1s^1$ valence = 1

- Oxygen: $_8O$ $1s^2$ $2s^2$ $2p^4$



The oxygen valence layer has two doublets and two single electrons, so the valence number is 2.

III. octet rule

Lewis' original idea is to explain the particular stability of noble gases by the presence of eight electrons (four pairs) on the valence layer. He generalizes this idea to molecules and states the byte rule in the form: atoms bind together to give a molecule, saturate their outer layer and take the electronic configuration of the nearest noble gas. An electronic configuration whose outer layer contains one byte of electrons is particularly chemically stable.

Therefore, Lewis admits that any molecular arrangement such that each atom of the molecule is surrounded by eight electrons and acquires the electronic configuration of rare gases, exception: hydrogen adopts an electronic configuration similar to that of helium, a rare gas of the first period.

1 Byte Rule Exception

a. Incomplete byte: It concerns some elements of the second period (**B**, **Be**,...) for example, the boron atom is surrounded by 6 electrons.

b. Byte extension: It concerns some elements of the third period (**P**, **S**,……….)

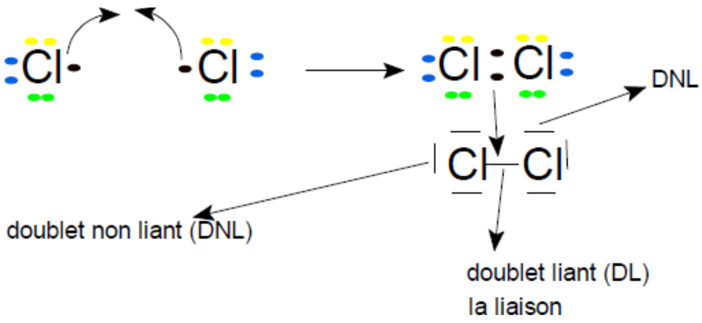
For example, in PCl_5 the phosphorus atom is surrounded by 10 electrons.

c. Lewis diagram (or formula)

The chemical properties of an atom depend on its outer electronic layer (valence layer). The Lewis formula of an atom represents this layer, it consists in materializing the electrons of the valence layer by dots arranged around the symbol of the element and the empty box by a rectangle.

Lewis proposed in 1919 a model to which he defined covalent bonding as the result of sharing electrons between two atoms. The Lewis diagrams make it possible to represent the bond, by visualising the distribution of the valence electrons of the atoms within the neutral molecules and the ions. Shared electron pairs (binding doublets) and non-binding doublets are denoted by dashes (─) or dots (:).

Example: Cl_2



2. Formal charge

The formal charge (**CF**) of an atom in a Lewis formula is given by the following relationship:

$$\mathbf{CF = n_V - (n_{DNL} + \frac{n_{DL}}{2})}$$

$\mathbf{n_V}$: number of valence electrons of the atom alone.

$\mathbf{n_{DNL}}$: number of non-binding electrons of free pairs (DNL) after formation of the molecule.

$\mathbf{n_{DL}}$: number of shared binding electrons.

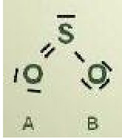
If the atom has more electrons in the molecule than in the free state then it carries a formal negative charge and vice versa.

Example: $\mathbf{SO_2}$

$$CF(S) = 6 - 2 - \frac{1}{2} x\ 6 = 1$$

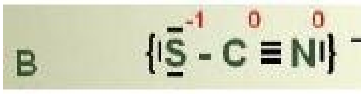
$$CF(O_A) = 6 - 4 - \frac{1}{2} x\ 4 = 0$$

$$CF(O_B) = 6 - 6 - \frac{1}{2} x\ 2 = -1$$

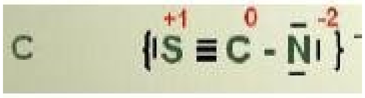


The most stable chemical structures are those with formal charges closest to 0 and will have negative charges on the most electronegative atoms. In these structures the rearrangement of electrons is the weakest.

A Lewis structure is favoured when the formal loads are the smallest. Example: Ion thiocyanate $\mathbf{SCN^-}$; $\mathbf{\chi_N = 3.0; \chi_S = 2.5}$



Both structures are correct



Formal charges are higher than molecules A and B. In Lewis structures, thiocyanate will be closer to structures A and B than molecule C. There will even be a preference for structure A because charge -1 is on the most electronegative atom, i.e. nitrogen.

3. Connection types concerned

They are classified according to the electronegativities of the linked atoms. The difference in electronegativities between the atoms of the bond determines its nature.

a. Liaison covalente

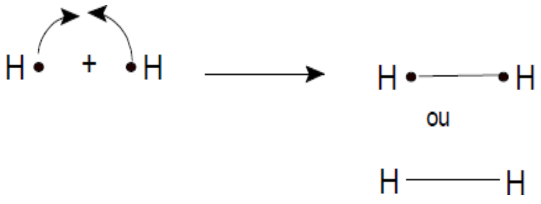
The covalent bond is the pooling of an electronic doublet of two atoms in contact and similar electronegativities (χ). The two electrons that form the bond are halfway to each atomic nucleus.

$\Delta\chi = \chi_A = \chi_B \leq 1$**,** in this case both elements belong to block **p**.

A. + B. ------> A-------- B

If $\chi_A = \chi_B$, pure covalent bond.

Example: Formation of the covalent bond within the hydrogen molecule $\mathbf{H_2}$



b. polarised bond

As atoms have different electronegativities, the covalent bond between two different atoms is polarized. The electrons of the bond are attracted by the more electronegative element, in this case the bond is called polar.

Example: $\mathbf{H_3C^+\ OH^-}$

c. Ionic bond

When the electronegativity difference between the atoms is very large, (**$\Delta\chi$ > 2**, in this case, one of the elements belongs to the **s** block), the electrons of the bond are attracted by the most electronegative atom and the bond is said to be of the ionic type. There is electron transfer from the least to the most electronegative element and formation of two ions.

Example: **Na^+Cl^-** (electronegativity: **Na** = **0.9**; **Cl** = **3.0**).

d. Dative Binding

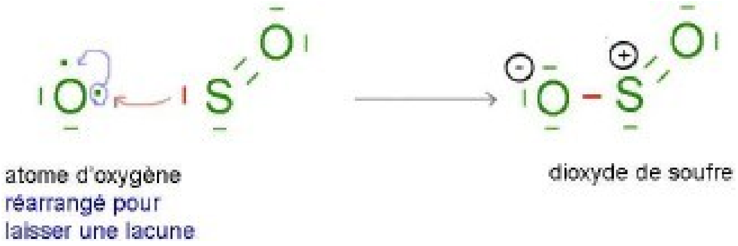
If the doublet initially belongs to a single donor, the covalent bond is called a dative bond (or coordination). It forms between a chemical species with an electronic gap (or empty cell) and a species with an electronic doublet.

Examples:

NH_3^+

N donor; **H** acceptor

SO2



S donor; **O** acceptor

e. Multiple links

Double or triple bond, to the **σ** bond are added one or two **π** bonds, weaker than the **σ** bonds, but still in the category of strong bonds.

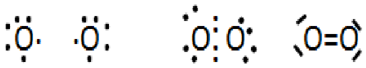
- Simple covalent bonding: results from the pooling of two atoms of a single electron pair. Each atom provides an electron, it is called "**σ-bond**".

Example: **H_2** **H—H**

- Double covalent bond: results from the pooling of two pairs of electrons between two atoms. Each atom provides 2 electrons.

Example:

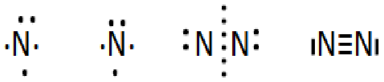
O_2



- Triple covalent bond: results from the pooling between two atoms of three pairs of electrons. Each atom provides 3 electrons.

Example:

N_2



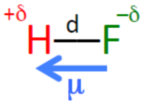
In addition, there are weaker bonds between molecules, such as Van der Waals bonds, which ensure the cohesion of liquids and solids. There is another type of bond called a hydrogen bond which can be intermolecular or intramolecular.

4. Bond polarity and dipole moment

- Homonuclear diatomic molecule **A_2**: the pooled electrons are symmetrically distributed in the bond: the molecule is said to be apolar or does not admit a dipole moment.
- Heteronuclear diatomic molecule **AB** (**B** more electronegative than **A**): the pooled electrons are closer to **B** than to **A**: the molecule is said to be polar or to have a dipole moment (denoted $\vec{\mu}_{AB}$).

It is usually represented by an arrow conventionally oriented from the center of negative charges to the center of positive charges.

Exemple: **HF**



$$\mu = q \times d$$

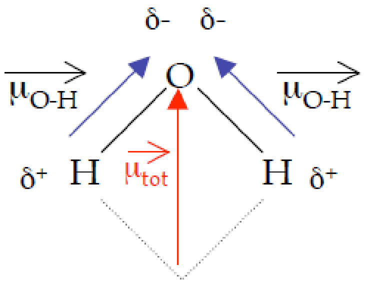
d: distance separating the nuclei (internuclear) = the length of the bond.

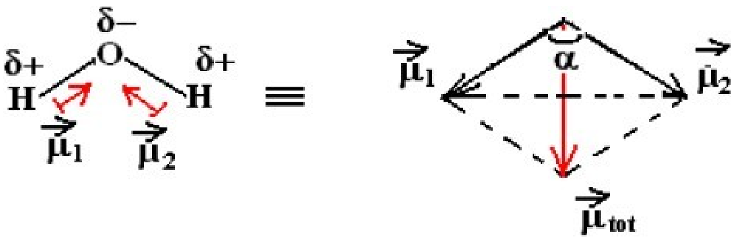
The unit of the dipole moment in the international system (SI) is the Coulomb.meter (abbreviated **C.m**), is poorly adapted, for this we use more **the Debye** (abbreviated **D**), defined by **$1D = 3.34.10^{-30}$ C.m**

- Polyatomic molecules: The permanent dipole moment of a polyatomic molecule is the vector sum of the different dipole moments of all bonds.

$$\mu = \Sigma\ \mu_i$$

Example: $\mathbf{H_2O}$





$\vec{\mu}_1 = \vec{\mu}_2 = \vec{\mu}_{O-H}$

In case of center of symmetry : $\Sigma\ \vec{\mu} = 0$

Example: $\mathbf{CO_2}$ **O=C=O** ; **μ = 0**.

5. Partial ionic character (CI)

The percentage of partial ionic character **(%CI)** measures the iconicity rate in a bond of a chemical bond**,** it is calculated according to the following relationship:

$$\%CI\ ionique = \frac{\mu_{réelle}}{\mu_{théorique}} \times 100$$

Where: **real μ** is that measured and **theoretical μ** is that calculated theoretically (**theoretical μ** = **q x d)**

6. Molecular Geometry

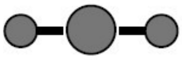
The geometry of a molecule is determined by the definition of the relative position of the molecule in space, these relative positions depend on two parameters: the lengths of the bonds and the angles between atoms forming the molecule.

The Lewis diagram makes it possible to explain the formation of a single, double or triple bond but it cannot tell us about the type of bond or the geometry of the molecule. The introduction of **VSEPR** (Valence Shell Electrons Pairs Repulsion) and hybridization theories makes it possible, after analysis of the Lewis scheme, to predict the geometry of single molecules or ions of the AXnEp type where **A** is the central atom bound to **n** atoms **X** and having **p** pairs of free electrons **E** (non-binding doublet). The sum (**n+p**) called the total number of doublets provides information on the basic geometry of the molecule.

a. Gillespie's Theory

Gillespie's theory or **VSEPR** expresses that the binding and non-binding doublets around the central atom are arranged in such a way that their mutual repulsions are minimal (therefore maximum distances), so the electronic doublets are as far away as possible and thus reduce the interaction energy and give the molecule more stability.

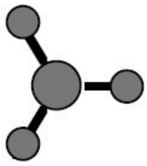
AX_2



linear

α = 180°

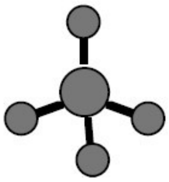
AX_3



trigonal plane

α = 120°

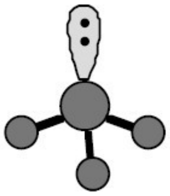
AX_4



tetrahedral

α = 109°28

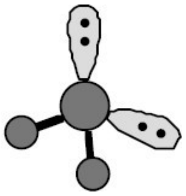
AX_3E



pyramid trigonal

α < 109°28

AX_2E_2



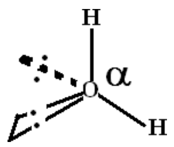
bent

α < 109°28

Example: The Lewis scheme for **H_2O** would give:

$$H-\overline{\underline{O}}-H$$

That is 4 doublets (2 not shared) around **O**, which will undergo mutual repulsions and give the molecule a spatial configuration (α > 90°), which will give a tetrahedral form:



b. Chemical bonding in the quantum model: Atomic Orbital Hybridization (AO):

The use of normal atomic orbitals does not explain the different geometric shapes of molecules involving identical atomic orbitals. For this, the notion of hybridization of atomic orbitals is used. Hybridization is the formation of equivalent hybrid orbitals by linear combination of atomic orbitals (**s** and **p**) or (**s**, **p** and **d**) of the same atom, we can have this phenomenon after excitation of the electron. It consists of the mixing of orbitals of an atom so as to form new hybrid orbitals that make it possible to better qualitatively describe the bonds between atoms. The resulting hybrid orbitals are very useful in explaining the shape of molecular orbitals of molecules. The theory of hybridization makes it possible to explain the geometry of certain molecules. It also gives the values of the angles between the directions of the bonds in a polyatomic molecule.

c. Hybridization of s and p orbitals

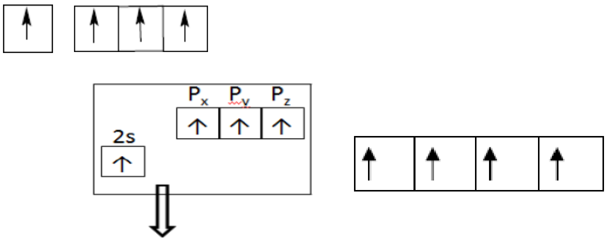
This type of hybridization is of interest to the elements of the second period of the periodic table. There are three types of hybridization: $\mathbf{sp^3}$, $\mathbf{sp^2}$ and **sp**.

- $\mathbf{Sp^3}$ **hybridization**: This is the formation of four $\mathbf{sp^3}$ hybrid orbitals from an **s** orbital and three **p** orbitals ($\mathbf{p_x}$, $\mathbf{p_y}$ and $\mathbf{p_z}$)**.** These hybrid orbitals are oriented towards the four vertices of a tetrahedron.

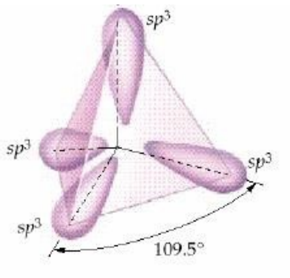
The electronic configuration of the valence layer of carbon in the ground state is $\mathbf{2s^2\ 2p^2}$, in this configuration the four external electrons are not all located in the same type of atomic orbital, which does not explain the tetravalence of carbon, carbon must unpair an electron of **2s** and promote it in the empty orbital of **2p**.

$_6\mathbf{C}$ $\mathbf{1s^2\ 2s^2\ 2p^2}$ **ground state**

$_6\mathbf{C^*}$ $\mathbf{1s^2\ 2s^1\ 2p^3}$ **excited state**



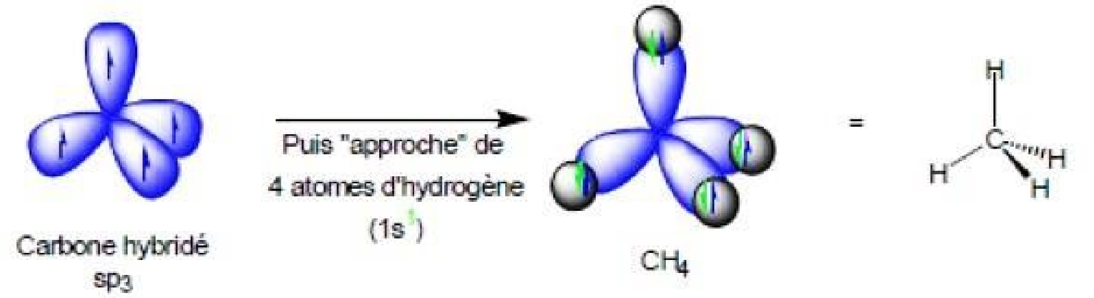
Four $\mathbf{sp^3}$ hybrid orbitals

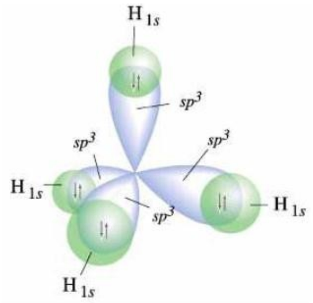


Since the **s** orbitals are spherical and the **p** orbitals point along the three Cartesian axes, we cannot simply explain the obtaining of a tetrahedral molecule.

OA **2s** and the **3** OA **2p** of the **C** atom are "mixed" to form **4** **sp^3** hybridized OA.

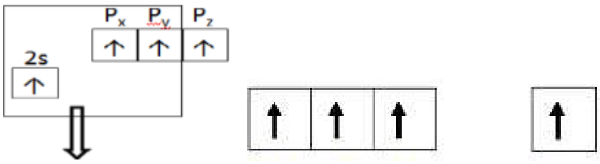
The **sp^3** hybridization makes it possible to explain the spatial configuration of molecules such as **CH_4** following scheme:





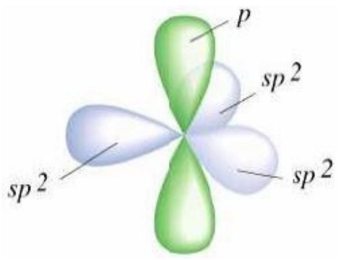
In the **CH_4** molecule, the four **C-H** bonds are identical. They make an angle of 109°28'. A regular tetrahedral structure was adopted with carbon at the center of the polyhedron and hydrogen atoms at the vertices. The connections are made by axial overlap (**σ** connection).

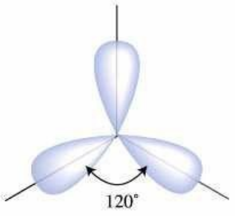
- **Hybridization sp^2:** This is the formation of three hybrid orbitals: **sp^2** from an **s** orbital and two **p** orbitals (**p_x** and **p_y** for example). The orbital **p_z** remains unchanged. It is a combination between an **s** orbital and two **p** orbitals (**p_x** and **p_y** for example). The **p_z** orbital remains unchanged, so 3 equivalent **sp^2** hybrid orbitals are obtained and a pure or free **p** orbital forms a lateral overlap bond (bond).



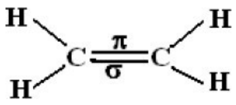
3 sp^2 hybrid orbitals and p orbital

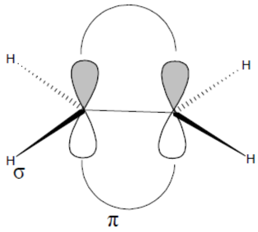
Three identical trigonal **sp^2** orbitals (120° angle) plane and there remains the **p** orbital Unchanged

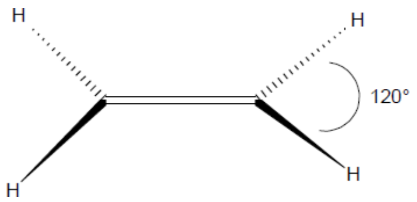


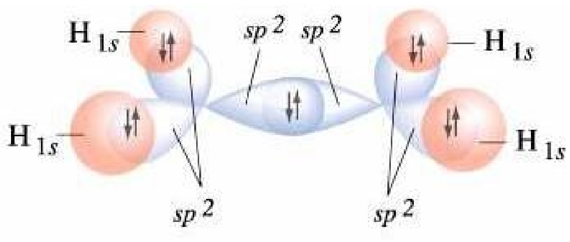


Sp^2 hybridization makes it possible to explain the spatial configuration of molecules such as **C_2H_4**.A carbon of this type allows by axial overlap the formation of three **σ** bonds with three atoms, Example: two hydrogens and one carbon CAS of ethylene; they are coplanar at 120°, one from the other, perpendicular to this plane remains a **2p** atomic orbital which did not participate in the hybridization which gives rise by lateral overlap with another **P^2** orbital, that of another **sp** carbon with a **π** bond, thus resulting in the formation of a double bond.

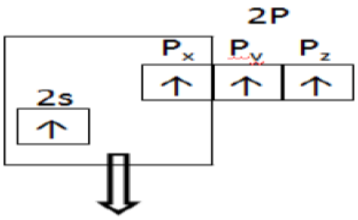




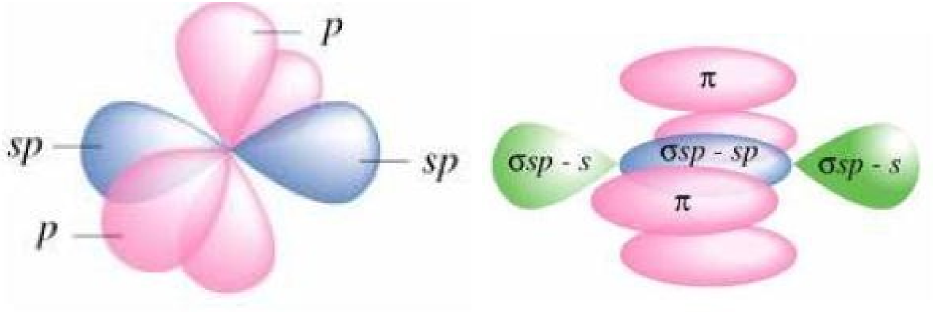




- **Sp hybridization:** They are obtained by linear combination of an **s** orbital with a **p** orbital (**p_x** for example). The orbitals **p_y** and **p_z** remain unchanged giving overlaps **π**, i.e. a linear configuration with **α = 180°**. So we have a triple bond.

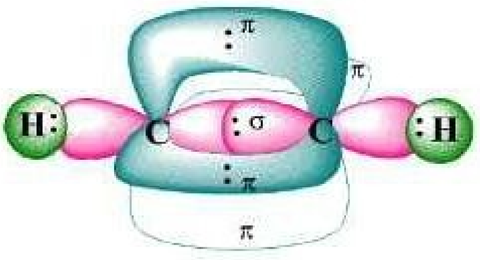


2 sp hybrid orbitals and **2 p** orbitals



Example: acetylene **C_2H_2** (**H-C≡C-H**).

The molecule is linear. The two **C-H** bonds are identical and make an angle of 180° between them.



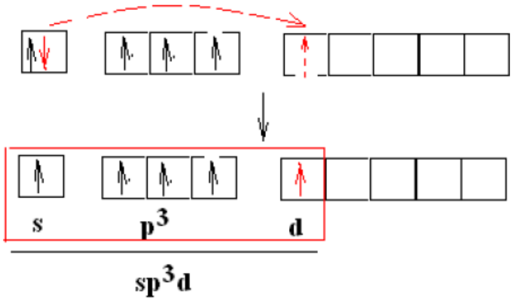
- **Hybridization of the s, p and d orbitals**

This is the formation of equivalent hybrid orbitals by linear combination of **s**, **p** and **d** orbitals of the same atom. They are of types **sp^3d^x** and **d^xsp^y** .

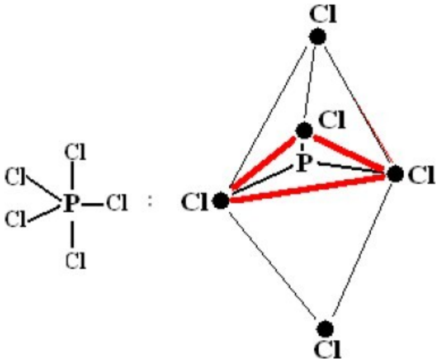
Example: **sp^3d** hybridization: Case of **PCl_5** (5 bonds around phosphorus)

$_{15}P\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3\ 3d^0$

To make 5 bonds, the phosphor must hybridize to **sp^3d** (combination of an **s** orbital, 3 **p** orbitals and 1 **d** orbital), i.e. 5 **sp^3d** hybrid orbitals as follows:

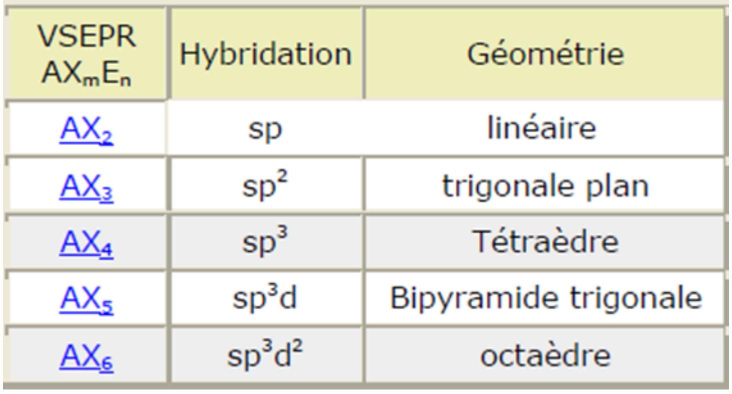


Either a pyramid geometry with a triangular base



The most frequent cases of hybridization of atomic orbitals correspond to the geometric shapes already described in the **VSEPR** Method.

7. Correspondence between hybridization and VSEPR



VSEPR AX_mE_n	Hybridation	Géométrie
AX_2	sp	linéaire
AX_3	sp^2	trigonale plan
AX_4	sp^3	Tétraèdre
AX_5	sp^3d	Bipyramide trigonale
AX_6	sp^3d^2	octaèdre

Exercises

Exercise I

Exercise I.1

I) We have 0.4 mole of H_2S

1. What is the mass of H_2S?

2. What are the numbers of moles of H and S?

3. What are the masses of H and S ?

4. How many atoms of H and S ?

5.What is the number of H_2S molecules ?

II) Calculate the molecular mass of: $C_{12}H_{22}O_{11}$, SiO_2, $CaCO_3$.

III) A sample of $CaCO_3$ contains 4.45 moles.

What is the mass of this sample?

What are the masses of Ca^{2+} and CO_3^{2-}?

Exercise I.2

In a first experiment, 0.56 g of iron reacted with 4.10 g of sulfur. All the iron was consumed and 0.88 g of iron sulfide was formed.

In a second experiment, 3.50 g of iron reacted with 0.64 g of sulfur.
All the sulfur was consumed and 1.76 g of iron sulfide was formed.

1. Do these results follow Proust's law of definite proportions ?
2. How much iron sulfide will be formed if 2 g of sulfur and 2 g of iron are used ?

Exercise I.3

I) A compound contains 43.64% phosphorus and 56.36% oxygen (percentages by mass).
What is the empirical formula of this compound, knowing that its molar mass is 283.88 g/mol?

II) Aluminum reacts with oxygen to form alumina (Al_2O_3), which contains 52.9% aluminum.
Calculate the atomic mass of aluminum.
The atomic mass of oxygen is 16 g/mol.
P = 30.97 g/mol.

Exercise I.4

1. How many grams of K_2SO_4 are needed to prepare 200 mL of a 0.5 M solution ?
2. How many grams of NaOH and $Ca(OH)_2$ are needed to prepare 25 mL of 1 N solutions ?
3. How many grams of $Fe_2(SO_4)_3$ are needed to prepare one liter of a 0.2 N $Fe_2(SO_4)_3$ solution ?
4. Determine the concentration of a $Na_2S_2O_3$ solution, knowing that 200 mL of this solution contains 3.162 g of $Na_2S_2O_3$.

(K = 39.1 g/mol, S = 32 g/mol)

5.How many mL of concentrated HCl (density 1.19, 37.23% by mass) are needed to prepare a 2 N HCl solution ?

Exercise II

Exercise II.1

a) The electron beam in a cathode ray tube is subjected to the action of an electric field **E** over a length **L**.
Calculate the expression of the **deflection Y_0** experienced by the beam at the exit of the field.

b) After measuring a deflection **Y_0**, this deflection is canceled by the opposing action of a magnetic induction field **B**, having the same effective length **L** as the electric field **E**.
Calculate the **charge-to-mass ratio e/m** of the electrons.
Given:

$Y_0 = 4.4$ cm, $E = 2 \times 10^4$ V/m, $L = 10$ cm, $B = 10^{-3}$ T

Exercise II.2

In Millikan's apparatus, the motion of droplets with different charges, depending on the variation of the electric field, gave the following results:

1. In the absence of an electric field (**$E = 0$**), the free fall of a droplet in air is 3.2 cm in 10 seconds.
Calculate the **radius** and the **mass** of the droplet.
2. When an electric field **$E = 450\,000$ V/m** is applied, the droplet rises at a terminal speed **$V_1 = 0.118$ mm/s**.
Calculate the **charge q_1** of the droplet.
3. The droplet is in **equilibrium** between the two capacitor plates when **$E = 247{,}000$ V/m**.
Calculate the **charge q_2** of the droplet.
4. At the same electric field as above, the droplet descends with a terminal velocity **$v_2 = 0.1587$ mm/s**.
Calculate the **charge q_3** of the droplet.
5. Compare the different charges calculated and deduce the **elementary charge**.

Given data:

$\eta = 1.82 \times 10^{-5}$ MKS units (viscosity)

$g = 9.81\ m/s^2$, $\rho = 1.26 \times 10^3\ kg/m^3$ (density of the droplet)

Exercise II.3

A **Bainbridge-type mass spectrometer** is used to separate two types of ions. One of the ions is the **^{12}C isotope** of carbon.

The ion speed at the exit of the velocity selector is **$v_0 = 600$ km/s**, and the separation is then produced by a magnetic field **B = 0.3 Tesla**.

1. What is the **special characteristic** of the ions entering the analyzer ?
2. Express the **distance d** separating the impact points in terms of **N_a, e, B, v_0**, and the isotopic masses **M_1** and **M_2**, knowing that the unknown ion follows a **trajectory of greater radius** than that of ^{12}C.
3. Determine the **atomic mass** of the unknown ion.

Given data:

$d = 4.15$ cm, $N_a = 6.023 \times 10^{23}\ mol^{-1}$, $e = 1.6 \times 10^{-19}$

Exercise II.4

1. Calculate the **average mass of natural iron**, knowing that it is a mixture of four isotopes:

Isotope	Abundance (%)	Atomic Mass (g)
^{54}Fe	5.82%	53.939
^{56}Fe	91.66%	55.935
^{57}Fe	0.21%	56.935

Isotope	**Abundance (%)**	**Atomic Mass (g)**
^{58}Fe	0.33%	57.933

2. Calculate the **binding energy** of the **^{58}Fe nucleus**, then deduce the **binding energy per nucleon**.

Given: $c = 3 \times 10^8$ m/s, $M(^{58}\text{Fe}) = 57.93328$ u, $m_n = 1.00893$ u, $m_p = 1.00758$ u

Exercice III

Exercice III. 1

If possible, determine the number of neutrons, protons, and electrons present in each of the following atoms or ions :

$$^{19}_{9}F,\ ^{40}_{20}Ca,\ ^{24}_{12}Mg^{+2},\ ^{52}_{24}Cr^{+3},\ ^{127}_{53}I^{-},\ ^{108}_{47}Ag^{+},\ ^{79}_{34}Se^{-2},\ ^{222}_{86}Rn,\ ^{56}_{26}Fe^{+2},\ ^{56}_{26}Fe^{+3},\ ^{36}_{18}Cl^{-}.$$

Exercise III.2

Next to each nuclide, write the type of radiation it emits and write the corresponding nuclear reactions:

$$^{15}_{8}O(\beta^{+}),\ ^{222}_{86}R(\alpha),\ ^{106}_{47}Ag(\beta^{-}),\ ^{12}_{6}C(\beta^{-}).$$

Exercise III.3

In a nuclear reactor, one of the reactions is:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow\ ^{94}_{38}Sr + ^{140}_{Z}Xe + x^{1}_{0}n$$

A) Determine and justify the values of Z and x.

B) Calculate the mass defect and the energy released (in joules and MeV) by the fission of one uranium-235 nucleus.

C) Estimate the energy released by the fission of 5g of uranium. Calculate the mass of oil that would release the same energy through combustion.

Atomic masses provided:

^{235}U: 234.99332 u

^{94}Sr: 93.894 u

^{140}Xe: 139.981 u

neutron: 1.00866 u

1 u = 1.66×10−271.66 \times 10^{-27}1.66×10−27 kg

Energy content of oil: 42 MJ/kg

Exercise III.4

Fusion reaction in the sun:

$$4\,{}_{1}^{1}H \rightarrow {}_{2}^{4}He + 2\,{}_{x}^{0}e + 2\bar{\gamma}$$

A) Identify x.

B) What is the energy (in MeV and joules) released by the formation of one helium nucleus ?

C) The radiated power of the Sun is 3.9×10^{26} watts.

What is the mass lost each second ?

D) The mass of the Sun is 2×10^{30} kg. Its age is 4.6 billion years. What mass has it lost since it began emitting radiation ?

Given:

H = 1.0073 u

He = 4.0015 u

Positron/electron = 0.55×10−30.55 \times 10^{-3}0.55×10−3 u

Exercise III.5

The half-life of radioactive sulfur 1635S is 88 days.
Calculate the mass of sulfur remaining undecayed after 176 days, knowing that the initial mass was 1 g.

Exercise III.6

It is known that 6.5×10^{-6} g of radon is in equilibrium with 1 g of radium.

A) Calculate the half-life of radon. The half-life of radium is TRa=1590T, Ra = 1590TRaRa=1590 years.
Given: Ra = 226, Rn = 222

B) 1 gram of pure radium emits 3.68×10^{10} alpha particles per second. Deduce Avogadro's number.

Exercise III.7

A ruined object contains a known amount of Pb (206) in equilibrium with U(238)238U (Pb/U = 3.9%).
Given that the half-life of U (238) is T= 4.56×10^{9} years, determine the age of the object.

Exercises IV

Exercise IV.1

An electron accelerated by a potential difference of **V = 121.09 volts** excites a hydrogen atom after transferring all its energy to it.

1. Calculate the **wavelength** emitted by the atom when it returns to its **ground state**.
2. Determine the **energy level** *n* in which the electron was found in its excited state.

Given:

R_H =109677,8 cm^{-1} ; c=3.108 m/s.

Exercise IV.2

Calculate the **wavenumbers**, **frequencies**, and **wavelengths** of the **first four lines** in the **visible emission spectrum** of the hydrogen atom.
Data: R_H=109677.8 cm^{-1}R, c=3.0×108m/s

Exercise IV.3

1. Using **Bohr's theory**, calculate the **Bohr radius** a0, for the **n = 1 orbit**, where the electron orbits the nucleus.
2. Calculate the **ionization energy** of the hydrogen atom—that is, the **minimum energy required** to remove an electron from its **ground state** (final speed = 0).

Exercise IV.4

1. Which **electronic transition** corresponds to the **spectral line of wavelength** λ=4340.5 A°\lambda = 4340.5 A° in the **hydrogen emission spectrum** ?
2. Compare this wavelength with that of the **same transition** for the **hydrogen-like ion He^+**.

Given: R_H=1.0967×107 m^{-1}

Exercise IV.5

The hydrogen atom's electron is excited from its ground state with energies equal to **10.20 eV**, **12.08 eV**, and **12.74 eV**.

1. Determine the **energy levels** of the electron for each case.
2. Draw the corresponding **energy level diagram**. Which **absorption series** does each case belong to?
3. What is the **wavelength** of each **electronic transition** ?

Given:

c=3.0×108 m/s, c = 3. 10^{8}

h=6.62×10−34 J\cdotpsh = 6.62 .10^{-34} , h=6.62×10^{-34}J.s

Ionization energy = **13.59 eV**

Exercise IV.6

Calculate the constant a in the formula:

$$\sqrt{\nu} = a.z$$

for a **hydrogen-like ion**, for a **transition** from an outer orbit n2 to an inner orbit n1

Here, ν\nuν is the **frequency**, and ZZZ is the **nuclear charge**.

Also calculate the **radius** and **energy** of the orbit.

Given (CGS units):

m=9.10^{-28} g ; e=4,8.10^{-10} C.G.S ; h=6,6.10^{-27} C.G.S ; n1=1 ; n2=2.

Exercises V

Exercise V.1

1. Using the relationships between the three quantum numbers **n**, **l**, and **m**, determine the **number of orbitals** in the **first three energy levels** of the hydrogen atom.

2. Give the usual designations of the following orbitals:

$\Psi_{3,0,0}$, $\Psi_{3,2,0}$,$\Psi_{3,2,0}$, $\Psi_{2,1,-1}$,$\Psi_{2,1,-1}$

Exercise V.2

Given 5 electrons from the same atom, defined by the following quantum numbers:

1- n=3 l=1 m=0 s=+1/2

2- n=4 l=0 m=0 s=-1/2

3- n=3 l=2 m=1 s=-1/2

4- n=3 l=0 m=0 s=+1/2

5- n=3 l=1 m=-1 s=-1/2

Identify the **subshell** corresponding to each of these electrons.

Exercise V.3

Are the following sets of quantum numbers for a single electron **possible or not** ?

1-n=2 l=0 m=0 4- n=1 l=0 m=1

2- n=2 l=1 m=-1 5- n=4 l=1 m=-2

3-n=2 l=2 m=0 6 - n=0 l=0 m=0

Give the values of the **four quantum numbers** characterizing each electron of a **carbon atom** (Z = 6).

Exercise V.4

We consider an electron in the **$3S^1$** state. What are the **four quantum numbers** characterizing this electron ?

Exercise V.5

1. Indicate the **quantum numbers** that characterize the **unpaired electron** of **gallium** (Z = 31).

1. What is the **atomic number** of the atom whose **X^{2+} cation** has the **same electron configuration** as argon (Z = 18)?

2. What is the **atomic number** of the atom that has **7 electrons** in the **3d** subshell ?

Exercises VI

Exercise VI.1

Consider the following atoms:
N (Z = 7), K (Z = 19), Sc (Z = 21), Cr (Z = 24), Mn (Z = 25), Fe (Z = 26), Cu (Z = 29)
Zn (Z = 30), Ag (Z = 47), Au (Z = 79)

1. Give the **electronic configurations** of the atoms.

Present the **valence electrons** for each atom and the number of **core electrons**.

2. Place these atoms in the **periodic table** by **group** and **period**.

Exercise VI.2

1. Cesium (Cs) belongs to the same group as potassium (K) and the same period as gold (Au).
Give its electronic configuration and its atomic number.
2. Molybdenum (Mo) belongs to the same group as chromium (Cr, Z = 24) and to the fifth period.
Give its electronic configuration and its atomic number.

Exercise VI.3

An element X has less than 18 electrons and possesses two unpaired electrons.

1.What are the possible electronic configurations of X ?

2. What is the actual configuration of X, knowing that it belongs to the same period as lithium (Li, Z = 3) and to the same group as tin (Sn, Z = 50) ?

Exercise VI.4

An element X belongs to **Group IB** and is found in the **6th period**.

1. Give the **electronic configuration** according to **Klechkowsky's rule**.

2. Find the **atomic number Z** of element X.

3. Give the **real electronic configuration**.

4. What other **elements** are in this group with **atomic numbers lower than that of X?** Give the **atomic number Z** for each.

Exercise VI.5

Consider the following elements: 16S and 47Ag

1. Establish the **electronic configuration** of each element; determine (in table form):

   - the **valence electrons**
   - the **core electrons**
   - the **period** and **group**

2. Determine the **atomic numbers Z** of elements X, Y, and D, knowing that:

   - $X^{-2} = [_{18}Ar]\ 4s^2\ 3d^{10}\ 4p^6$
   - $Y^{+3} = [_{18}Ar]\ 4s^2\ 3d^{10}\ 4p^6$
   - Element D belongs to the **same period as ^{47}Ag** and the **same group as ^{16}S**

3. Among these elements, identify those belonging to the **metallic family** (according to **Sanderson's theory**) – present in **table form**.

Exercise VI.6

1. Arrange in **increasing atomic radius** order:

   $^{4}Be^{2+}$, ^{2}He, $^{3}Li^{+}$, $^{1}H^{-}$

2. Arrange in **increasing ionization energy** order:

   Ne (Z = 10), O (Z = 8), Na^{+}, Na (Z = 11)

3. Arrange in **increasing electronegativity** order:

   O (Z = 8), Al (Z = 13), F (Z = 9)

Justify your reasoning for all three rankings.

Exercises VII

Exercise VII.1

Represent, using the **Lewis model**, the following elements of the periodic table:

H, He, Li, Be, B, C, N, F, Ne

Exercise VII.2

1. Give the Lewis notation for the following molecules and ions:

H_2, Cl_2, H_2O, H_3O^+, NH_3, NH_4^+, CH_4, C_2H_6, SF_4, SF_6, PCl_3, PCl_5, NCl_3

2. Among these compounds, which ones do not follow the octet rule?

3. Based on the electronic structures of sulfur and phosphorus, explain the formation of the molecules SF_6 and PCl_5.

4. Predict the possible valences of phosphorus.

Both chlorides PCl_3 and PCl_5 exist.

Explain why only NCl_3 is known, and why NCl_5 does not exist.

Exercise VII.3

1. Consider the following molecules: **BF_3, CO_2, CH_4, C_2H_6, C_2H_2**

Specify the **hybridization states** of the **carbon and boron atoms**.

2. The molecule **butadiene** ($CH_2 = CH–CH = CH_2$) is **planar**.

Determine the **hybridization states** of the carbon atoms.

Exercise VII.4

1. Write the molecular orbital diagram, give the electronic structure, calculate the bond order, and provide the Lewis structure for each of the following molecules or

molecular ions :

O_2, O_2^+, O_2^-, O_2^{2-}

2. Rank these molecules in order of increasing stability.

3. Are the two bonds in the O_2 molecule identical ?

4. Assign a bond length to each molecule from the following values:

1.12 Å, 1.21 Å, 1.26 Å, 1.49 Å

Exercise VII.5

Briefly define Gillespie's theory (VSEPR theory) and, using this theory, determine the geometry of the following molecules:

MgF_2, $AlCl_3$, CH_4, PCl_5, H_3O^+, H_2O, $AsCl_3$, CO_2

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