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Course handout

ELEMENTS OF CHEMISTRY
COURSE MATERIAL AND SOLVED EXERCISES

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PREFACE

This course handout is intended for first-year ST students (LMD and Engineering programs)

The content of this handout summarizes everything a student needs to know about the structure of matter, which is an essential part of general chemistry.

It focuses primarily on the fundamental concepts of the structure of matter.

This handout consists of six chapters.

The first chapter is devoted to a review of some fundamental concepts (states of matter, atoms, molecules, and solutions).

The second chapter covers the main constituents of matter namely, the atom as well as some physical properties of mass and charge.

In this same chapter, we describe the experiments that demonstrated:

The electron, the proton, and the neutron (Crookes, J.J. Thomson, and Millikan experiments). This chapter also covers the structure of the atom and isotopes, as well as their separation and stability.

The third chapter describes the process of radioactivity, nuclear reactions, the law of radioactive decay, etc.

The fourth chapter addresses the electronic structure of the atom in a simple, clear, and accessible manner and discusses the quantization of energy in the semi-atomic model (wave-particle duality of light, optical spectrum of hydrogen, classical models of the atom, and the

spectra of hydrogenoids ions).

This chapter prepares the transition to the quantum model of the atom, introducing a theory necessary for the rigorous description of the atom's properties: wave mechanics (De Broglie's hypothesis, Heisenberg's uncertainty principle, and electronic configurations).

The fifth chapter is devoted to the periodic classification of elements in the modern periodic table (rows and groups), chemical families, and the evolution and periodicity of the physicochemical properties of elements (atomic and ionic radii, ionization energy, electron affinity, and electronegativity).

The sixth chapter is devoted to chemical bonding, in which various types of bonds are discussed: covalent bonding in Lewis theory, polar covalent bonding, dipole moment and partial ionic character of the bond, molecular geometry: Gillespie or VSEPR theory, chemical bonding in the quantum model: molecular orbital theory (LCAO method), formation and nature of bonds, and molecular energy diagrams.

The study of polyatomic molecules, or the theory of atomic orbital hybridization, is presented in a simple and clear manner. The concepts in each chapter are illustrated with examples.

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Abstract

This course handout presents the fundamental principles of chemistry, from the description of matter, its physical states, and its transformations to the study of its microscopic structure. It explains the composition of the atom, the properties of subatomic particles, radioactivity, and nuclear phenomena. The arrangement of electrons around the nucleus is examined through atomic models and quantum mechanics, providing an understanding of electronic configurations. The handout also covers the periodic table and the periodic properties of elements to explain their chemical behavior. Finally, it presents the different types of chemical bonds, molecular polarity, and molecular geometry to explain the formation and properties of molecules. Altogether, these concepts provide an essential foundation for the study and interpretation of chemical phenomena.

Keywords: General chemistry, matter, atomic structure, radioactivity, periodic table, chemical bonding, molecular geometry.

ملخص

يقدم هذا المطبوَع البيداغوجي المبادئ الأساسية للكيمياء، بدءًا من وصف المادة وحالاتها الفيزيائية وتحولاتها، وصولًا إلى دراسة بنيتها المجهرية. كما يشرح تركيب الذرة وخصائص الجسيمات دون الذرية والنشاط الإشعاعي والظواهر النووية. وتُدرس كيفية توزيع الإلكترونات حول النواة من خلال النماذج الذرية وميكانيكا الكم، مما يتيح فهم التوزيعات الإلكترونية. ويتناول المطبوَع أيضًا الجدول الدوري والخواص الدورية للعناصر لتفسير سلوكها الكيميائي. وأخيرًا، يعرض أنواع الروابط الكيميائية المختلفة وقطبية الجزيئات والهندسة الجزيئية لفهم تكوين الجزيئات وخصائصها. وتشكل هذه المفاهيم مجتمعةً أساسًا ضروريًا لدراسة الظواهر الكيميائية وتفسيرها

الكلمات المفتاحية: الكيمياء العامة، المادة، البنية الذرية، النشاط الإشعاعي، التوزيعات الإلكترونية، الجدول الدوري، الروابط الكيميائية ، الهندسة الجزيئية..

Résumé

Ce polycopié de cours présente les principes fondamentaux de la chimie, depuis la description de la matière, de ses états physiques et de ses transformations jusqu'à l'étude de sa structure microscopique. Il explique la composition de l'atome, les propriétés des particules subatomiques, la radioactivité ainsi que les phénomènes nucléaires. L'organisation des électrons autour du noyau est étudiée à travers les modèles atomiques et la mécanique quantique, permettant de comprendre les configurations électroniques. Le polycopié aborde également le tableau périodique et les propriétés périodiques des éléments afin d'expliquer leur comportement chimique. Enfin, il présente les différents types de liaisons chimiques, la polarité et la géométrie moléculaire pour comprendre la formation et les propriétés des molécules. L'ensemble de ces notions constitue une base essentielle pour l'étude et l'interprétation des phénomènes chimiques.

Mots-clés: Chimie générale, matière, structure atomique, radioactivité, configurations électroniques, tableau périodique, liaisons chimiques, géométrie moléculaire.

CHAPTER I

FUNDAMENTAL CONCEPTS

1. Introduction

Chemistry is based on the study of matter, its composition, properties, and transformations. Understanding fundamental concepts such as the states of matter, phase changes, atoms, molecules, the mole, and various physicochemical quantities is essential for analyzing chemical phenomena. This chapter presents the basic notions related to the structure of matter, the laws governing its behavior, and the qualitative and quantitative aspects used to characterize substances and solutions. These concepts provide the essential foundation for the further study of general chemistry.

2. States and macroscopic characteristics of matter

2.1. Definition of matter

Matter is anything that has mass and occupies a volume in space.

2.2. States of matter

Classically, there are three states of matter, which are:

• Solid state

Has a defined volume and shape.

• Liquid state

Has a defined volume but no specific shape; it takes the shape of its container.

• Gaseous state

Has no defined volume or shape; it takes the volume and shape of its container.



Figure I.1 : State of matter

3. Change in the state of matter

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

Example: water



Figure. I.2: Change in the state of water



Figure I.3: Phase changes of matter

4. Concepts of atoms, molecules, moles, and Avogadro's number

4.1 Atoms

- The atom is the smallest part of an element that can exist, with a mass of around 10^{-26} kg and a radius of around 1Å.
- The atom consists of a nucleus around which electrons move. The nucleus is made up of nucleons (protons and neutrons) and contains almost all of the atom's mass.

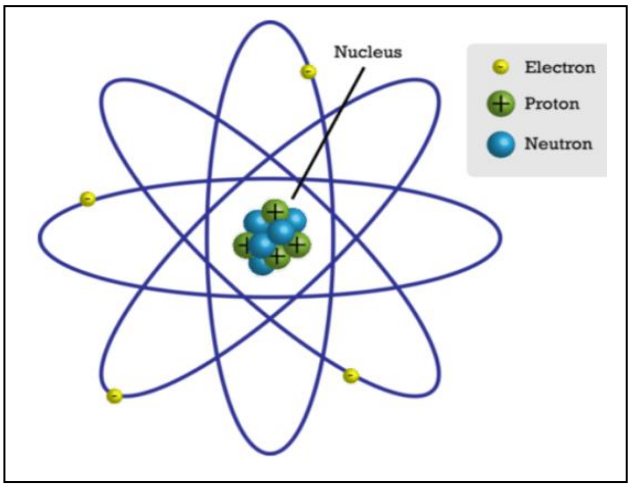


Figure I.4: Composition of an atom

4.2 The molecule

Atoms combine to produce molecules. A molecule consists of one, two, or more atoms.

Example: H_2O, C_6H_6.



Figure I.5: Molecule of H_2O and C_6H_6

4.3 The mole, the number of Avogadro (N_A)

Mole

The mole is the unit of measurement for the amount of matter.

- The number of atoms contained in one mole is called Avogadro's number

  $N_A = 6.023 \times 10^{23}$

1 mole (of atoms, ions, molecules, etc.) = 6.023×10^{23} (atoms, ions, molecules, etc.)

5. Atomic mass unit, atomic and molecular molar mass, volume Molar

5.1 Atomic mass unit (amu)

The atomic mass unit is a unit of measurement for the mass of particles (electrons, protons, neutrons, etc.).

$$1\text{a.m.u} = \frac{1}{12}\text{M}_\text{C} = \frac{1}{12}.\frac{12}{\text{N}_\text{A}} = \frac{1}{\text{N}_\text{A}} = \frac{1}{6.023.10^{23}} = 1.66.10^{-24}\text{g} = 1.66.10^{-27}\text{kg}$$

5.2 Atomic mass

Is the mass of one mole of atoms.

Example: M_C = 12.0 g.mol^{-1} and M_O = 16.0 g.mol^{-1}

M_O: molar mass of oxygen

5.3 Molecular molar mass

Is the mass of one mole of molecules.

Example: The molar mass of water H_2O:

M_{H2O}= 2.1+16 =18 g.mol^{-1}

5.4 Volume molar

The molar volume V_m of a substance is the volume occupied by one mole of that substance.

$$\mathbf{V_m = \frac{V}{n}} \qquad \textbf{(I.1)}$$

For an ideal gas under standard temperature and pressure (STP) conditions (n = 1mole, T= 0°C, p = 1atm), one mole of gas molecules always occupies the same volume:

$$\boldsymbol{V_m = \frac{RT}{P} = 22.4L/mol} \qquad \textbf{(I.2)}$$

6. Law of conservation of mass (Lavoisier)

In chemical reactions "Nothing is lost, nothing is created, everything is transformed" (Lavoisier 1743-1794)

Example:

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$$

- In a chemical reaction, the elements are conserved.

- In a chemical reaction, the mass of the reactants disappeared is equal to the mass of the products formed (Lavoisier's Law).

7. Qualitative aspect of the matter

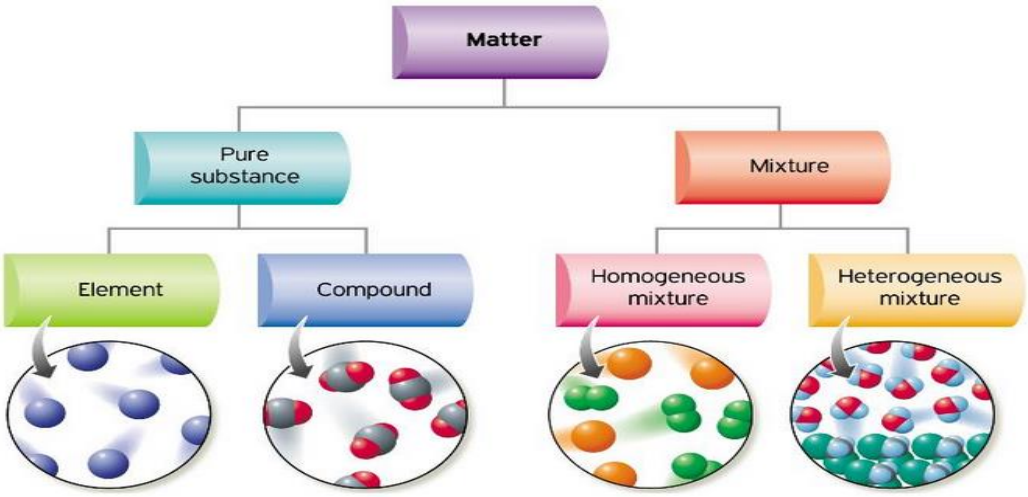


Figure I.6 : Classification of matter

7.1 Pure substance

Is a substance composed of a single type of chemical entity (atom, ion, or molecule). A pure substance is either an element (simple pure substance, example: (Cu, Fe, H_2, O_2) or a compound (composed of several elements, example: (pure water H_2O).

7.2 A mixture

Is a substance consisting of several types of chemical entities mixed together. Mixtures are either homogeneous or heterogeneous:

a. **Homogeneous mixture**

Its components cannot be seen with the eye.

Examples: sugar + water, salt + water.

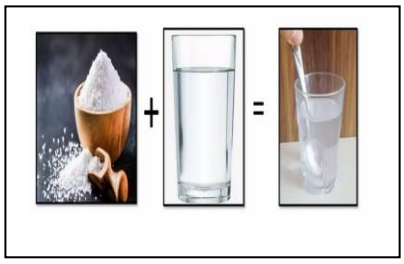


Figure I.7 : Homogeneous mixture

b. Heterogeneous mixture

Has two or more distinct phases.

Its components can be seen with the eye.

Examples: water + sand + oil.



Figure I.8 : Heterogeneous mixture

7.3 Solutions, solute, solvent, aqueous solution, dilution, and saturation

• Solution

A solution is a homogeneous mixture of two or more components. In liquid, gaseous, or solid phase.

• Solvent

A solvent is any liquid substance that has the ability to dissolve other substances.

• Solute

A solute is a chemical species (molecular or ionic) dissolved in a solvent.

- **Aqueous solution**

The homogeneous mixture (solvent + solute) is called an aqueous solution if the solvent is water.

- **Dilution**

Dilution is a process that consists of obtaining a final solution with a lower concentration than the initial solution by adding solvent.

The initial solution is called the stock solution and the diluted solution is called the daughter solution. During dilution, the amount of dissolved chemical species does not change.

$$\mathbf{n_{stock} = n_{daughter} \Rightarrow C_0V_0 = C_1V_1} \qquad \mathbf{(I.3)}$$

With $n_{stock} = C_0V_0$, $n_{dauther} = C_1V_1$

8. Quantitative aspect of matter

8.1 Number of moles

The number of moles is the ratio between the mass of the compound and its molar mass:

$$\mathbf{n = \frac{m}{M}} \qquad \textbf{(I.4)}$$

n: number of moles;

m: mass of compound in g;

M: molar mass of compound in g/mol

8.2 Molarity (C_M)

Molar concentration or molarity (C_M) represents the number of moles of solute per liter of solution.

$$\mathbf{C_M = \frac{n}{V}} \qquad \textbf{(I.5)}$$

8.3 Molality (C)

Molality (C) represents the amount of solute contained in 1000 g of solvent.

$$\mathbf{C = \frac{n_{solute}}{m_{solvent}}} \qquad \textbf{(I.6)}$$

8.4 Mass concentration (Weight concentration) C_m

The mass concentration of a chemical substance in solution is the mass of solute present per liter of solution, it is noted as $\mathbf{C_m}$ and expressed in $g.L^{-1}$.

$$\mathbf{C_m = \frac{m}{V}} \qquad \textbf{(I.7)}$$

There is a relationship between molar concentration and mass concentration:

$$\mathbf{C_m = \frac{m}{V} = \frac{n.M}{V} = C_M.M} \qquad \textbf{(I.8)}$$

8.5 Normality (N)

Represents the number of gram equivalents of solute per liter of solution (eq.g/L).

A gram equivalent is the amount of substance containing one mole of the particles in question (H^+, OH^-, e^-, etc.).

$$\mathbf{N = \frac{eq.g}{V}} \qquad \textbf{(I.9)}$$

Relationship between Normality (N) and Molarity (M):

$$\mathbf{N = Z.\ C_M} \qquad \textbf{(I.10)}$$

8.6 Weight or mass fraction

The mass fraction w_i of component i is the ratio of the mass m_i of that component to the total mass m_{total} of the mixture.

$$\mathbf{W_i = \frac{m_i}{m_T}} \qquad \textbf{(I.11)}$$

8.7 Molar fraction

The molar fraction of a component in a solution is the ratio of the number of moles of that component to the total number of moles.

$$\mathbf{X_i = \frac{n_i}{n_T} \quad with \quad \sum X_i = 1} \qquad \textbf{(I.12)}$$

8.8 Volumic mass and density

- **Volumic mass**

  It describes the mass of a certain volume of solution under specific temperature and pressure conditions.

$$\boldsymbol{\rho = \frac{m}{V}} \qquad \text{Kg/m}^3 \text{ or g/cm}^3 \qquad \textbf{(I.13)}$$

- **Density of a liquid or solid**

  Is the ratio of the density of that liquid or solid to the density of water.

$$\mathbf{d = \frac{\rho}{\rho_{water}}} \qquad \textbf{(I.14)}$$

- **Density of a gas**

  Is the ratio of the density of that gas to the density of air.

$$\mathbf{d = \frac{\rho}{\rho_{air}}} \qquad \textbf{(I.15)}$$

If the volume considered is the molar volume, then m = M (molar mass), given that the density of dry air is equal to 1.293 g/L.

$m_{air} = \rho_{air} . V_{mol} = 1.293 \times 22.4 = 29$ g Therefore:

$$\mathbf{d = m_{gas} / m_{air} = \boldsymbol{d} = \boldsymbol{M}/29} \qquad \textbf{(I.16)}$$

Conclusion

This chapter introduced the fundamental concepts of chemistry related to matter and its transformations. The notions of atoms, molecules, the mole, and Avogadro's number provide the basis for understanding the microscopic composition of matter. The study of pure substances, mixtures, and solutions, together with quantitative parameters such as concentration, molar mass, and density, offers the necessary tools for describing and analyzing chemical systems. These concepts constitute an essential foundation for the study of chemical reactions and more advanced applications of chemistry.

Exercises

Exercise 01

1) A solution with a volume of V = 250 mL is prepared by dissolving 12 mmol of sucrose in water.

What is the molar concentration of sucrose?

2) What is the amount of benzoic acid contained in a volume V = 23.0 mL of a benzoic acid solution with a molar concentration C = 1.5×10^{-2} mol/L?

3) Calculate the amount of sodium chloride (NaCl) and water required to obtain 300 g of a NaCl solution with a mass percentage of 10%.

Data: Density of water = 1 g/cm³, M(Na) = 23, M(Cl) = 35.5 g/mol

Solution

1) $C = \frac{n}{V} = \frac{12.10^{-3}}{250.10^{-3}} = 4{,}8\ 10^{2}\ mol/l$

Determination of the amount of substance

$n = C \times V = 1.5 \times 10^{-2} \times 23 \times 10^{-3} = 3.5 \times 10^{-4}$ mol

In 300 g of solution, there are 30 × 0.1 = 30 g of NaCl

Molar mass of NaCl = 58.5 g/mol

$n = \frac{m}{M} = \frac{30}{58{,}5} \Longrightarrow n = 0{,}51 mol$

Mass of water (solvent) = mass of solution – mass of NaCl (solute) = 300 – 30 = 270 g

ρ_{water} = 1 g/cm³, so the volume of water is 270 mL.

Exercise 02

We want to prepare 1 liter of a 1 N sulfuric acid solution. We have sulfuric acid with a concentration of 96% and a density of 1.84. What volume of acid must be taken?

We take 20 mL of this prepared H_2SO_4 solution and add enough water to bring the volume to 100 mL. What is the molar concentration of the resulting solution?

Solution

d= $\frac{\rho_{H2SO4}}{\rho_{eau.}\ 1}$, $\rho = \frac{m}{V} \Rightarrow m = \rho.V$ = 1.84x1000 = 1840 g

100g de $H_2SO_4 \longrightarrow 96g\ of\ pure\ H_2SO_4$

1840g ⟶ m'

m'= 1766.4g

n= $\frac{m'}{M_{H2SO4}} = \frac{1766,4}{98}$ = 18.02 mole

C= $\frac{n}{V} = 18{,}02\ mol/l$

N = 2.M= 2. 18,02 = 36,04 N= N_0

$V_0 = \frac{N_1.V_1}{N_0} = \frac{1.\ 1}{36,04}$ = 0. 02747l = 27.47 ml

2) N_0 = 1N, $C_0 = \frac{N_0}{K} = \frac{1}{2} = 0.5M$, V_0 = 20 ml

V_1 = 100 ml, C_1= ?

$C_1 = \frac{C_0.V_0}{V_1}$ = 0.1 mol/l

CHAPITRE II

PRINCIPAL CONSTITUENTS OF MATTER

1. Introduction

Understanding the structure of matter is one of the fundamental objectives of chemistry and physics. This chapter explores the relationship between matter and electricity through Faraday's experiments and presents the discovery of the atom's constituents. The contributions of Crookes, Thomson, Millikan, and Rutherford are discussed to explain the identification and characterization of electrons, protons, neutrons, and the atomic nucleus. The chapter also introduces atomic structure, isotopes, mass spectrometry, nuclear binding energy, and the factors governing nuclear stability, providing a comprehensive foundation for the study of atomic and nuclear chemistry.

2. Faraday's experiment

Faraday observed that the destruction of chemical bonds by electrolysis produced considerable amounts of electricity.

There is a relationship between matter and electricity.

At the anod: $O^{-2} \rightarrow \frac{1}{2}O_2 + 2e^-$

At the cathode : $2H^+ + 2e^- \rightarrow H_2$

$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

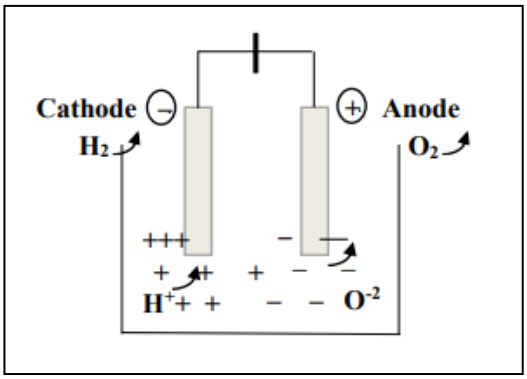


Figure II.1: Faraday's electrolysis

3. Identification of the constituents of matter

3.1. Electron

a. Crooks' experiment (1879) and characteristics of cathode rays

Crookes' experiment demonstrates that negative particles (electrons) exist in atoms. This experiment is carried out in a discharge tube (electrical discharge) containing a rare gas.

The pressure of the gas (air, helium, neon, etc.) in the tube is reduced to 10^{-6} atm. When a high potential difference (pd) of approximately 1000 volts per cm is applied between the two metal electrodes placed at the extremity of a glass tube containing gas. The gas remains dark, but the glass of the tube becomes fluorescent opposite the negative electrode (the cathode). This fluorescence is due to the impact on the glass of rays emitted by the cathode (cathode rays). CROOKS considered that this radiation caused 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.

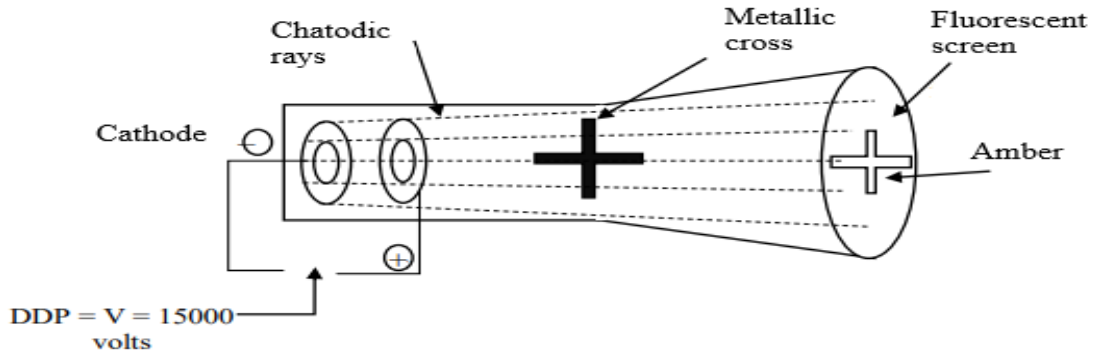


Figure II.2: Crooks' experiment

b. Joseph John Thomson's experiment: 1895.

In this experiment, Joseph John Thomson determined the e/m ratio of the electron by studying the movement of cathode rays in an electric and magnetic field.

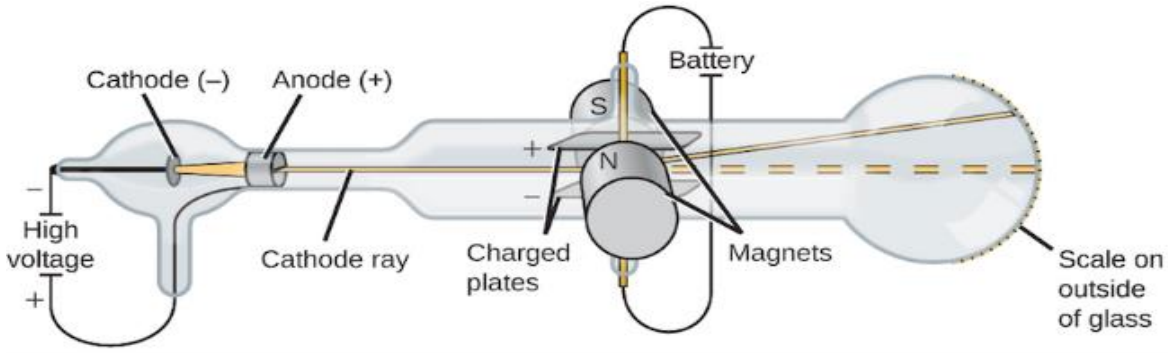


Figure II.3: J.J. Thomson's experiment

In the presence of an electric field

In the presence of an electric field $\vec{E}$, electrons enter the capacitor at a velocity V_0 , where they are subjected to an electric force: $\overrightarrow{F_e} = q\vec{E}$

Along Ox: uniform rectilinear movement. Along Oy: uniformly accelerated movement.

$$\text{Ox: } \begin{cases} V = cst \\ \gamma = 0 \\ x = v.t \end{cases} \qquad \text{Oy: } \begin{cases} v = \gamma t \\ \gamma = cst \\ y = \frac{1}{2}\gamma t^2 \end{cases}$$

We have

- $\overrightarrow{F_e} = m_e \overrightarrow{\gamma_y} = E.q$

$\gamma_y = \frac{q}{m_e}.E$

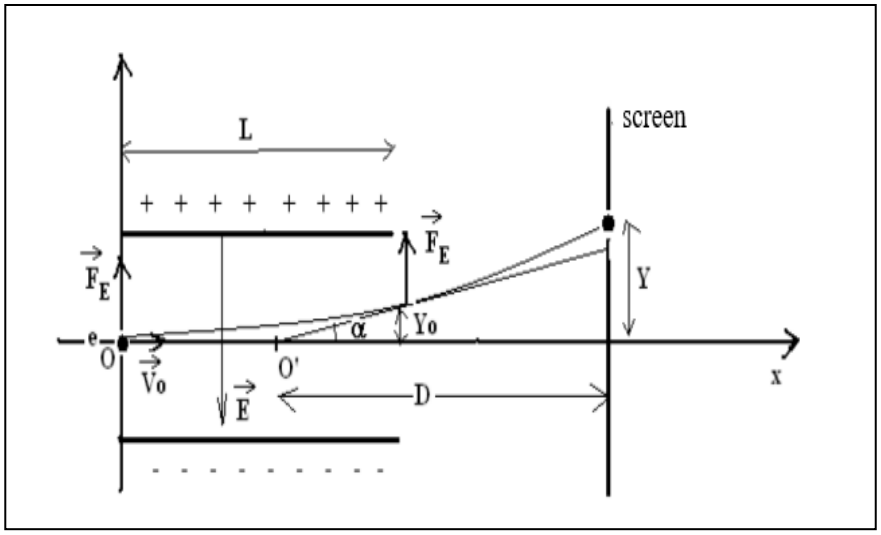


Figure II.4: Presence of an electric field

Along Ox

$t = \frac{x}{v_0}$

$y = \frac{1}{2}\frac{q}{m_e}.\frac{E.x^2}{v_0^2}$

At the condensation outlet

x= L

$y_0 = \frac{1}{2}.\frac{e}{m}.\frac{E.L^2}{V_0^2}$

.**To the simultaneous action of fields $\vec{E}$ and $\vec{B}$**

$$\begin{cases} \overrightarrow{F_e} = q.\vec{E} \\ \overrightarrow{F_B} = qv_0B \end{cases} \Rightarrow q.E = q.v_0.\vec{B}$$

$$v_0 = \frac{E}{B}$$

We have

$$y = \frac{1}{2}\frac{q}{m_e} E \frac{x^2}{V_0^2}$$

We replace: x with L and y with Y.

We obtain:

$$y_0 = \frac{1}{2}.\frac{e}{m_e}\frac{E.L^2}{E^2}.B^2 = \frac{1}{2}.\frac{e}{m_e}.\frac{B^2.L^2}{E}$$

So

$$\frac{e}{m_e} = \frac{2.E.y_0}{B^2L^2}$$

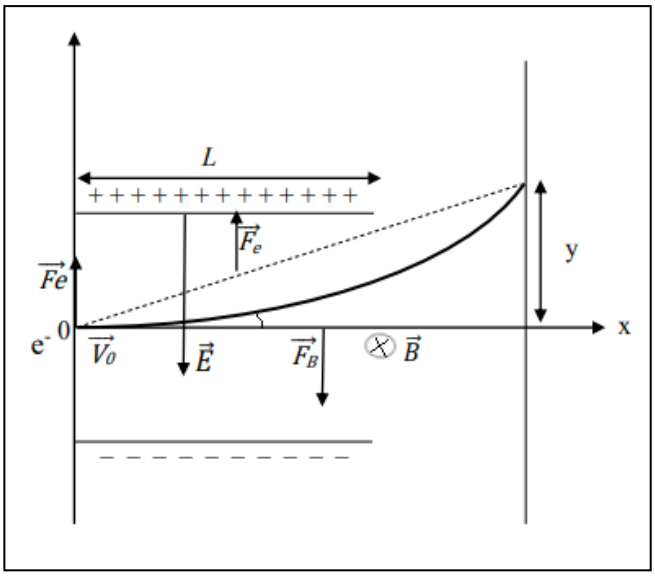


Figure II.5 : Simultaneous action of fields $\vec{E}$ and $\vec{B}$

$$\frac{e}{m_e} = 1.759.10^{11}\text{C/kg} \qquad \textbf{(II.1)}$$

Under the action of the magnetic field alone

$$F_m = e.v_0.B.\sin\alpha = e.v_0.B \qquad \sin\alpha = 1$$

$$\left|\overrightarrow{F_c}\right| = m_e.\frac{v_0^2}{r} = e.v_0.B \Rightarrow r = \frac{m_e.v_0}{e.B}$$

$$\mathbf{r = \frac{m_e.v_0}{e.B}} \qquad \textbf{(II.2)}$$

c. Millikan's experiment: Determination of the charge of the electron: 1911

The experiment is based on the displacement

of a drop of ionized (charged) oil in a capacitor.

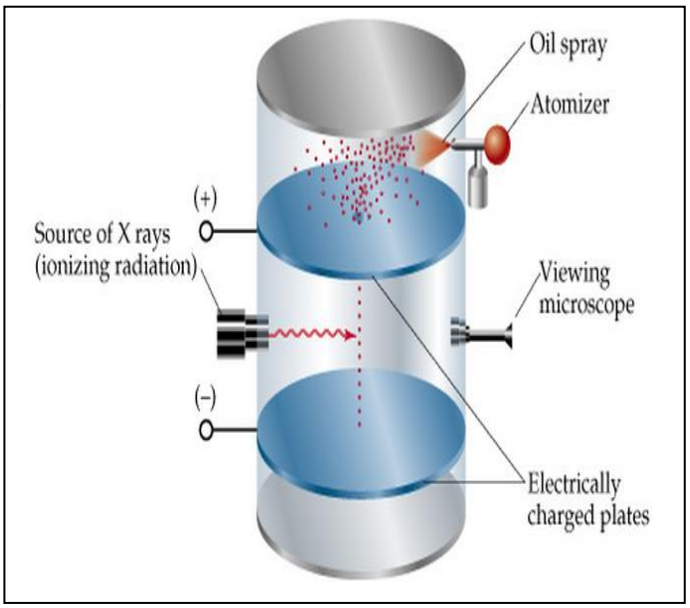


Figure II.6: Millikan's experiment

a) In the absence of an electric field

Fs: Stock force, which always

opposes the movement of the drop (air friction force).

$\vec{A}$: Archimedes' force (which opposes weight).

$\vec{P}$: Weight of the oil drop.

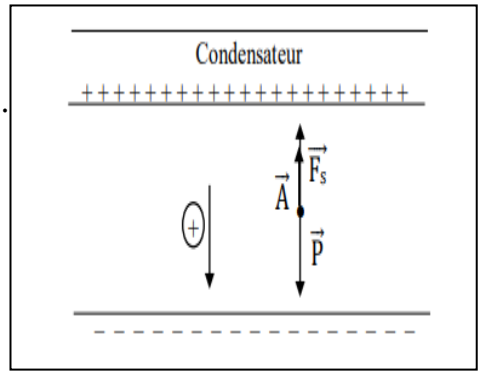


Figure II.7: the absence of an electric field

$$P = m.g = \rho.v.g = \frac{4}{3}.\pi.r^3.\rho.g$$

$$A = \frac{4}{3}.\pi.r^3.\rho_a.g$$

$$F_s = 6\pi.\eta.r.v_0$$

$$\sum \vec{F} = \vec{P} + \vec{F_s} + \vec{A}$$

$$\sum \vec{F} = \vec{0}$$

η: Premittivity of air.

r: Radius of the drop.

v_0: Velocity of the drop.

ρ_a: Volumic mass of air.

g: Gravity.

ρ: Volumic mass of oil.

Since the velocity is constant, the acceleration $\gamma = 0$.

$$\frac{4}{3}.\pi.r^3.\rho.g - \frac{4}{3}.\pi.r^3.\rho_a.g - 6.\pi.\eta.r.v_0 - 0$$

$$\frac{4}{3}r^2.(\rho - \rho_a).g - 6.\eta.v_0 = 0$$

$$\mathbf{r^2 = \frac{9}{2}.\frac{\eta.v_0}{(\rho-\rho_a).g}} \qquad \textbf{(II.3)}$$

b) In the presence of electric fields

The charged droplet rises and reaches a new maximum velocity V'$_0$.

$\sum \vec{F} = \vec{F_e} + \vec{P} + \vec{F_s} + \vec{A}$

$\sum \vec{F} = \vec{0}$

$P + F'_s - A - F_e = 0$

$F_e = P + F'_s - A = qE$

$F_s = P - A$

$F_e = F_s + F'_s$

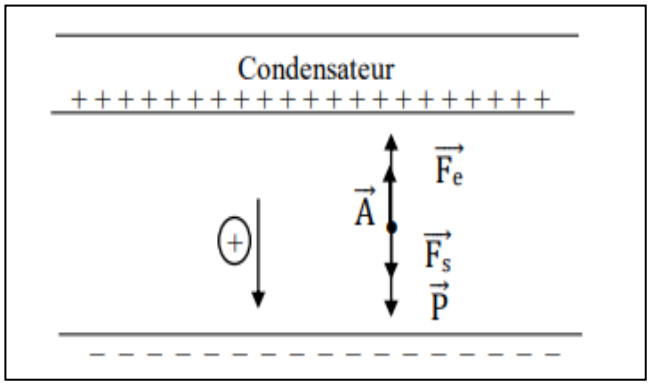


Figure II.8 : Presence of electric fields

$6.\pi.\eta.r(v_0 + v'_0) = q.E$

$$\mathbf{q = \frac{6.\pi.\eta.r(v_0+v'_0)}{E}} \qquad \textbf{(II.4)}$$

v_0: free fall velocity.

v'_0: rising velocity.

When the drop stops v'$_0$= 0

$\sum \vec{F} = \vec{0}$

$P - A - F_e = 0 \quad (F_s = 0)$

$\frac{4}{3}.\pi.r^3.(\rho' - \rho) \quad = qE$

$q = \frac{\frac{4}{3}.\pi.r^3.(\rho' - \rho)}{E}$

m_e = 9.1 × 10^{-31} kg

e/m = 1.759 × 10^{11} coulomb/kg,

|e| = 1.602 × 10^{-19} coulomb.

Then m = e /1.759 × 10^{11}

m = 1.602 × 10^{-19} / 1.579 × 10^{11}

m = 9.1 × 10^{-31} kg = 5.5 × 10^{-4} uma

Applying different voltages produces different values of q. Millikan showed that all values of q were multiples of the elementary charge of the electron (e = 1.602×10^{-19}). This value represents the smallest electrical charge that an oil droplet can contain; it is the elementary charge of the electron.

q = n. e (n: 1, 2, 3,..)

3.2 The nucleus and its components

3.2.1 Rutherford's experiment (1911-1919)

The experiment consists of bombarding a very thin sheet of metal (gold) with radiation containing helium nuclei (He^{2+}).

Most of the particles α (He^{2+}), pass through the gold foil without being deflected, while others pass through with only slight deflection (1/100) and very few nuclei are turned back by the foil (1/20,000).

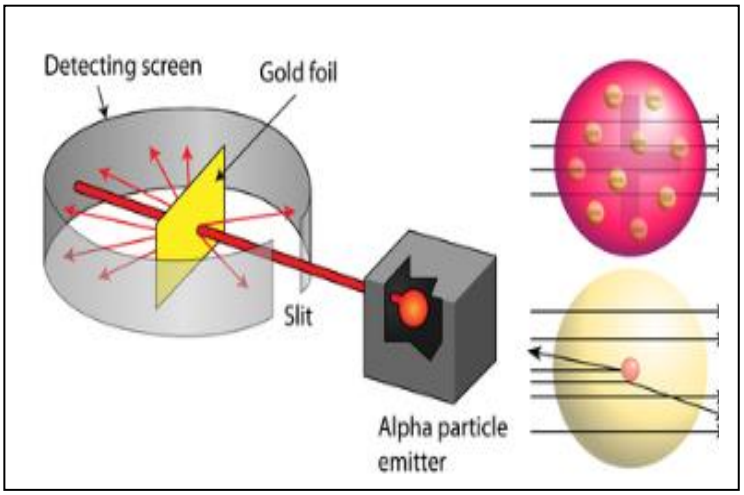


Figure II.9: Rutherford's experiment

These results inspired Rutherford to conclude that the positive charge is concentrated in a dense, small nucleus at the center of the atom, and that most of the space in an atom is actually empty, in other words Rutherford deduced that the atom consists of a positively charged nucleus, around which negatively charged electrons move and remain within a sphere.

4. Composition of the atomic nucleus

The nucleus has a diameter of around 10^{-4} Å. It is composed of stable elementary particles called nucleons.

Protons are positively charged:

$q_p = +e = 1.602\times10^{-19}$ C.

The mass of the proton:

$m_p = 1.673\times10^{-27}$ kg ≈ 1836 m_e.

Neutrons have no charge, and their mass is:

$m_n = 1.675\times10^{-27}$kg.

All of the atom's mass is concentrated in the nucleus.

5. Characteristics of the atom

The atom consists of a nucleus and a cloud of electrons. The nucleus contains protons and neutrons, which are nucleons. The mass of the nucleus is almost equal to the mass of the atom (the mass of electrons is negligible compared to that of nucleons).

5.1 Atomic number and mass number

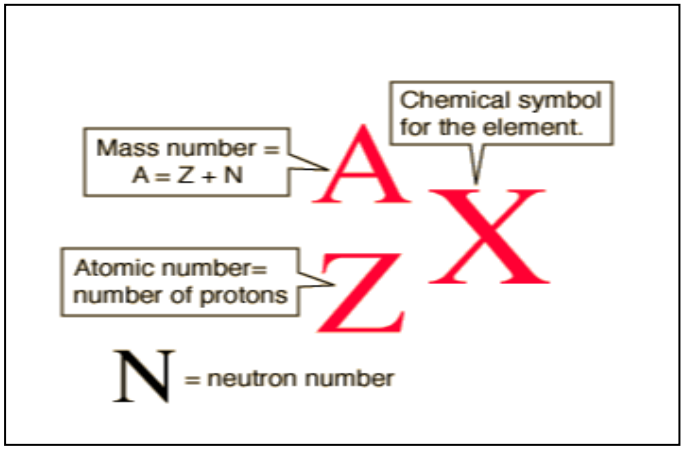
5.1.1 Atomic number Z

The atomic number is the number of protons and also refers to the number of electrons around the nucleus, since the atom is electrically neutral.

5.1.2 Mass number A

The mass number represents the number of nucleons (protons and neutrons).

The nucleus of an atom is represented by the symbol:



Note:

If the element is ionized (charged), the number of electrons is different from the number of protons.

Example $^{35}_{17}Cl$

Z = 17

A = 35

N = 35 – 17 = 18

- ***Isotopy and relative abundance of different isotopes***

Isotopes are atoms of the same element that have the same number of protons in their nucleus, but a different number of neutrons. This indicates that isotopes have different atomic masses, but similar chemical properties.

Example: Carbon isotopes

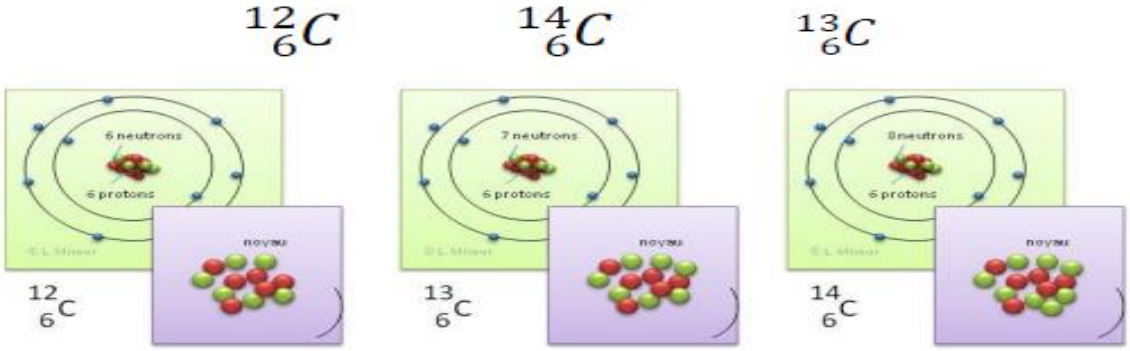


Figure II.10: Isotopes of Carbon

5.1.3 Average atomic mass of a chemical element

The average atomic mass is calculated using the following formula:

$$\mathbf{M} = \frac{\sum \mathbf{X_i M_i}}{\mathbf{100}} \qquad \textbf{(II.5)}$$

x_i: Molar percentage

M_i: Mass of isotopes

Example:

Oxygen with three isotopes: 99.76%, : 0.04%, 0.2%

$^{16}O: 99.76\%, \quad ^{17}O : 0.04\%, \quad ^{18}O : 0.2\%$

$$M(O) = \frac{16x99.76 + 17x0.04 + 18x0.2}{100}$$

M(O) = 16.0044 g/mol

5.1.4 Isotope separation Mass

Spectrometry can be used to identify the different isotopes of an element by determining their masses and isotopic abundances.

- ***Banbridge spectrometry***

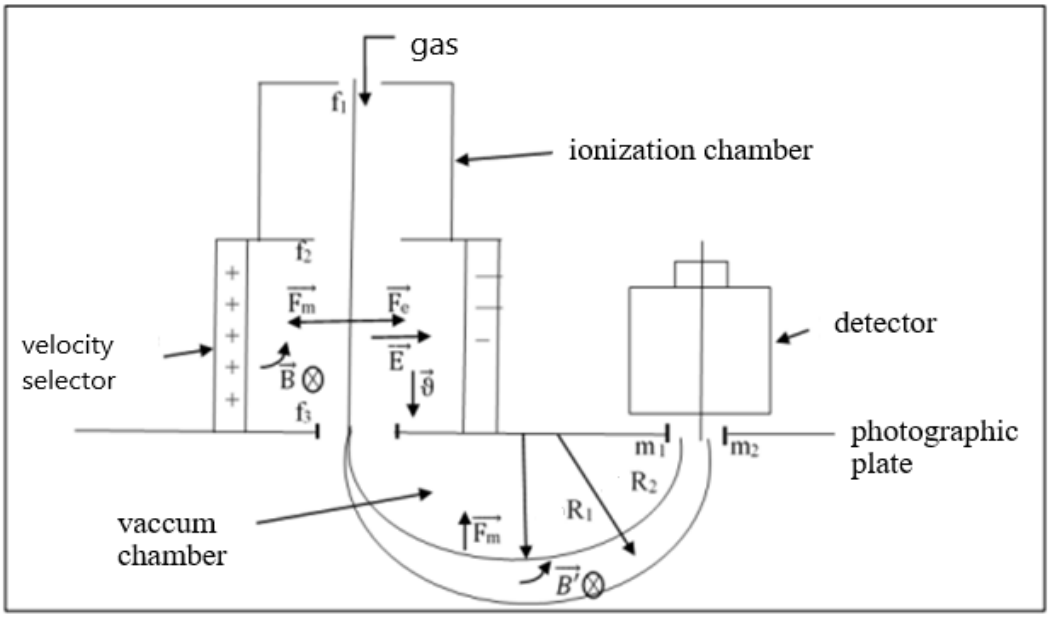


Figure II.11: Schematic representation of the Bainbridge spectrometer principle

The Banbridge experiment follows these steps:

1. Ionization of the elements contained in the sample to be analyzed. The ions pass through a velocity filter where they are exposed to an electric field E and a magnetic field B. The ions follow a trajectory at the same speed.
   $\overrightarrow{\mathrm{F_m}} = \overrightarrow{\mathrm{F_e}}$

Electric force $\overrightarrow{F_e} = \mathrm{q}\vec{\mathrm{E}}$

Magnetic force

$\overrightarrow{F_m} = q\overrightarrow{v_0}\vec{B}$

$\left|\overrightarrow{\mathrm{F_e}}\right| = \left|\overrightarrow{\mathrm{F_m}}\right|$

$\mathrm{q.E} = \mathrm{q.v.B} \Rightarrow \mathbf{v} = \frac{\mathbf{E}}{\mathbf{B}}$

$$\mathbf{v} = \frac{\mathbf{E}}{\mathbf{B}} \qquad \textbf{(II.6)}$$

2. At the exit of the velocity filter, a new magnetic field is applied in the analyzer. Under the effect of this field, the ions describe semicircles with radius R. The ions are exposed to the magnetic force.

$F_m = m\gamma$

We have $F'_m = q.v.B'$

In equilibrium: $q.v.B' = m\frac{v^2}{R}$

$$q.B' = \frac{m}{R}.\frac{E}{B}$$

$$v = \frac{E}{B}$$

$$\frac{m}{R} = \frac{q.B'.B}{E}$$

$$\mathbf{\frac{m}{R} = Cst} \qquad \textbf{(II.7)}$$

$$\frac{m_i}{R_i} = \frac{m_R}{R_R} \Rightarrow \mathbf{m_i = \frac{m_R.R_i}{R_R}}$$

Calculate distance d

$$F_m = m\gamma = m\frac{v^2}{R} = qBv \Rightarrow R = \frac{m.v}{q.B} \Rightarrow m = \frac{R.q.B}{v}$$

$$\text{Isotope } R_1\text{: } R_1 = \frac{m_1.v}{q.B}$$

$$\text{Isotope } R_2\text{: } R_2 = \frac{m_2.v}{q.B}$$

$$\text{Isotope } R_i\text{: } R_i = \frac{m_i.v}{q.B} \quad \text{with} \quad R_i = \frac{D_i}{2}, m_2 > m_1$$

$$\mathbf{d = 2(R_2 - R_1) = \frac{2v}{qB}(m_2 - m_1)} \qquad \textbf{(II.8)}$$

6. Binding energy and cohesion of nuclei

6.1. Mass defect

The mass defect Δm is always positive. It is defined as:

$$\Delta m = (Z \cdot m_p + (A-Z) \cdot m_n) - m_{noyau} \qquad \textbf{(II.9)}$$

6.2 Bond energy

Binding energy is the energy required to break a nucleus into nucleon particles.

$$E_L = \Delta m.C^2 \qquad \textbf{(II.10)}$$

Δm: Mass defect of the nucleus (in kg)

C: Speed of light in a vacuum (m/s)

This energy is positive since it is received by the system in question (nucleus).

E_L : Binding energy of the nucleus (in J, eV, or MeV)

7. Nucleus stability

a- Determination of cohesion energy per nucleon: Aston curve

The Aston curve below shows the variation of

$E_{liaison\ /nucleon}$ (A) as a function of the nucleon number A.

The stability of a nucleus increases with the binding energy per nucleon, which is around **8 MeV/nucleon** for most stable nuclei.

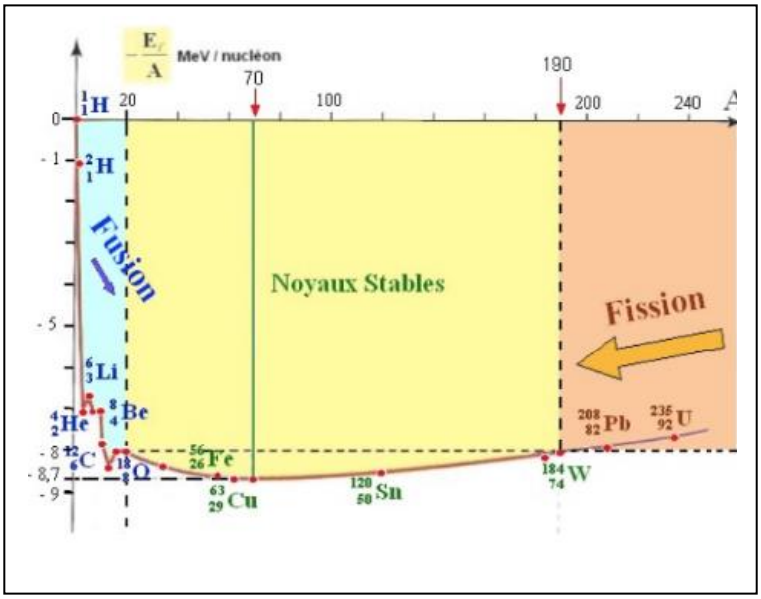


Figure II.12 : Cohesion energy per nucleon: Aston curve

b- Stability and number of nucleons: Curve number of neutrons = f (Z: number of protons)

Stability zone

The diagram shows the variation in mass number A as a function of atomic number Z in nuclei

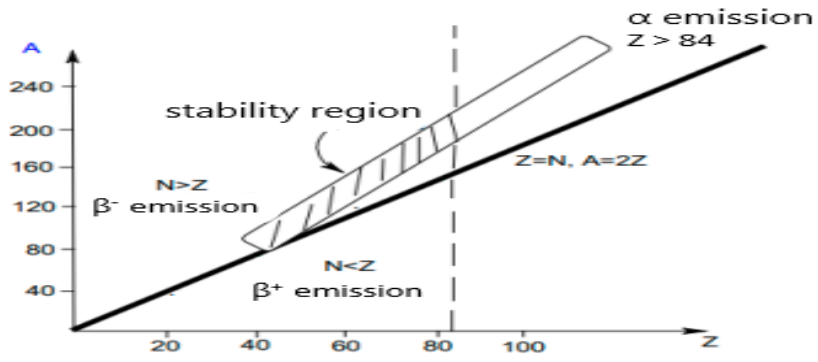


Figure II.13: Stability and number of nucleons

Between 1≤ Z≤20, all nuclei are stable with Z≈N.

Between 20≤ Z≤84, nuclei are less stable N>Z, requiring more neutrons to compensate for the electrostatic repulsion of the proton.

All nuclei for which Z≥ 84 are highly unstable and radioactive (α emission).

Conclusion

This chapter has highlighted the main constituents of matter and the experimental discoveries that led to our current understanding of atomic structure. The properties of electrons, protons, neutrons, and atomic nuclei were examined, along with the concepts of atomic number, mass number, and isotopes. Techniques such as mass spectrometry were presented for determining isotopic masses and abundances. Finally, the notions of mass defect, binding energy, and nuclear stability were introduced, emphasizing their importance in explaining the cohesion and behavior of atomic nuclei.

Exercises

Exercise 1

An electron beam traveling at a velocity v enters the space between the plates of a capacitor, where a uniform electric field E perpendicular to the direction of the beam and a magnetic field B perpendicular to both E and v are present.

1- Derive the expression for y_o at the exit of the capacitor.

The two fields E and B act simultaneously, and their intensities are adjusted so that the beam is not deflected.

2- Give the expression for the velocity v of the electrons.

3- Determine the charge-to-mass ratio e/m of the electrons

Data: E = 5.10^4 volts·m^{-1}, B = 10^{-3} tesla, l = 10 cm, y_o = 1.76 cm

Solution

along ox :

$\overrightarrow{F_e} = m\,\vec{\gamma}$

$0 = m\gamma \Rightarrow \gamma = 0 \Rightarrow v = cst$

$$v = \frac{dx}{dt} \Rightarrow \int dx = \int v dt \Rightarrow \boldsymbol{x = vt}$$

Along oy :

$F_e = m\gamma \Rightarrow q\,E = m\gamma \Rightarrow \gamma = \frac{e\,E}{m} = cost$

$$\gamma = \frac{dv}{dt} \Rightarrow \int dv = \int \gamma dt \Rightarrow v = \gamma t$$

$$v = \frac{dy}{dt} \Rightarrow \int dy = \int v\,dt \Rightarrow \int dy = \int \gamma t\,dt$$

$$y = \frac{1}{2}\gamma t^2 \Rightarrow y = \frac{1}{2}\frac{e\,E}{m}t^2$$

at the capacitor output $l = v\,t \Rightarrow t = \frac{l}{v}$

$$\boldsymbol{y = \frac{1}{2}\frac{e}{m}E\,\frac{l^2}{v^2}}$$

2) Equation for particle velocity:

$F_m = F_e \Rightarrow evB = eE \Rightarrow \boldsymbol{v = \frac{E}{B}}$

3) The mass charge of $\frac{e}{m}$:

$$y = \frac{1}{2}\frac{e}{m}E\ \frac{l^2}{v^2} = \frac{1}{2}\frac{e}{m}E\frac{l^2}{E^2}B^2 = \frac{1}{2}\frac{e}{m}\frac{l^2}{E}B^2$$

$$\boldsymbol{\frac{e}{m} = \frac{2\,y\,E}{l^2B^2} = 1,76\,.\,10^{11}Cb/Kg}$$

Exercise 2 (Millikan Experiment)

1. Using the apparatus employed by Millikan, observe the free fall of an oil droplet in

the air. Its velocity is 0.32 mm/s, neglecting the air resistance on the droplet.

Calculate its radius and mass.

2. The droplet is then placed between the plates of a capacitor. It rises, and its velocity is 0.118 mm/s when the electric field is E = 4.5 × 10^5 volts/m.

Calculate the charge q carried by the droplet.

3. During the experiment, the droplet's charge varies, and it can be stopped between the plates when the electric field E' = 2.47 × 10^5 volts/m.

- Calculate the new charge q' carried by the droplet.

- Deduce the elementary charge from all these measurements.

Data: Specific mass of the liquid used φ = 1.26 × 10^3 kg/m^3;

Acceleration due to gravity g = 9.81 m/s^2

Viscosity coefficient of air η = 1.82 × 10^{-5} decapoise (MKSA).

Solution

Calculation of the radius:

$P = R \Rightarrow mg = 6\pi\eta v_0 r \Rightarrow \rho\frac{4}{3}\pi r^3 g = 6\pi\eta v_0 r\pi$

$(\rho = \frac{m}{v} \Rightarrow m = \rho v = \rho\ \frac{4}{3}\pi r^3)$

$$r^2 = \frac{6\pi\eta v_0}{\frac{4}{3}\pi\rho g} = \frac{9}{2}\frac{\eta v_0}{\rho\, g} \Rightarrow r = \sqrt{\frac{9}{2}\frac{\eta v_0}{\rho\, g}}$$

$$r = \sqrt{\frac{9}{2}\frac{1{,}82.10^{-5}.0{,}32.10^{-3}}{1{,}26.10^{3}.9{,}81}} = 1{,}45.10^{-6}$$

$$\boldsymbol{r = 1{,}45.10^{-6}\,m}$$

Calculation of mass:

$$\rho = \frac{m}{v} = \frac{m}{\frac{4}{3}\pi r^3} \Rightarrow m = \frac{4}{3}\pi\rho r^3$$

$$m = \frac{4}{3}.3{,}14.1{,}26.10^{3}.(1{,}45.10^{-6})^3 = \boldsymbol{1{,}61.10^{-14}Kg}$$

2) Calculation of the charge q:

Fe = R + P

$$qE = 6\pi\eta v_0' r + mg$$

We know that: $m\, g = 6\pi\eta v_0 r$

$$q\, E = 6\pi\eta v_0' r + 6\pi\eta v_0 r$$

$$q\, E = mg\left(\frac{v_0'}{v_0} + 1\right) \Rightarrow q = \frac{mg}{E}\left(\frac{v_0'}{v_0} + 1\right)$$

$$q = \frac{1{,}61.10^{-14}.9{,}81}{4{,}5.10^{5}}\left(\frac{0{,}118.10^{-3}}{0{,}32.10^{-3}} + 1\right)$$

$$\boldsymbol{q = 4{,}8\,.10^{-19}Cb}$$

2) Calculation of the charge q' :

$$F_e' = P \Rightarrow\ q'E' = mg \Rightarrow\ q' = \frac{mg}{E'}$$

$$q' = \frac{1{,}61.10^{-14}.9{,}81}{2{,}47\,.10^{5}} = \boldsymbol{6{,}39\,.10^{-19}Cb}$$

We observe that: q-q' = $q - \ q' \simeq 1{,}6.10^{-19}Cb$

Furthermore:

q ≃ 3 e

q' ≃ 4 e

Exercise 3 (Atomic Composition):

In the periodic table, the following data are listed for the element copper:

atomic number 29; mass number 63

1- State the number of protons, neutrons, and electrons that make up the copper atom

2- Calculate the mass of the copper atom

3- How many protons, neutrons, and electrons does the Cu^{2+} ion have?

Data: m (proton) ≈ m (neutron) = 1.67×10^{-27} kg, m (electron) = 9.1×10^{-31} kg

Solution

$$^{63}_{29}Cu$$

A = 63

Z (Number of protons) = 29.

A = Z + N ⇒ N = A - Z = 63 – 29 = 34 (Number of neutrons).

Number of electrons = 29.

m (Cu) = 29 x (m_p) + 34 x (m_N) + 29 x (m_{e^-})

= 29 x 1.67×10^{-27} +34 x 1.67×10^{-27} + 29 x 9.1×10^{-31}

= (29 +34) x 1.67×10^{-27} + 29 x 9.1×10^{-31} = 105.21 x 10^{-27} + 263.9 x 10^{-31}

M (Cu) ≈ 105.21 x 10^{-27} Kg.

For Cu^{2+}

Z (Number of protons) = 29.

A = Z + N ⇒ N = A - Z = 63 – 29 = 34 (Number of neutrons).

Number of electrons = 27.

Exercise 04: (Banbridge Spectrograph)

The Banbridge spectrograph is used to separate the isotopes of an element x, with (12) C used as a reference element since it is lighter than the isotopes of x. Four impact points are obtained on the photographic plate, with distances of 32 cm, 64 cm, 66.64 cm, and 69.32 cm, respectively.

1- Find the relationship between the distance between the impact points and the exit of the velocity filter and the masses of the isotopes.

2- Calculate the mass of each isotope.

1- Calculate the average atomic mass of element X, given that the percentages of the isotopes, from lightest to heaviest, are 77.60%, 11.11%, and 11.29%.

Solution

1) In the analyzer, we have:

$F_m = m\,\gamma_n$ avec $\gamma_n = \frac{v^2}{R}$

$$qvB = m\frac{v^2}{R} \Rightarrow \boldsymbol{R = \frac{m\,v}{q\,B}}$$

2)

$$\frac{R}{m} = \frac{v}{q\,B} = cost$$

$$\frac{R_c}{m_c} = \frac{R_{x1}}{m_{x1}} = \frac{R_{x2}}{m_{x2}} = \frac{R_{x3}}{m_{x3}} = \frac{R}{q\,B}$$

$$\frac{R_c}{m_c} = \frac{R_{x1}}{m_{x1}} \Rightarrow m_{x1} = \frac{m_c R_{x1}}{R_c} = \frac{12.64}{32} = \boldsymbol{24\ u.m.a}$$

$$\frac{R_c}{m_c} = \frac{R_{x2}}{m_{x2}} \Rightarrow m_{x2} = \frac{m_c . R_{x2}}{R_c} = \frac{12.\ 66{,}64}{32} = \boldsymbol{25\ u.m.a}$$

$$\frac{R_c}{m_c} = \frac{R_{x3}}{m_{x3}} \Rightarrow m_{x3} = \frac{m_c . R_{x3}}{R_c} = \frac{12.\ 69{,}32}{32} = \boldsymbol{26\ u.m.a}$$

3) Average atomic mass:

4) $M_{moy} = \frac{\sum M_i . X_i}{\sum X_i} = \frac{X_1 . M_{x1} + X_2 . M_{x2} + X_3 . M_{x3}}{X_1 + X_2 + X_3}$

5) $M_{moy} = \frac{77{,}6\ .24 + 11{,}11\ .25 + 11{,}29\ .26}{100} = \boldsymbol{24{,}33\ u.m.a}$

CHAPITRE III

Radioactivity – Nuclear reactions

1. Introduction

Radioactivity is a fundamental nuclear phenomenon that involves the spontaneous transformation of unstable atomic nuclei into more stable forms through the emission of particles and radiation. This chapter introduces the different types of natural radioactivity, namely alpha (α), beta (β), and gamma (γ) radiation, as well as the principles of artificial radioactivity and nuclear reactions. It also presents the kinetics of radioactive decay, including decay laws, half-life, and activity, and highlights the major applications of radioactivity in energy production, medicine, and archaeological dating. Understanding these concepts is essential for studying nuclear processes and their impact on science and technology.

2. Natural Radioactivity

It was discovered in 1898 by Henri Becquerel. It is the property of an unstable atomic nucleus to spontaneously transform into nuclei of another chemical species, emitting radiation and particles.

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

- **α Radiation**

These are helium nuclei or helium (notation or α) emitted essentially by heavy nuclei (Z > 83) during their transformation into smaller nuclei.The general nuclear equation is as follows:

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

Example

$^{232}_{90}\mathrm{Th} \rightarrow {}^{228}_{88}\mathrm{Ra} + \alpha$

$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + \alpha$

- **β Radiation**

There are two types of β radioactivity: β- and β+.

When the N/Z ratio is too high, a neutron tends to transform into a proton, producing a particle with the same characteristics as an electron, called β^-

$$^{1}_{0}n \rightarrow {}^{1}_{1}P + {}^{0}_{-1}e$$

Since electrons cannot exist inside a nucleus, they are emitted (ejected).The nuclear equation is:

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

Example

$$^{108}_{47}Ag \rightarrow {}^{108}_{48}Cd + {}^{0}_{-1}e$$

They are more penetrating but less ionizing than alpha particles. They penetrate the body to a thickness of a few millimeters. They are dangerous to the body.

- **β^+ Radiation**

Nuclei with too many protons (or too few neutrons, therefore located to the right of the stability curve) emit a positron that comes from the decay of a proton into a positron, a neutron, and an electron neutrino.

$$^{1}_{1}P \rightarrow {}^{1}_{0}n + {}^{0}_{+1}e\ (\beta^+)$$

Example

$$^{60}_{27}Co \rightarrow {}^{60}_{26}Fe + {}^{0}_{+1}e\ (\beta^+)$$

- **ɣ Radiation**

Very high-energy electromagnetic radiation of the same nature as light (i.e., photons). With this type of radioactivity, there is no emission of particles or disintegration.

In general, when a nucleus is formed during α or β decay, it does not immediately reach its fundamental state, but is found in an excited state. The transition from the excited state to the fundamental state liberates a γ photon.

$$^{A}_{Z}X^{*}\ (\text{unstable}) \rightarrow {}^{A}_{Z}X\ (\text{stable}) + \gamma$$

Example

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th}^{*} + \alpha \rightarrow {}^{234}_{90}\mathrm{Th} + \gamma$$

3. Artificial radioactivity and nuclear reactions

This concerns radioactivity caused in certain nuclei as a result of human intervention.There are three types:

a. Nuclear fission

b. Nuclear fusion

c. Transmutations

a. Nuclear fission

Atoms with very high mass numbers A, when bombarded by neutrons, can be broken down into smaller atoms and regenerate neutrons.

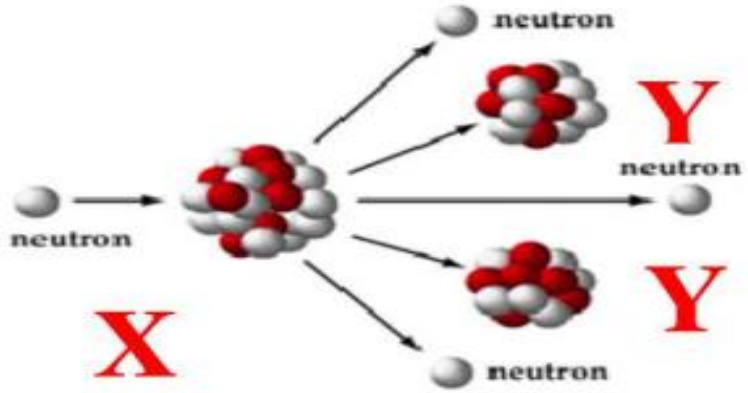


Figure III.1: Nuclear fission

Example

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{139}_{56}\mathrm{Ba} + {}^{94}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}\mathrm{n}$$

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{139}_{54}\mathrm{Xe} + {}^{95}_{38}\mathrm{Sr} + 2\,{}^{1}_{0}\mathrm{n}$$

b. Nuclear fusion

This is the union of two smaller nuclei into a larger nucleus with the emission of a considerable amount of energy.

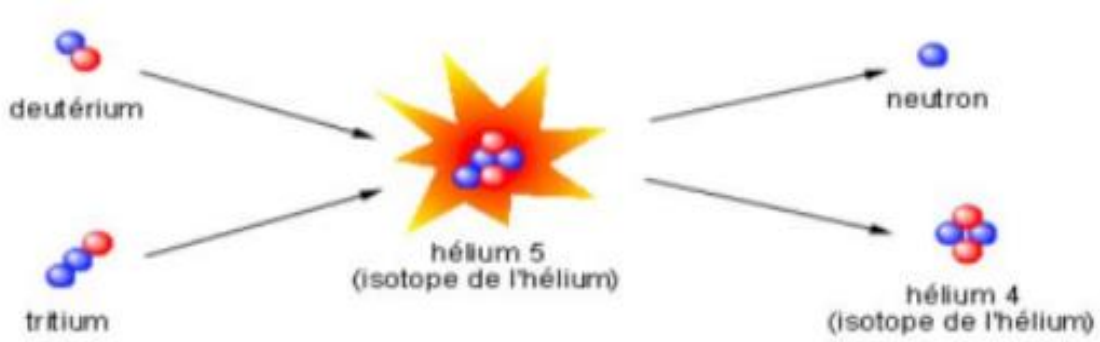


Figure III.2: Nuclear fusion

Some of the known fusion reactions are as follows:

$$^{2}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{1}_{0}\mathrm{n} + \text{radiation energy}$$

$$^{2}_{1}\mathrm{H} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{1}_{1}\mathrm{H} + {}^{3}_{1}\mathrm{H} + \text{radiation energy}$$

$$^{6}_{3}Li + {}^{2}_{1}H \rightarrow 2\,{}^{4}_{2}He + radiation\ energy$$

c. Nuclear transmutations

These reactions produce nuclides with a mass number equal to or very near that of the nuclide that was used as the original focus, and the nuclides formed are stable or radioactive.

Example

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

Abbreviated notation for this reaction:

$$^{14}\mathrm{N}\,(\alpha, \mathrm{P})\,^{17}\mathrm{O}$$

$$^{6}_{3}\mathrm{Li} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{7}_{3}\mathrm{Li} + {}^{1}_{1}\mathrm{H}$$

Abbreviated notation for this reaction:

$$^{6}\mathrm{Li}\,(\mathrm{d}, \mathrm{P})\,^{7}\mathrm{Li}$$

$$^{23}_{11}\mathrm{Na} + {}^{1}_{1}\mathrm{H} \rightarrow {}^{23}_{12}\mathrm{Mg} + {}^{1}_{0}\mathrm{n}$$

Abbreviated notation for this reaction:

$$^{23}\mathrm{Na}\,(\mathrm{P}, \mathrm{n})\,^{23}\mathrm{Mg}$$

Table I.1: The most common nuclear particles and their symbols

Particle	Name	Symbol
α	Alpha	${}_{2}^{4}\mathrm{He}^{+2}, {}_{2}^{4}\alpha$
γ	gamma	${}_{0}^{0}\gamma$
β^-, e^-	Electron	${}_{-1}^{0}\mathrm{e}$
B^+	Positon	${}_{+1}^{0}\mathrm{e}$
n	neutron	${}_{0}^{1}\mathrm{n}$
P	Proton	${}_{1}^{1}\mathrm{P}$, ${}_{1}^{1}\mathrm{H}^{+}$
d, D	Deuterium	${}_{1}^{2}\mathrm{H}$
t, T	Tritium	${}_{1}^{3}\mathrm{H}$

4. Radioactive disintegration kinetics

4.1 Radioactive decay law

The decay of a radioactive element can be very rapid, taking just a few milliseconds, or extremely long, taking several thousand years. This decay is defined by the law of first-order reaction velocity.

for either reaction (**B** is not radioactive)

$$X \rightarrow \gamma + \text{particle}$$

At t = 0 N_0 0

at t≠0 N (number of particles remaining after a given time t)

$N_0 - N$ (disintegrated after a given time t)

at time t+dt, there are N+dN < N, with (dN < 0).

dN is the number of nuclei that disintegrate in the time interval dt.

$$-\frac{dN}{dt} = \lambda N \qquad \textbf{(III.1)}$$

λ is the disintegration constant; its units: s^{-1} , min^{-1}, h^{-1}, day^{-1}, …

It represents the probability of disintegration per second. $\lambda > 0$

$$-\frac{dN}{dt} = \lambda N$$

$$\frac{dN}{N} = -\lambda dt$$

$$\int_{N_0}^{N}\left(\frac{dN}{N}\right) = \int_0^t -\lambda dt \Leftrightarrow [\ln(N)]_{N_0}^{N} = -\lambda[(t)]_0^t$$

$\ln N - \ln N_0 = -\lambda t$

$\ln (N/N_0) = -\lambda t$

$N/N_0 = e^{-\lambda t}$

$$\mathbf{N = N_0\, e^{-\lambda t}} \qquad \textbf{(III.2)}$$

This law can be written in another form depending on the mass or mole number of the radioactive element studied.

1 mol $\rightarrow N_A$

n mol of the element (m/M) $\rightarrow$N

So $m/M = 1\ mol \times N/N_A$

$$\text{therefore} \quad \mathbf{N = m.\ N_A/M} \qquad \textbf{(III.3)}$$

in the same way $N_0 = m_0.\ N_A/M$

Replacing N and N_0 with their formula

we obtain: $m.\ N_A/M = (m_0.\ N_A/M).\ e^{-\lambda t}$

therefore

$$\mathbf{m = m_0\, e^{-\lambda t}} \qquad \textbf{(III.4)}$$

Or

$$\mathbf{n = n_0\, e^{-\lambda t}} \qquad \textbf{(III.5)}$$

n: number of moles of the element.

m: mass of the radioactive element at time $t \neq 0$

m_0: mass of the radioactive element at time t=0

4.2 Radioactive period (T) or half-life ($t_{1/2}$)

The half-life time, or period, is the time after which half of the initial nuclei have disintegrated. It is obtained by replacing t = T and $N_t = N_0 / 2$.

$$\int_{N_0}^{\frac{N_0}{2}} \frac{dN}{N} = -\lambda \int_0^T dt \Rightarrow (\ln N)_{N_0}^{\frac{N_0}{2}} = -\lambda(t)_0^T$$

$$\Rightarrow \ln\frac{N_0}{2} - \ln N_0 = -\lambda T$$

$$\Rightarrow \ln N_0 - \ln 2 - \ln N_0 = -\lambda T$$

$$\Rightarrow \ln 2 = \lambda T$$

$$\Rightarrow \mathbf{t_{1/2} = T = \frac{\ln 2}{\lambda}} \qquad \textbf{(III.6)}$$

4.3 Activity of a radioactive nucleus

This is a disintegration velocity denoted by A. It represents the number of nuclei of a radioactive element that disintegrate per unit of time. It is also the number of particles or photons emitted per unit of time.

$N=N_0 e^{-\lambda t}$

$A = \lambda N \Rightarrow N = \frac{A}{\lambda}$

$A_0 = \lambda N_0 \Rightarrow N = \frac{A}{\lambda}$

$$\frac{A}{\lambda} = \frac{A_0}{\lambda} e^{-\lambda t}$$

$$\Rightarrow \mathbf{A = A_0 e^{-\lambda t}} \qquad \textbf{(III.7)}$$

- **Unit of activity**

Disintegration per second **dps** or per minute **dpm** or per hour **dph**.

The becquerel Bq: 1 Bq = 1 disintegration.s^{-1} (dps)

The curie Ci: **1 Ci = 3.7 x 10^{10} dps (Bq)**

5. Applications of radioactivity

Energy production: Radioactivity, especially nuclear fission, is widely used for energy production (such as electricity) in nuclear reactor power stations and atomic bombs..

In medicine: It is used in cases of cancer, particularly gynecological, urological, ENT, or cerebral tumors. The tumors are destroyed by ionizing radiation created by the radioactive material used. The radioactive sources used in brachytherapy are: Cesium 137, Iridium 192, Iodine-125. These three elements deliver high doses of radiation. This method allows the tumor to be irradiated while protecting neigh boring organs as much as possible and, in some cases, avoiding surgical treatment. Once treatment is complete, the radioactive sources are removed from the patient. For small tumors, brachytherapy is 80% to 90% effective.

Datation of archaeological objects

The use of radioactive ^{14}C makes it possible to determine the age of archaeological artifacts.

^{14}C is oxidized into CO_2 and then absorbed by plants through photosynthesis. The concentration in living plants is kept constant, but when the plant dies, the concentration of ^{14}C decreases (it diminishes) due to decay. The activity

of ^{14}C is 15.3 decays per minute per gram of C.

The decay period is 5730 years.

6. Dangers of radioactivity

Pathological effects: lesions, cancer and leukemia Genetic effect: gene modification. Similarly, each type of radiation has its own characteristics:

• α radiation: low penetrating power, stopped by the skin, very dangerous if ingested.

• β radiation: higher penetrating power (1 cm into flesh), stopped by interaction with nuclei

• γ radiation: very high penetrating power, passes through the human body

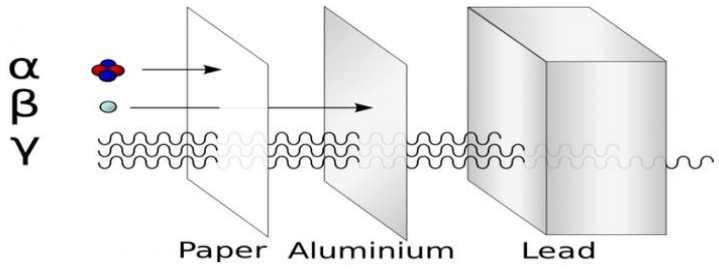


Figure III.3: Protection from radioactive radiation

Conclusion

This chapter has explored the fundamental principles of radioactivity and nuclear reactions. The characteristics of natural and artificial radioactivity, including α, β, and γ emissions, were examined along with nuclear fission, fusion, and transmutation processes. The mathematical description of radioactive decay, half-life, and activity provides important tools for understanding nuclear transformations. Finally, the numerous applications of radioactivity in medicine, energy production, and archaeology demonstrate its scientific and technological significance, while emphasizing the need to consider its potential biological and environmental risks.

Exercices

Exercise 01

Complete the following nuclear reactions:

$^{210}_{84}Po \longrightarrow \cdots + \ ^{206}_{82}Pb$

$^{40}_{21}Si \longrightarrow \ ^{40}_{20}Ca + \cdots$

$^{32}_{15}P \longrightarrow \cdots + \ ^{32}_{16}S$

$\alpha + \ ^{9}_{4}Be \ \longrightarrow \ ^{12}_{6}C + \cdots$

$\ldots\ldots + \ ^{7}_{3}Li \ \longrightarrow 2^{4}_{2}He$

$^{214}_{84}Po^{*} \longrightarrow \ ^{214}_{84}Po + \cdots$

Solution

$^{210}_{84}Po \longrightarrow \ ^{4}_{2}He(\alpha) + \ ^{206}_{82}Pb$

$^{40}_{21}Si \longrightarrow \ ^{40}_{20}Ca + \ ^{0}_{+1}e(\beta^{+})$

$^{32}_{15}P \longrightarrow \ ^{0}_{-1}e(\beta^{-1}) + \ ^{32}_{16}S$

$^{4}_{2}He(\alpha) + \ ^{9}_{4}Be \ \longrightarrow \ ^{12}_{6}C + \ ^{1}_{0}\eta$

$^{1}_{1}H \ + \ ^{7}_{3}Li \ \longrightarrow 2^{4}_{2}He$

$^{214}_{84}Po^{*} \longrightarrow \ ^{214}_{84}Po + \ ^{0}_{0}e(\gamma)$

Exercise 02

Thorium (^{237}Th) is radioactive and emits alpha particles. The radioactive half-life, or half-life T, of thorium is 18 days. At t = 0, we have a radioactive source of thorium with mass m_0 = 1 µg.

Write the equation for its decay, knowing that it produces radium Ra.

Calculate the radioactive decay constant λ of thorium.

Calculate the mass of thorium remaining at the two times t1 = 36 days and t2 = 6 months.

At what time is the mass of thorium remaining 0.0156 µg?

Solution

$^{237}_{90}Th \longrightarrow {}^{235}_{88}Ra + {}^{4}_{2}He(\alpha)$

2) Based on the radioactive decay law $N = N_0 e^{-\lambda t}$, the remaining mass m of thorium at time t is given by the equation: $m = m_0 e^{-\lambda t}$, where m0 is the initial mass at time t = 0 and λ is the radioactive decay constant.

After a time $t_{1/2}$ equal to one half-life has elapsed, half of the initial mass remains

Soit $\frac{m_0}{2} = m_0 e^{-\lambda t} \Rightarrow \frac{1}{2} = e^{-\lambda t_{1/2}} \Longrightarrow \lambda = \frac{ln\,2}{t_{\frac{1}{2}}} = \frac{ln2}{18}$ = **0,0385 j^{-1}**

3) After 36 days, the remaining mass is m = $e^{-36\lambda}$ = **0,25µg.**

After 6 months, or approximately 180 days, the remaining mass is **m = 9.8 × 10^{-4} µg.**

4) We have : m = $m_0\, e^{-\lambda t}$ such that 0,0156 = $e^{-\lambda t} \Rightarrow \ln 0{,}0156 = -\lambda t \Rightarrow \lambda = \frac{-ln0{,}0156}{\lambda}$

T = 108 days.

Exercise 03

The wreck of a small boat was recently discovered off the coast. To estimate the age of the boat, a well-preserved piece of wood was taken from it. Measurement of the number of (^{14}C) decays yielded 1,307 decays per minute. The same measurement performed on a piece of recent wood, of the same type and mass as the one used previously, yields a value of 1,720 decays per minute.

Given: half-life of $_{14}$C: $t_{1/2}$ = 5,500 years

Determine the age of the boat

Solution

A = 1307 dpm ; A_0 = 1720 dpm

$$\lambda = \frac{\ln 2}{t_{1/2}}$$

$$A = A_0 e^{-\lambda t} \Rightarrow \frac{A}{A_0} = e^{-\lambda t} \Rightarrow ln\frac{A}{A_0} = -\lambda t = -\frac{ln2}{T}t$$

$$t = -\frac{T\ ln\frac{A}{A_0}}{ln2} = -\frac{5500\ ln\frac{1307}{1720}}{\ln 2} = 2188{,}75\ ans$$

t = 2188,75 ans

CHAPTER IV

ELECTRONIC STRUCTURE OF THE ATOM

1. Introduction

The electronic structure of the atom is a fundamental concept for understanding the physical and chemical properties of matter. This chapter introduces the wave-particle duality of light and matter, highlighting the interaction between electromagnetic radiation and atoms. It presents the hydrogen atomic spectrum, the Bohr atomic model, and the quantum mechanical description of the hydrogen atom. The chapter also examines polyelectronic atoms, quantum numbers, atomic orbitals, and the principles governing electronic configurations. These concepts provide the theoretical basis for understanding chemical bonding, periodic properties, and atomic behavior.

2. Wave-particle duality

Just as particles, light possesses a corpuscular nature (photon, electron, etc.) and a wave nature (λ, ν).Light (photon) is electromagnetic radiation that has both of these properties.

2.1. Wave aspect of light

Light is a combination of electric and magnetic fields that propagate through space in a wave-form movement. These electromagnetic or light waves propagate through space at a constant velocity c (velocity of light).

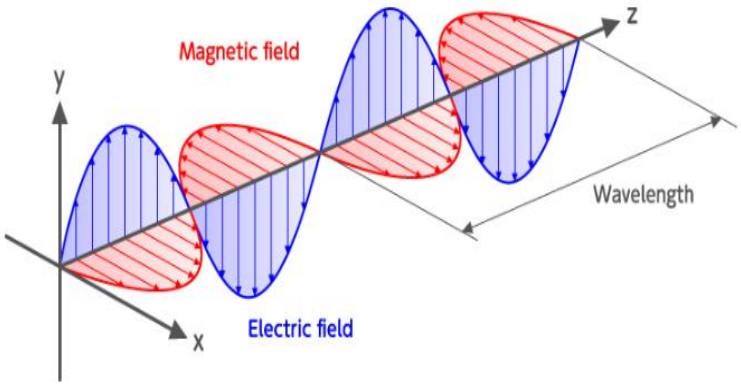


Figure IV.1: The wave nature of light

- ✓ This wave is characterized by its wavelength λ or by its wave number $\bar{\upsilon}$:

$$\lambda = 1/\bar{\upsilon} = c/\nu = c\,.T \qquad \textbf{(IV.1)}$$

ν: frequency;

c: celerity or velocity of light

($C = 3.10^8$ m/s).

- ✓ The period T is the time after which the vibrating vector

($\vec{E}$ and $\vec{B}$) returns to the same amplitude and in the same direction.

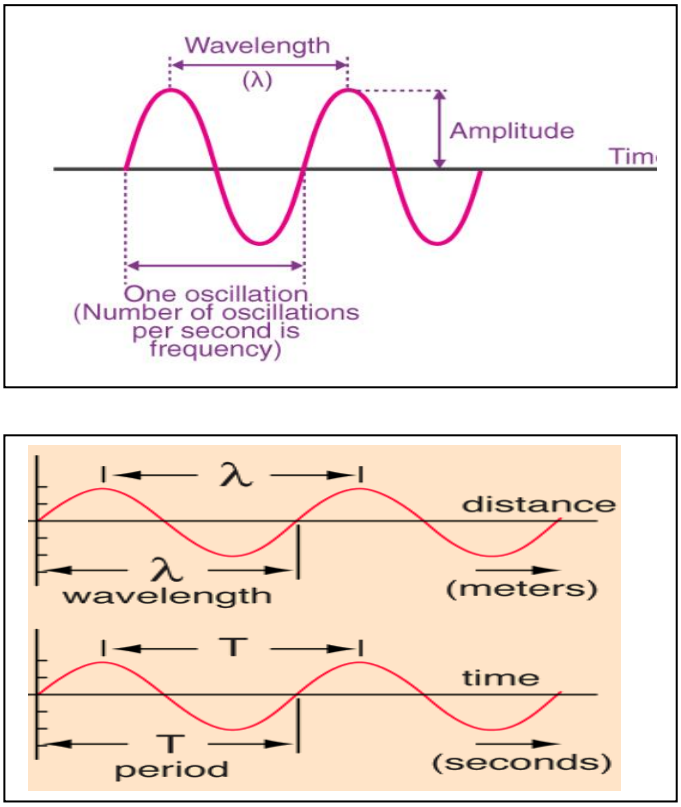


Figure IV.2 : The Characteristics of a Wave

The electromagnetic spectrum is composed of all electromagnetic waves.

Depending on their wavelength, electromagnetic waves are classified into various categories, grouped together on the electromagnetic spectrum. Light, visible to the human eye, occupies a portion of the electromagnetic waves with wavelengths between 400 nm (violet) and 700 nm (red).

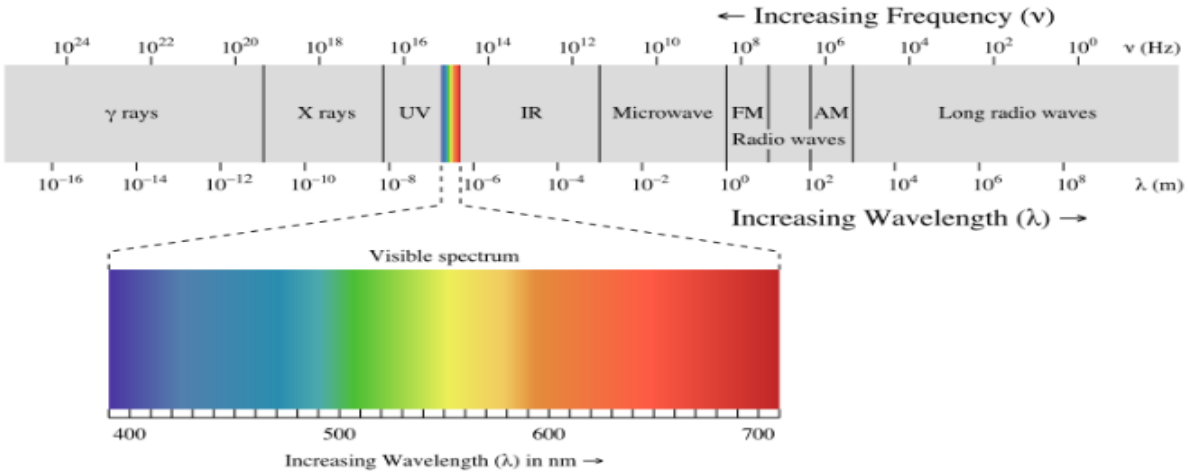


Figure IV.3: Illustration of colors on the electromagnetic spectrum

2.2. Corpuscular aspect of light

Photons of mass equal to zero and travel at the speed of light in a vacuum.

Each photon contains an amount of energy E proportional to the frequency of the wave

$$\mathbf{E = h \nu = h c / \lambda} \qquad \mathbf{(IV.2)}$$

Where

h is Planck's constant ($h = 6.62 \times 10^{-34}$ J·s).

$1eV = 1{,}6.10^{-19}J$

$1m = 10^{-9}$ nm

- **Photoelectric effect**

If a metal plate is illuminated with monochromatic light of frequency υ greater than the threshold frequency ν0, electrons are emitted from this surface. This phenomenon is called the photoelectric effect. The excess energy relative to the characteristic energy of the metal E0 = hν0 is dissipated in the form of kinetic energy taken by the electrons.

$E_{ph} = E_0 + E_C$

If: $E_{ph} \geq E_0$

There is a photoelectric effect.

If: $E_{ph} < E_0$

There is no photoelectric effect.

$E_C = E - E_0 = \frac{1}{2} m_e v^2$

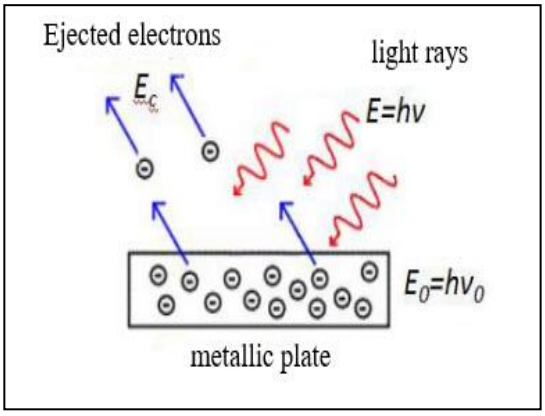


Figure IV.4: Photoelectric effect

Where

m_e is the mass of the ejected electron ,

v is the velocity of the ejected electron .

3. Interaction between light and matter

3.1 Spectrum of the hydrogen atom

A. Continuous spectrum: This is produced when white light passes through a prism.This spectrum is formed from all wavelengths of visible light (example.rainbow).

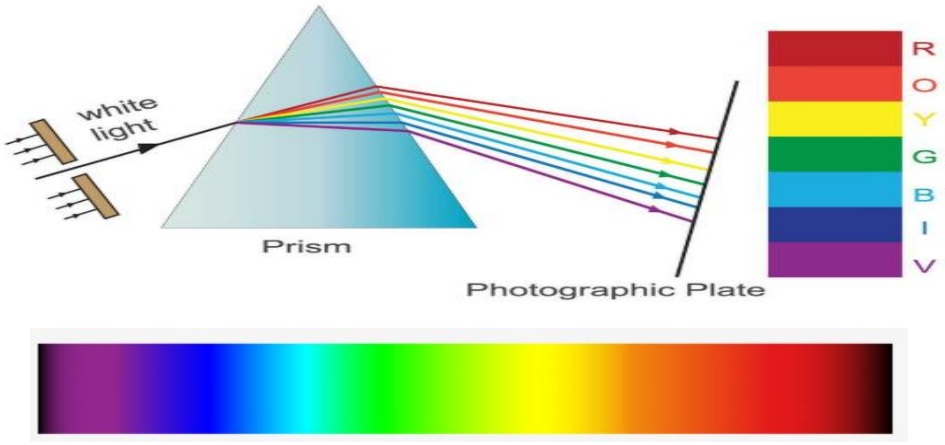


Figure IV.5: Continuous spectrum

B. Discontinuous spectrum or line spectrum

When hydrogen gas is subjected to a high-intensity electrical discharge, it emits several lines through a prism that selects monochromatic radiation (of the same frequency and wavelength), each of these lines corresponding to a specific wavelength. The spectrum obtained on the photographic plate is a spectrum consisting of very fine lines of various colors separated by wide dark spaces.

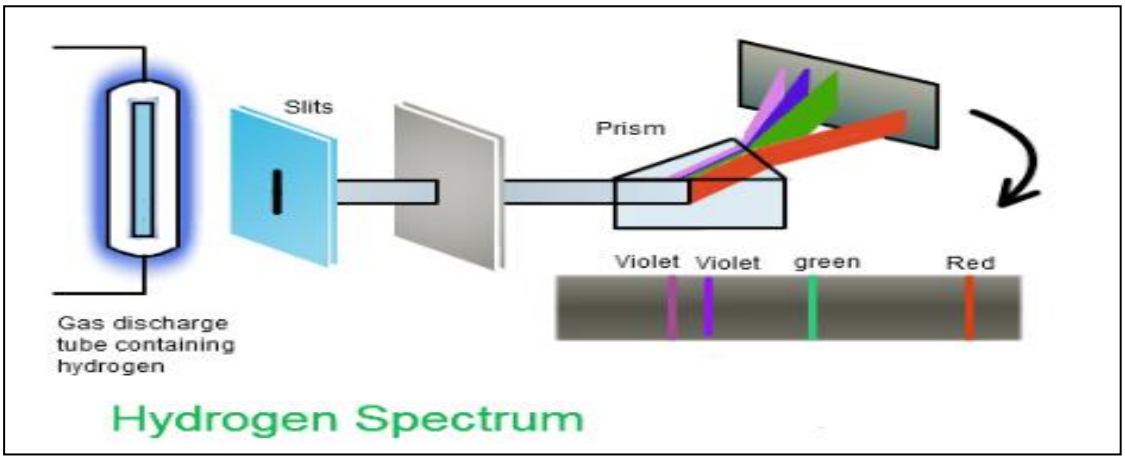


Figure IV.6: Emission spectrum of hydrogen

- The electron of the hydrogen atom can only occupy certain energy levels, i.e., the energy of the hydrogen atom is quantified.
- For a hydrogen atom, when an electron moves from a higher energy level to a lower one, it emits light of a specific wavelength, which can be calculated using Planck's equation: $\Delta E = h\upsilon = hc/\lambda$
- ΔE: energy change.
- υ: frequency of the emitted light.
- λ: wavelength of the emitted light.

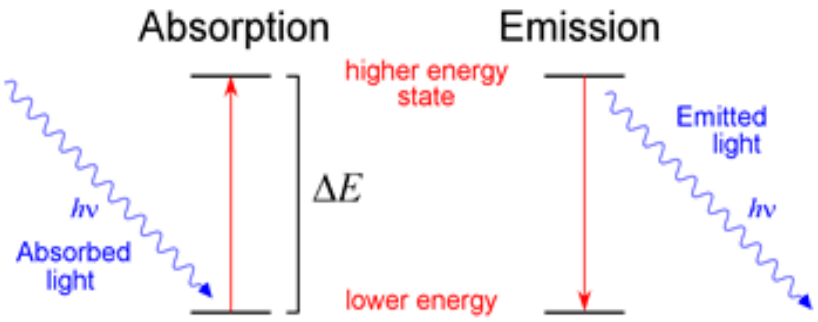


Figure IV.7: Absorption and Emission

Experience has shown that the emission spectrum of the hydrogen atom has a large number of lines in the ultraviolet, visible, and infrared ranges. The first lines studied are in the visible range. They are known as the "Balmer series."

- The lines are classified into series in various wavelength ranges.These spectra were discovered by Lyman (UV), Balmer (Visible), Pascen, Brackett, and Pfund (IR).

The RITZ-RYDBERG formula

The Balmer-Rydberg empirical relationship is a formula that defines the wavelengths of spectral lines of the hydrogen atom based on two integers, n_1 and n_2. Empirically determined by Balmer in 1885 for the visible series of hydrogen, it was generalized by Rydberg in 1888. The formula is as follows:

$$\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{C} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \textbf{(IV.3)}$$

Where:

n_1 and n_2 are positive integers ($n_1 > 0$ and $n_2 > n_1$).

λ: corresponding wavelength

$\bar{\nu}$: Nombre d'onde (m^{-1}).

R_H: Rydberg constant for hydrogen, found experimentally:

$R_H = 109677.6\ cm^{-1}$

Note: Relationship between wavelength ($\boldsymbol{\lambda}$), frequency ($\boldsymbol{\nu}$), and wave number $\boldsymbol{\bar{\nu}}$

$$\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{c}\ (\mathbf{m^{-1}}) \qquad \textbf{(IV.4)}$$

$$\boldsymbol{\nu}(\mathbf{s^{-1}}, \mathbf{Hz}) = \frac{c}{\lambda} \qquad \textbf{(IV.5)}$$

- **Notion of a series of lines**

The Spectral Lines for Atomic Hydrogen

Table IV.1: Various series of emission lines from the hydrogen atom.

Series	n_1	n_2	Spectral Region
Lyman	1	2, 3, 4….	Ultraviolet
Balmer	2	3, 4, 5….	Visible
Paschen	3	4, 5, 6….	Infrared
Brackett	4	5, 6, 7….	Infrared
Pfund	5	6, 7, 8….	Infrared

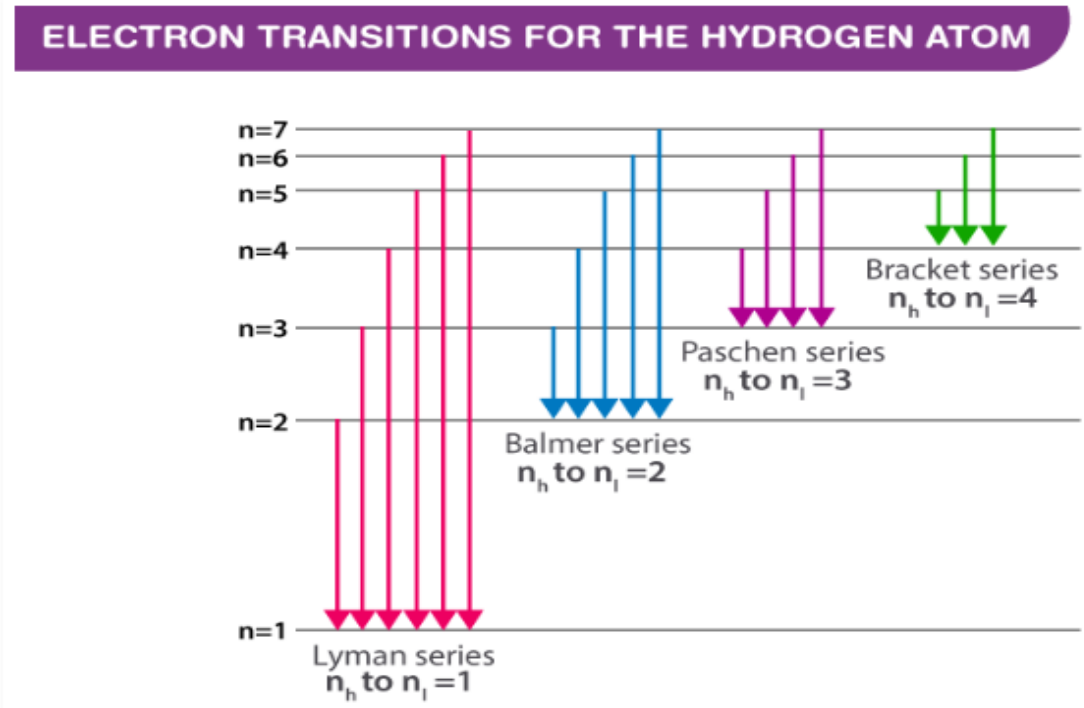


Figure IV 8 : Spectral lines of the hydrogen atom.

- **Differents shells (K, L, M, N,O …) of the hydrogen atom and their associated transitions.**

The first line (α) : $n_i \rightarrow n_i + 1$

The second line (β) : $n_i \rightarrow n_i + 2$

The third line (γ): $n_i \rightarrow n_i + 3$

The limited line: $n_i \rightarrow n_i + \infty$

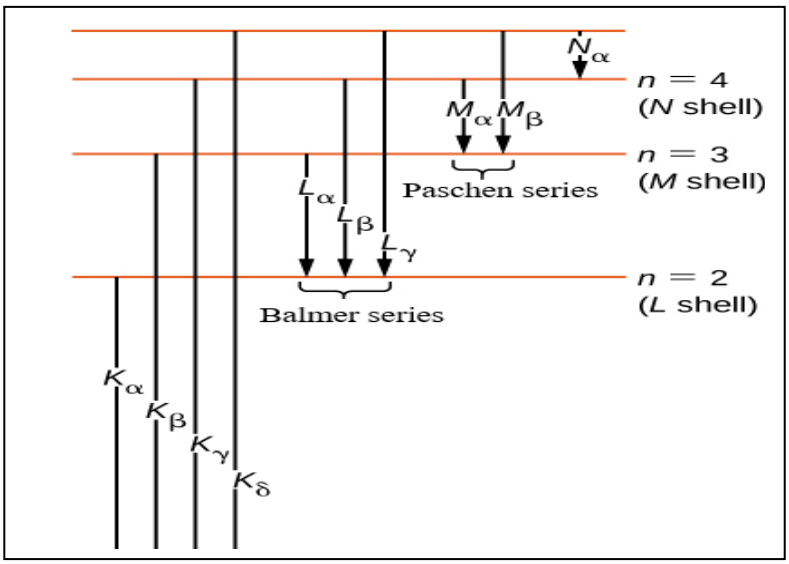


Figure IV.9: Transitions of different shells (K, L, M, N, O …) of the hydrogen atom

- **Excitation and ionisation state**

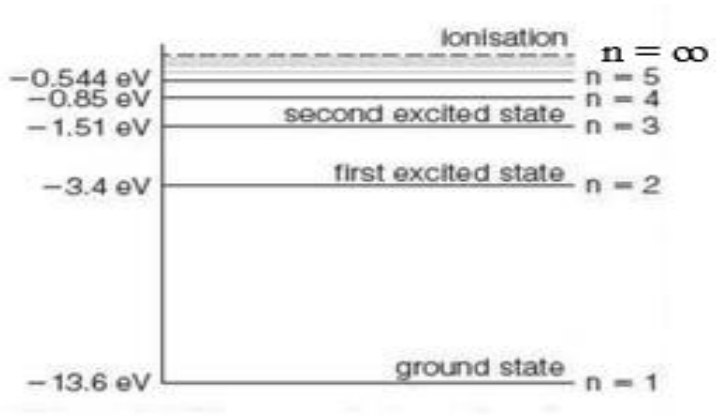


Figure IV.10: Excitation and ionisation state

First excited state: $n_i \rightarrow n_i + 1$

Second excited state: $n_i \rightarrow n_i + 2$

Ionisation state: $n_i \rightarrow n_i + \infty$

This phenomenon corresponds to the extraction of the electron from the atom:

$$\mathbf{H \rightarrow H^+ + e^-}$$

4. Bohr atomic model (1913)

- In an atom, the nucleus is stationary while the electron of mass m moves around the nucleus in a circular orbit of radius r;
- The electron can only be found in specific orbits that do not emit energy; these are called “stationary orbits”;
- When an electron moves from one level to another, it emits or absorbs energy:When an electron moves from one level to another, it emits or absorbs energy: $\mathbf{\Delta}E = h.\boldsymbol{\nu}$
- The electron's angular momentum can only take integer values (quantization of angular momentum):

$$\mathbf{mvr} = \frac{\mathbf{nh}}{\mathbf{2\pi}} \qquad \textbf{(IV.6)}$$

h: Planck's constant ($6.62.10^{-34}$ J.s.

n: natural number

$$F_a = -Z.K.\frac{e^2}{r^2}$$

$$K = \frac{1}{4\pi\varepsilon_0}$$

$$Z = 1;\ F_a = -K.\frac{e^2}{r^2}$$

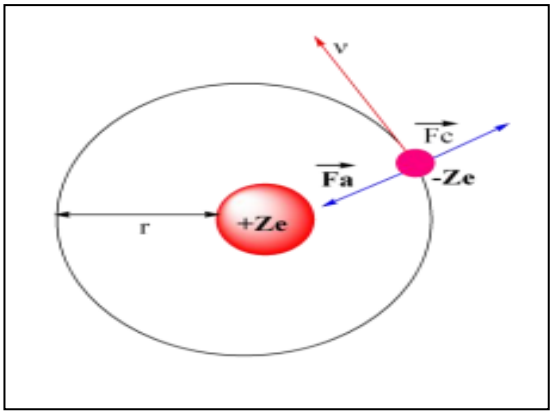


Figure IV.11: Various forces acting on an atom's electron

$$F_c = m.\frac{V^2}{r}$$

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

$$\overrightarrow{|F_c|} = |\overrightarrow{F_a}| \Rightarrow \frac{mv^2}{r} = K\frac{e^2}{r^2} \Rightarrow mv^2 = K\frac{e^2}{r} \quad (1)$$

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

$$mvr = \frac{nh}{2\pi}$$

$$m^2v^2r^2 = \left(\frac{nh}{2\pi}\right)^2 \Rightarrow mv^2 = \frac{n^2h^2}{4\pi^2r^2m} \quad (2)$$

$$k\frac{e^2}{r} = \frac{n^2h^2}{4mr^2\pi^2} \Rightarrow r_n = \frac{h^2}{4K\pi^2\, me^2}n^2$$

h, k, m, π, and e are constants, so r depends only on the value of the positive number(n) called the principal quantum number.

$$\mathbf{r_n = \frac{h^2}{4K\pi^2\, me^2}n^2} \qquad \textbf{(IV.7)}$$

For **n = 1,** $\mathbf{r_n = r_1 = 0.5290\ Å}$

$\mathbf{r_n = r_1 = 0.5290\ Å}$: First Bohr radius for the hydrogen atom, noted as $\mathbf{a_0}$.

With 1 Å (Angström) = 10^{-10} m

$r_n = n^2 a_0$

$$\mathbf{r_n = 0.529.n^2} \qquad \textbf{(IV.8)}$$

$K = \frac{1}{4\pi\varepsilon_0} = 9.10^9 \left(\frac{Nm^2}{C^2}\right)$; m= 9.110 .10^{-31} Kg ; e = 1.602.10^{-19} C

- For n = 2, second Bohr orbit $\mathbf{r_2 = 4 \times a_0}$;
- For n = 3, 3rd Bohr orbit $\mathbf{r_3 = 9 \times a_0}$;
- For n = 4, 4th Bohr orbit $\mathbf{r_4 = 16 \times a_0}$ .. etc…

➢ **Velocity of the hydrogen atom**

$$V = n\frac{h}{2\pi mr} = \frac{2\pi ke^2}{h}.\frac{1}{n} = 2.18.10^6.\frac{1}{n}$$

$$mVr = n\frac{h}{2\pi} \Rightarrow \mathbf{V_n = 2.18.10^6.\frac{1}{n}(m.s^{-1})} \qquad \textbf{(IV.9)}$$

➢ **Energy of the hydrogen atom**

The total energy E_t of the system is the sum of the potential energy E_p and the kinetic energy E_c:

$$E_c = \frac{1}{2}mv^2$$

$$E_p = \int_{\infty}^{r} \overrightarrow{|F_a|}.dr = \frac{-ke^2}{r}$$

$$mv^2 = \frac{ke^2}{r}$$

According to equation (1) $E_c = \frac{1}{2}.\frac{ke^2}{r}$

$$E_T = E_C + E_P = \frac{1}{2}.\frac{ke^2}{r} - \frac{ke^2}{r} = -\frac{1}{2}.\frac{ke^2}{r}$$

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

$$E_t = \frac{-ke^2}{2r} = \frac{-ke^2 4\pi^2 kme^4}{2h^2}.\frac{1}{n^2}$$

$$E_t = \frac{-2\pi^2 k^2 m e^4}{h^2} \cdot \frac{1}{n^2}$$

$$\mathbf{E_n = \frac{-2\pi^2 k^2 m e^4}{h^2} \cdot \frac{1}{n^2}} \qquad \textbf{(IV.10)}$$

$$n = 1, E_{n=1} = E_1 = \frac{-2\pi^2 k^2 m e^4}{h^2} \cdot \frac{1}{1^2} = -21.76.10^{-19}\ J = -13.6\ ev$$

$$E_n = E_1 \cdot \frac{1}{n^2} = \frac{-13.6}{n^2}\ (ev)$$

$$\mathbf{E_n = \frac{-13.6}{n^2}\ (ev)} \qquad \textbf{(IV.11)}$$

- The excitation energy of the hydrogen atom is the energy required to move the electron from orbit n_1 to orbit n_2 ($n_1 < n_2$).
- The ionization energy of the hydrogen atom is the energy required to move the electron from level n to a level n that tends towards ∞.

➢ **Transition between electronic levels**

According to Bohr's third postulate, when the electron in hydrogen transitions from an energy level $\boldsymbol{E_{ni}}$ to an energy level $\boldsymbol{E_{nf}}$,

The energy required is given by:

$$|\Delta E| = |E_{nf} - E_{ni}| = h\nu = \frac{hC}{\lambda} = \left|\frac{2\pi^2 k^2 m e^4}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\right|$$

$$\nu = \frac{|E_{nf} - E_{ni}|}{h}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{|E_{nf} - E_{ni}|}{hC} = \frac{1}{hC} \cdot \frac{2\pi^2 k^2 m e^4}{h^2} \cdot \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\mathbf{\bar{\nu} = \frac{1}{\lambda} = \frac{2\pi^2 k^2 m e^4}{C\,.h^3} \cdot \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)} \qquad \textbf{(IV.12)}$$

$$R_H = \frac{2\pi^2 k^2 m e^4}{C\,.h^3}$$

$$\bar{\nu} = \frac{1}{\lambda} = R_H.\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad n_f > n_i \qquad \textbf{Ritz's Empirical Formula} \quad \textbf{(IV.13)}$$

$R_H = 1.097373.10^7\ m^{-1}$ **(RYDBERG constant)**

- **Applications to hydrogenoids**

A hydrogenoid ion is a polyelectronic atom from which electrons have been removed, leaving only one in the outer shell. Its nucleus still has Z protons.

$_2He^+$; $_3Li^{2+}$; $_4Be^{3+}$

Example:

$$F_a = -Z.K.\frac{e^2}{r^2}$$

$$r_n = \frac{h^2}{4K\pi^2\, mze^2} n^2 = a_0 \frac{n^2}{z} = 0.529.\frac{n^2}{z}(A^0)$$

$$V = \frac{2\pi kze^2}{h}.\frac{1}{n} = v_0.\frac{z}{n} \Rightarrow \mathbf{V = 2.18.10^6.\frac{z}{n}\ (\frac{m}{s})} \qquad \textbf{(IV.14)}$$

$$\mathbf{r = \frac{0.53n^2}{z}\ \dot{A}} \quad \textbf{(IV.15)}$$

$$E_n = \frac{-2\pi^2k^2me^4}{h^2}.\frac{1}{n^2} = E_1.\frac{z^2}{n^2} = -13.6.\frac{z^2}{n^2}$$

$$\mathbf{E_n = -13.6.\frac{z^2}{n^2}\ \ ev} \qquad \textbf{(IV.16)}$$

$$\mathbf{\bar{\nu} = \frac{1}{\lambda} = R_H.Z^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)\ and\ n_f > n_i} \qquad \textbf{(IV.17)}$$

- **Poly-electronic atoms**

These are atoms that have more than one electron. In fact, in a polyelectronic atom with atomic number (Z), an electron ei is subject to:

- an attractive force from the nucleus with a charge of +Ze- a repulsive force from the other electrons.

For a given electron, there are electrons that act as a screen between the electron in question ei and the nucleus.

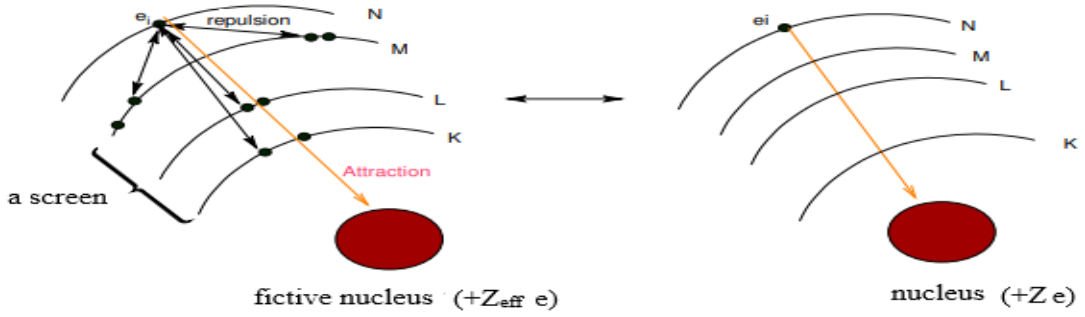


Figure IV.12: The representation of the attraction between the nucleus and the electrons

It is as if each electron sees a fictitious nucleus with a weaker (real) charge (+ Z_{eff} e < +Ze)

We therefore substitute the charge Z with the effective charge Z_{eff} in the term representing the nucleus-electron attraction. The effective nuclear charge Z_{eff} received by electron i is defined by:

$$\mathbf{Z_{eff} = Z - \sigma_i} \qquad \textbf{(IV.18)}$$

$\boldsymbol{\sigma_i}$: represents the screen constant.

Replacing Z with Z_{eff}, we obtain:

$$\mathbf{r_n = \frac{0.53 n^2}{Z_{eff}}\ \dot{A}} \qquad \textbf{(IV.19)}$$

$$\mathbf{E_n = -13.6.\frac{Z_{eff}^2}{n^2}} \qquad \textbf{(IV.20)}$$

$$\mathbf{\bar{\nu} = \frac{1}{\lambda} = R_H.Z_{eff}^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \text{ and } n_f > n_i} \qquad \textbf{(IV.21)}$$

5. The limitations of Bohr's model

The model:

- ✓ cannot explain the doubling of certain lines under the influence of a magnetic field.
- ✓ is only valid for hydrogen-like atoms, not for polyelectronic atoms, because it does not take into account the influence of a given electron on its neighbors.
- These limitations led to the development of a more "advanced" model: **the quantum model of the atom.**

6. Hydrogen atom in wave mechanics (or quantum mechanics)

6.1 Concepts of quantum wave mechanics

- **Wave-particle duality: De Broglie's postulate**

Every particle (corpuscle) with mass m and velocity v is associated with a wave of wavelength λ. We thus apply to matter (an electron) the combined nature of wave and particle. De Broglie's relation is written as:

$$\lambda = h / mv$$

λ : wavelength;

h: Planck's constant;

mv: quantity of movement

- **Heisenberg's uncertainty principle**

It is impossible to precisely define both the position and velocity of a particle. This is expressed by the relationship:

$\Delta x. \Delta px \geq h/2\pi$

Δx: uncertainty in position

Δpx = mΔv: uncertainty in quantity of movement.

According to this principle, it is therefore impossible to know precisely the trajectory of the electron around the nucleus. Consequently, we cannot assume that the electron describes a defined orbit as in Bohr's model.

6.2 Quantum number and atomic orbital

6.2.1 Principal quantum number

***n*:** This is a positive integer:

n ϵ N^* ***n = 1, 2, 3, …∞*** It defines the electron shell. The shells are designated by a symbol.

Table IV.1: Values of n and corresponding shell.

n	*1*	*2*	*3*	*4*	*5*
Shell/orbit	*K*	*L*	*M*	*N*	*O*

6.2.2 Secondary quantum number (azimuthal) l:

This number characterizes the sublayer (or sublevel) occupied by the electron.

l is an integer $0 \leq l \leq n-1$.

Table IV.2: The values of l and the corresponding sublayers

l	*0*	*1*	*2*	*3*	*4*
Subshell/orbital	*s*	*p*	*d*	*f*	*g*

6.2.3 Magnetic quantum number m:

This characterizes the quantum case occupied by the electron. $-l \leq m \leq +l$

m takes (2l+1) values

Table IV.3: Values of *l* and corresponding quantum cases

m	*0*	*-1, 0, 1*	*-2, -1, 0, 1, 2*	*-3, -2, -1, 0, 1, 2, 3*
Presentation of the boxes	□	□□□	□□□□□	□□□□□□□

6.2.4 The quantum number of spin (s):

The electron is always rotating around itself; this movement is called spin, and this rotation can occur in two opposite directions. These two rotations are associated with the two values s = +1/2 and s = -1/2.

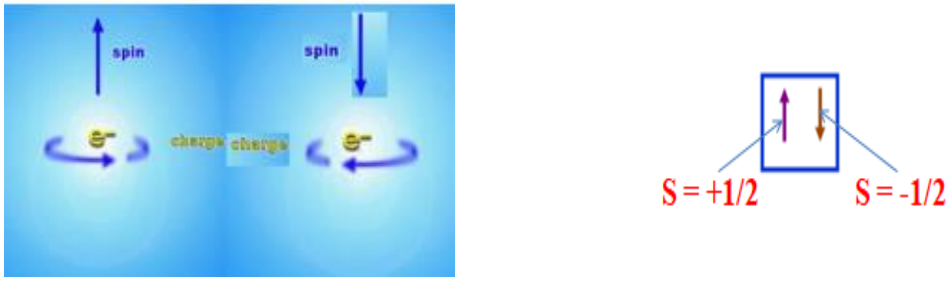


Figure IV.13: Quantum number of spin (s)

A level n can contain a maximum of $2n^2$ electrons:

For level n=1, the maximum number of electrons is 2.

For level n=2, the maximum number of electrons is 8.

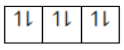
For level n=3, the maximum number of electrons is 18.

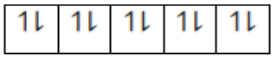
For level n=4, the maximum number of electrons is 32.

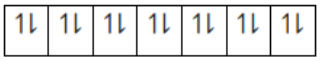
6.3 Quantum boxes

The orbitals (s, p, d, f) are represented by the following quantum boxes:

S orbitals: l = 0, m = 0 

p orbitals: l = 1, m = –1, 0, 

d orbitals: l = 2, m = –2, –1, 0, 

f Orbitales : l = 3, m = –3,–2,–1, 0, 1, 2, 

Each box can contain a maximum of two electrons with opposite spins.

6.4 Representation of atomic orbitals

6.4.1 S orbital

Orbitals (S) are characterized by l=0, m=0.

All orbitals (S) or (nS) have spherical symmetry.

6.4.2 P orbital

For l=1, we have m=-1, 0,+1, three P orbitals referred to as Px, Py, Pz orbitals, which have the same shape but each is elongated along one of the three perpendicular axes.

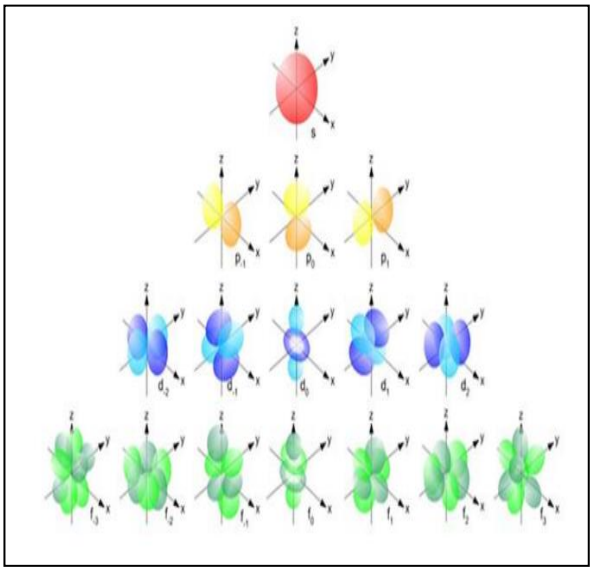


Figure IV.14: Representation of atomic orbitals

6.4.3 d orbital

If l=2, m=-2,-1,0,+1,+2:

so we have five d orbitals:

6.4.4 f orbital

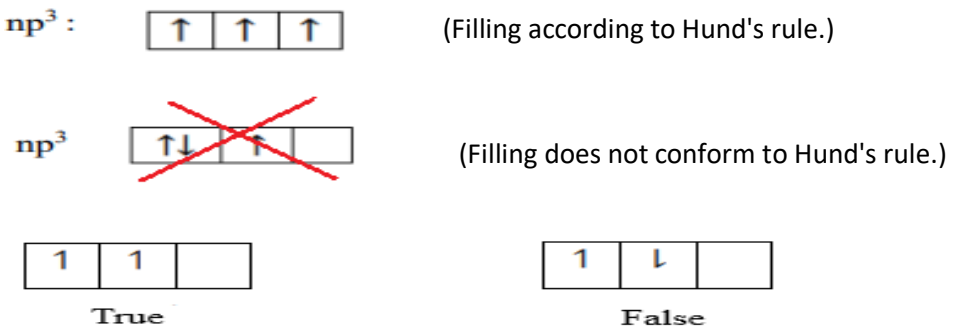
If l=3, m=-3,-2,-1,0,+1,+2,+3,

Therefore seven f orbitals

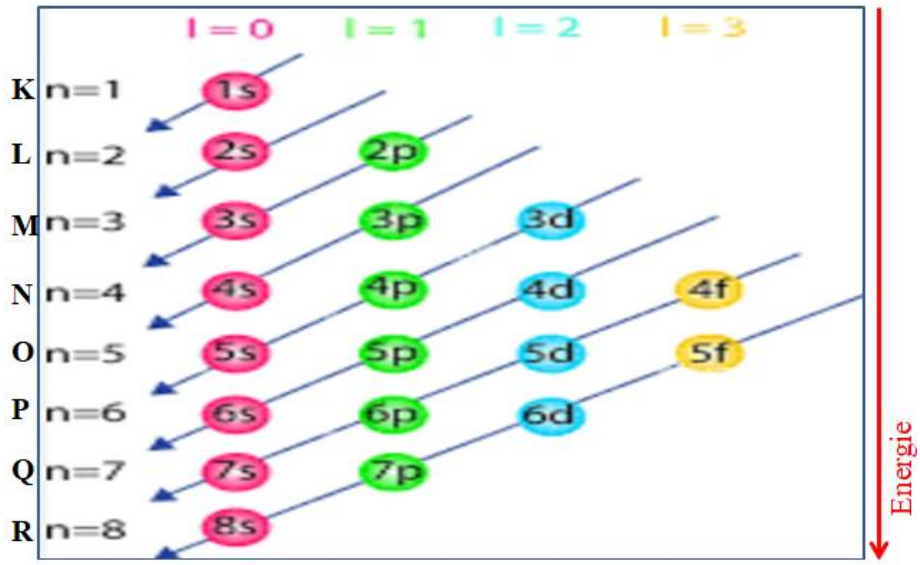
7. Electronic structure of polyatomic atoms (electronic configuration)

The electronic configuration of an atom is the distribution of Z electrons in the atom in a ground state across atomic orbitals.This filling of atomic orbitals is carried out using four general rules.

- ✓ **Pauli exclusion principle:** In an atom, two electrons cannot have identical quantum numbers: If two electrons in an atom occupy the same orbital (same values of n, ℓ, m), they must differ in their spin quantum number (one with spin +1/2 and the other with spin -1/2).
- ✓ **Hund's rule:** In the ground state, when electrons are placed in a multiple sublayer (p,d, f), they occupy the maximum number of orbitals with the same energy with single electrons that have parallel spins (same value of s).



- ✓ **KLECHKOWSKI'S RULE:** The subshells are filled in increasing order of the values of $n+l$. For two equal values, the subshell with the smallest n is filled first. For example, for 2p and 3s, we have $n+l$ = 2+1 and $n+l$ = 3+0, respectively; therefore, we fill 2p first (the smaller n), and only then do we fill 3s. 2p is filled first (smaller n), and only then is 3s filled.



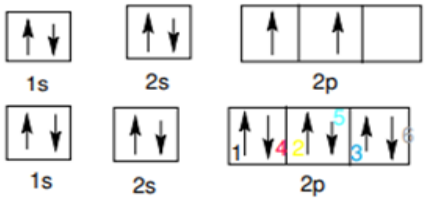
1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p…..

Figure IV.15: Order of Filling of Atomic Orbitals (Klechkowski's Rule)

Example

$_6C$: $1s^2\ 2s^2 2p^2$

$_{10}Ne$: $1s^2\ 2s^2 2p^6$



- **Core electrons**

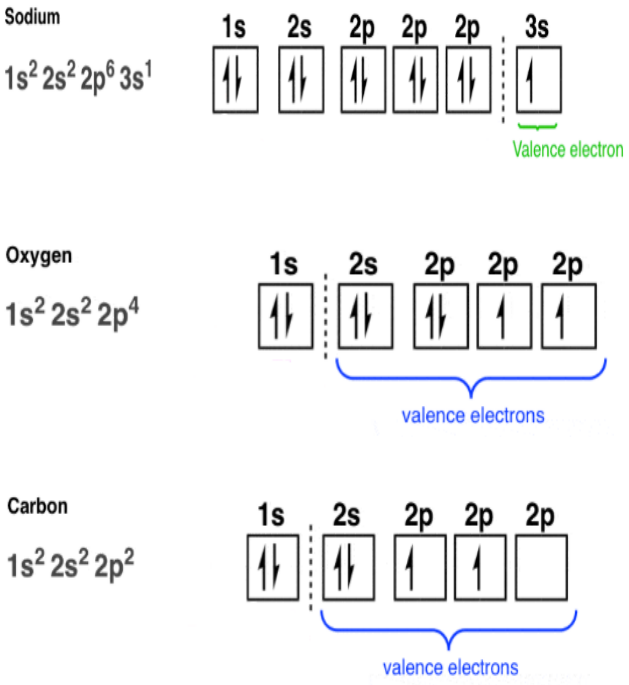
Core electrons are those that occupy the interior orbitals.

$_{16}S$: $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^4$

$_{18}Ar$: $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6$

- **Valence (or outer) shell of an atom**

The electrons in the outermost shell (the highest value of n) are called valence electrons (or peripheral electrons). In general, only valence electrons can be gained or lost during chemical reactions.



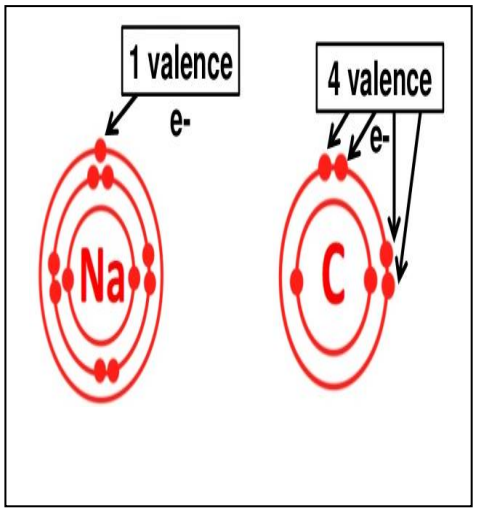


Figure IV.16: Valence shell of an atom

✓ **Aufbau Principle**

For a given element, they correspond to the configuration of the noble gas that precedes that element in the classification. The configuration of core electrons is symbolized by the symbol of the noble gas in parentheses.

Table IV.4: Aufbau principle

Noble gas	Symbol	number of electrons	
Helium	He	2	$2 < Z < 10$
Néon	Ne	10	$10 < Z < 18$
Argon	Ar	18	$18 < Z < 36$
Krypton	Kr	36	$36 < Z < 54$
Xénon	Xe	54	$54 < Z < 86$
Radon	Rn	86	$Z > 86$

Example

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

Aluminum $1s^2 2s^2 2p^6 3s^2 3p^1$ Becomes $[Ne]\ 3s^2 3p^1$

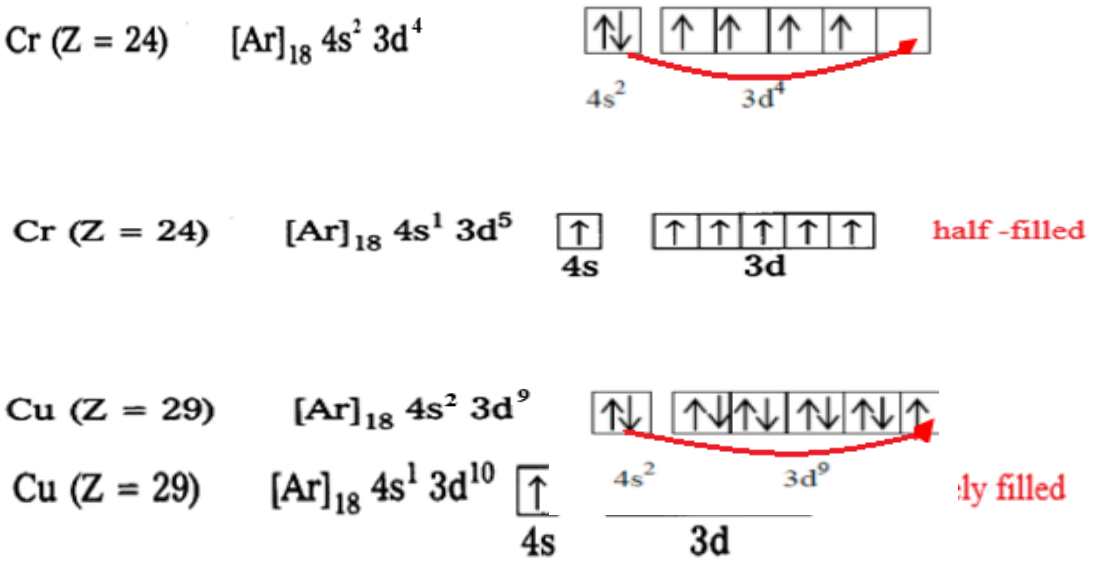
Argon $1s^2 2s^2 2p^6 3s^2 3p^6$

Calcium $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ Becomes $[Ar]\ 4s^2$

Note



- ✓ **Exceptions to Klochkowski's rule:** From level n=4 the filling of the OA does not strictly follow Klochkowski's rule.



Conclusion

This chapter has explored the evolution of atomic models from the classical Bohr model to the modern quantum mechanical description of the atom. The wave-particle duality of matter and light, together with the concepts of quantum numbers and atomic orbitals, has provided a deeper understanding of electron behavior within atoms. The electronic structure of hydrogen and polyelectronic atoms was analyzed through the principles of quantum mechanics and electron configuration rules. These concepts are essential for explaining the organization of the periodic table, chemical reactivity, and the formation of chemical bonds.

Exercises

Exercise 01

When light with a wavelength of 300 nm strikes a metal surface, electrons are emitted. The kinetic energy of these electrons is 0.74 eV. Calculate:

1- The maximum velocity of the emitted electrons

2- The extraction energy (in joules and eV)

3- The threshold wavelength λ_0.

Given: h = 6.62 × 10^{-34} Js; c = 3 × 10^{8} m/s; m_e = 9.1 × 10^{-31} kg

1) Maximum speed:

$E = E_0 + E_c$ avec $E_c = ½ m v^2$

$E_c = ½ m v^2 \Rightarrow v = \sqrt{\frac{2E_c}{m}}$

$$v = \sqrt{\frac{2.0{,}74.\ 1{,}6.10^{-19}}{9{,}1.\ 10^{-31}}} = 0{,}51.10^{6}\ m/s$$

2) Extraction energy E_0

$E_0 = E - E_c$

$$E = h\nu = \frac{hc}{\lambda} = \frac{6{,}62.10^{-34}.3.10^{8}}{300.\ 10^{-9}} = 6{,}62.10^{-19} joule = 4{,}13\ ev$$

$$E_c = 1{,}18\ .10^{-19}\ joule = 0{,}74\ ev$$

$$E_0 = E - E_c = 5{,}44.10^{-19}\ joule = 3{,}4\ ev$$

The wavelength λ_0:

$$E_0 = h\nu_0 = \frac{hc}{\lambda_0} \Rightarrow \lambda_0 = \frac{hc}{E_0}$$

$$\lambda_0 = \frac{6{,}62.\ 10^{-34}.3.10^{8}}{5{,}44.10^{-19}} = 3{,}65.10^{-7} m$$

$$\lambda_0 = 365\ nm$$

Exercise 02:

Apply Bohr's theory to the circular orbit described by the electron around the nucleus of a hydrogen atom, which is characterized by the value n = 3.

Determine

1. the radius of this orbit in (Å).

2. the energy of the electron in eV

3. the wavelength that causes the ionization of this atom, and deduce its corresponding energy in eV and joules.

Given: h = 6.62 × 10^{-34} Js; R_H = 1.1 × 10^7 m^{-1}; c = 3 × 10^8 m/s.

1) $r_n = 0{,}53.\ n^2$

$r_3 = 0{,}53.\ (3)^2 = 4{,}77$ Å

2) $E_n = \frac{-13{,}6}{n^2}$

$$E_3 = \frac{-13{,}6}{3^2} = 1{,}51ev$$

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

With $n_1 = 3$ et $n_2 = \infty$

$$\lambda = \frac{n_1^2}{R_H} = 8181.10^{-10}\ m = 818{,}1\ nm$$

$$\Delta E = \frac{hc}{\lambda} = \frac{6{,}62.10^{-34}\ .\ 3.\ 10^8}{8181.\ 10^{-10}} = 2{,}4.10^{-19}\ joule$$

Exercise 3: Hydrogen-like Atom

Consider the Li^{2+} ion

1- Calculate the radius of the n = 1 orbit
2- Calculate, in eV, the energy of the third ionization of the lithium atom.
3- Calculate the wavelength and frequency of the corresponding line between energy levels n = 4 and n = 1.
4- What is the smallest amount of energy that the B^{4+} ion must absorb to transition from the ground state to the excited state? If this energy were emitted by a photon, what would be the corresponding wavelength?
5- What are the frequencies of the following lines for the B^{4+} ion:

6- The limit line of the Lyman series and the second line of the Balmer series.

Given: R_H = 1.1 × 10^7 m^{-1}, c = 3.108 m/s, h = 6.62 × 10^{-34} J·s, EI = 13.6 eV (ionization energy of the hydrogen atom)

Solution

1) $r_n = 0{,}53\,.\ \frac{n^2}{Z}$

$r_1 = \frac{0{,}53.\ 1^2}{3} = \mathbf{0,17}$ Å

2) The third ionization of Li

$Li^{2+} \longrightarrow Li^{3+} + 1e^-$

$E_i = E_\infty - E_1 = 0 - E_1 = -\frac{Z^2.E_H}{n^2}$

$E_i = \frac{3^2.\ 13{,}6}{1^2} = \mathbf{122,4\ ev}$

3) Calculation of λ and υ :

$\frac{1}{\lambda} = Z^2.R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 3^2.R_H\left(\frac{1}{1} - \frac{1}{16}\right) = 9{,}3.10^7 m$

$\lambda = 0{,}1075.10^{-7}\ m = \mathbf{107,5}$ Å

Frequency υ

$\nu = \frac{c}{\lambda} = \frac{3.\ 10^8}{107{,}5\,.10^{-10}} = \mathbf{2,8\,.10^{16}s^{-1}\ Or\ Hz}$

The minimum energy required to transition from the ground state to the excited state:

The ion B^{4+} ; $Z = 5$

$\Delta E = E_2 - E_1 = Z^2E_H(\frac{1}{n_2^2} - \frac{1}{n_1^2})$

$\Delta E = 5^2.13{,}6.\left(\frac{1}{4} - 1\right) = \mathbf{-225\ ev}$

$|\Delta E| = 225\ ev$

Wavelength :

$\Delta E = h\nu = \frac{hc}{\nu}$

$\lambda = \frac{hc}{\Delta E} = \frac{6{,}62\,.10^{-34}.3.10^8}{225.\ 1{,}6.\ 10^{-19}} = 0{,}05516.10^{-7}m = \mathbf{55,16}$ Å

4) Frequency of the lines for the ion B^{4+}:

Lyman series: limit line: $n_1 = 1 \longrightarrow n_2 = \infty$

$$\frac{1}{\lambda} = Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{\nu}{c} \Rightarrow \frac{1}{\lambda} = Z^2 . R_H = \frac{\nu}{c}$$

$$\nu = Z^2 . R_H . c = 5^2 . 1{,}1 . 10^7 . 3 . 10^8 = \mathbf{82,5 . 10^{15} s^{-1}}$$

Balmer series: 2nd line: $n_1 = 2 \longrightarrow n_2 = 4$

$$\frac{1}{\lambda} = \frac{\nu}{c} = Z^2 R_H \left(\frac{1}{4} - \frac{1}{16}\right)$$

$$\boldsymbol{\nu = 15,47 . 10^{15} s^{-1}}$$

CHAPITRE V

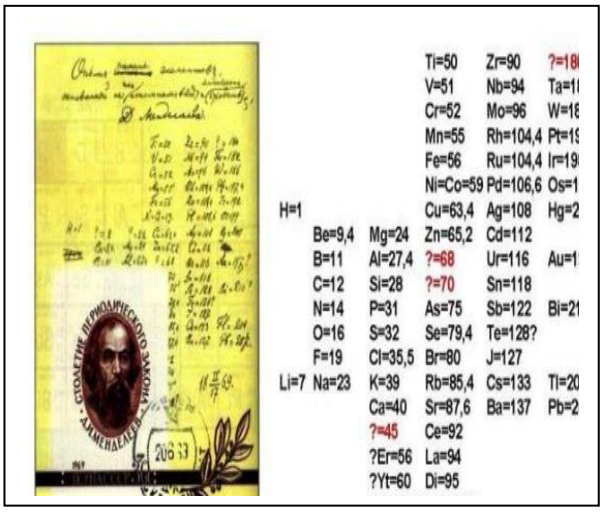
PERIODIC CLASSIFICATION OF ELEMENTS

1. Introduction

The periodic classification of elements is one of the most important achievements in chemistry, providing a systematic organization of all known chemical elements according to their atomic structure and properties. This chapter presents the evolution of the periodic table from Mendeleev's original classification to the modern periodic table based on atomic number. It examines the arrangement of elements into periods, groups, and electronic blocks, as well as the periodic trends of important physical and chemical properties such as atomic and ionic radii, ionization energy, electron affinity, and electronegativity. The chapter also introduces the use of Slater's rules for calculating effective nuclear charge and estimating atomic properties.

2. Mendeleev's periodic table

In Mendeleev's first classification (1869), Chemical families were classified according to their atomic masses. The originality of this classification consisted in the vacancy of certain boxes in the table.



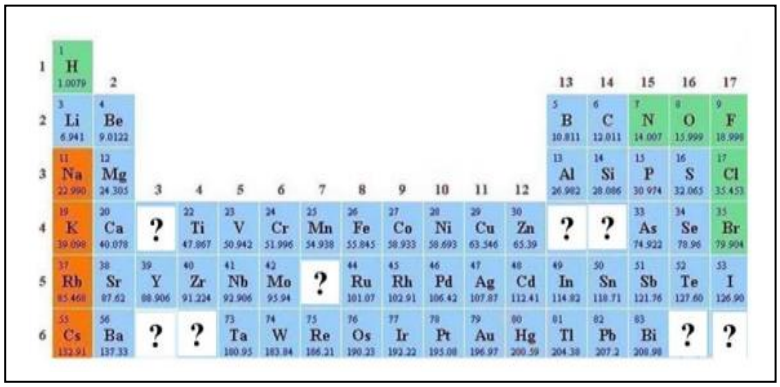


Figure V.1: Mendeleev's periodic table in 1869

3. Modern periodic classification

Mendeleev's classification arranged the elements in ascending order of their atomic masses, whereas in reality an element is defined by its atomic number Zand not by its atomic mass, which can vary due to the existence of isotopes. The modern classification is based on the ascending order of Z.

The periodic table is composed of four blocs.

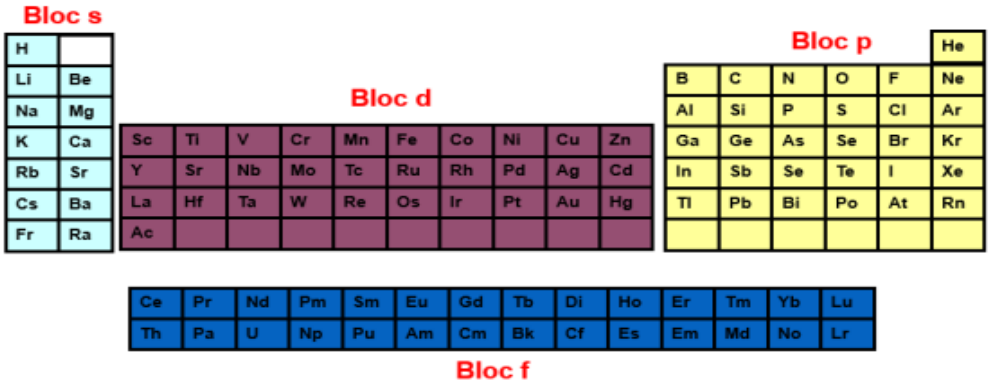


Figure V.2: Different blocs of the periodic table

- **Block s:**

External electronic structure: $\mathbf{ns^1}$ or $\mathbf{ns^2}$. Columns 1 and 2.

- **Block p:**

External electronic structure: $\mathbf{ns^2np^x}$ (with: $1 \leq x \leq 6$). Columns 13 to 18.

Note: $_2$He (configuration: $1s^2$) is classified in column 18 because it has the same properties as the elements in that column (inert gases).

- **Block d:**

External electronic structure: $\mathbf{ns^y(n-1)d^x}$ (with: $1 \leq x \leq 10$ and

$0 \leq y \leq 2$). Columns 3 to 12:"transition metals."

- **Block f:**

External electronic structure: $\mathbf{ns^2\ (n-2)f^x\ (n-1)d^y}$ (with n = 6 or 7, $0 \leq x \leq 14$; y = 0 or 1). Elements for which n = 6 are called "lanthanides"; those for which n = 7 are called "actinides" (these are all radioactive).

The periodic table is divided into:

4. Rows or periods

A row or period corresponds to an electron shell identified by its principal quantum number, denoted by **n**. There are seven known electron shells in the ground state, and therefore seven periods in the periodic table, numbered from **1** to **7**.

5. Groups and Periods: The elements in the same column with the same electronic configuration of the outer shell (valence electrons) form a family or group, which contain a similar chemical properties.

The periodic table has **18** vertical columns. Groups are numbered I to **VIII** using Roman numerals, and each group is divided into two subgroups: **A** and **B**.



Figure V.3: groups and periods in the periodic table

- **Subgroup A:**

The eight families (groups) are numbered from $\mathbf{I_A}$ to $\mathbf{VIII_A}$, represented by two blocks **s** and **p**.

An element belongs to subgroup **A** if the valence electrons are distributed in the sublayer (**ns**), (**ns np**) or **ns (n-1)d^{10} np**

- **Subgroup B:** These are groups numbered from $\mathbf{I_B}$ to $\mathbf{VIII_B}$, represented by block d (transition elements). An element belongs to subgroup **B** if its valence electrons are distributed in the **ns^2 (n-1)d** layer or **ns (n-2)f (n-1)d**.

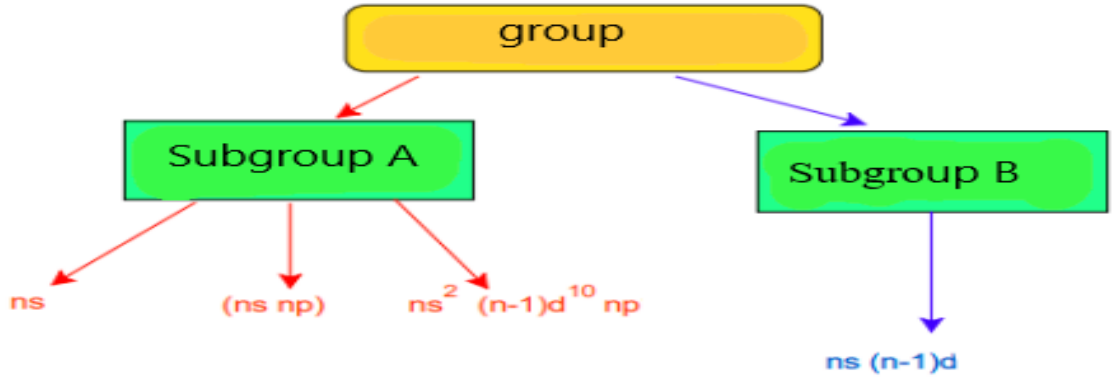


Figure V.4: Configuration of the valence shell of elements in subgroups A and B

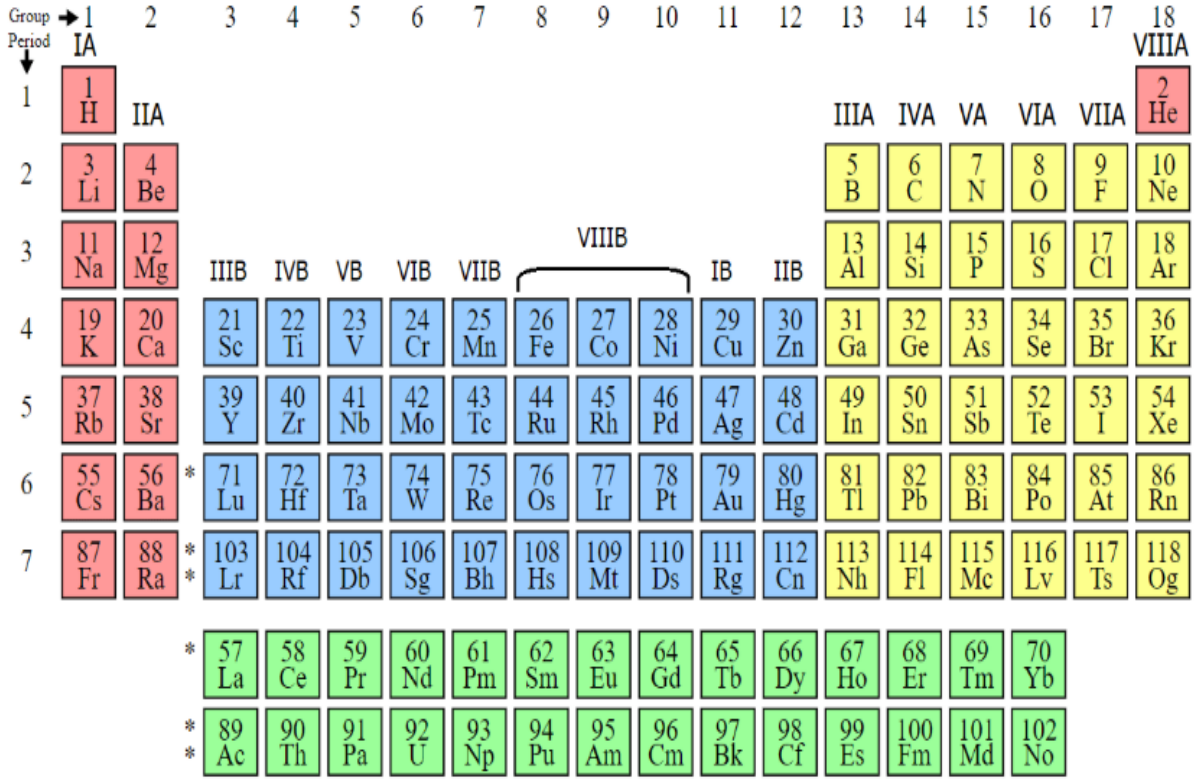


Figure V.5: Different groups and periods in the periodic table

6. Evolution and periodicity of the physical and chemical properties of elements

6.1 The principal families of the periodic table

- **Alkali metal family (column 1) :** Group $\mathbf{I_A}$: electronic configuration of type ns^1. Li, Na, K, Rb, Cs. The single electron in the valence shell can be easily lost, according to the ionization reaction**:** $\mathbf{X \rightarrow X^+ + e^-}$

- **Alkaline earth families (column 2):** group $\mathbf{II_A}$: ns^2 (Ca, Sr, Ba, and Ra). The two electrons in the valence shell can be easily lost, according to the reaction: $\mathbf{X \rightarrow X^{2+} + 2e^-}$

- **Chalcogens (column before halogens)**, also called sulfides: O, S, etc. Electronic configuration ns^2np^4 with n=2, 3, etc. They are missing two electrons to have a complete valence shell. They can capture two electrons, according to the reaction: $\mathbf{X + 2e^- \rightarrow X^{2-}}$

- **Halogen family (column 17):** group $\mathbf{VII_A\ ns^2np^5}$: F, Cl, Br, I ….

  They are missing one electron to have acomplete valence shell. They can therefore easily capture an electron, according to the reaction: $X + e^- \rightarrow X^-$

- **Rare gas (noble gas) (column 18)** family group $\mathbf{VIII_A\ ns^2np^6}$: He, Ne, Ar …

  These elements are very stable (complete s and p layers), chemically inert.

- **Family of transition elements (columns 3 to 11)**, these are elements that have incompletely filled (d) orbitals

- **Elements of the triads**, constitute group $\mathbf{VIII_B}$

- **Rare earth elements** are elements with (f) orbitals in the process of filling. The orbitals corresponding to the filling of the 4f orbital are called the Lanthanides, 6th period $57 \leq Z \leq 71$, while those corresponding to the filling of the 5f orbital are called the Actinides, 7th period $89 \leq Z \leq 103$.

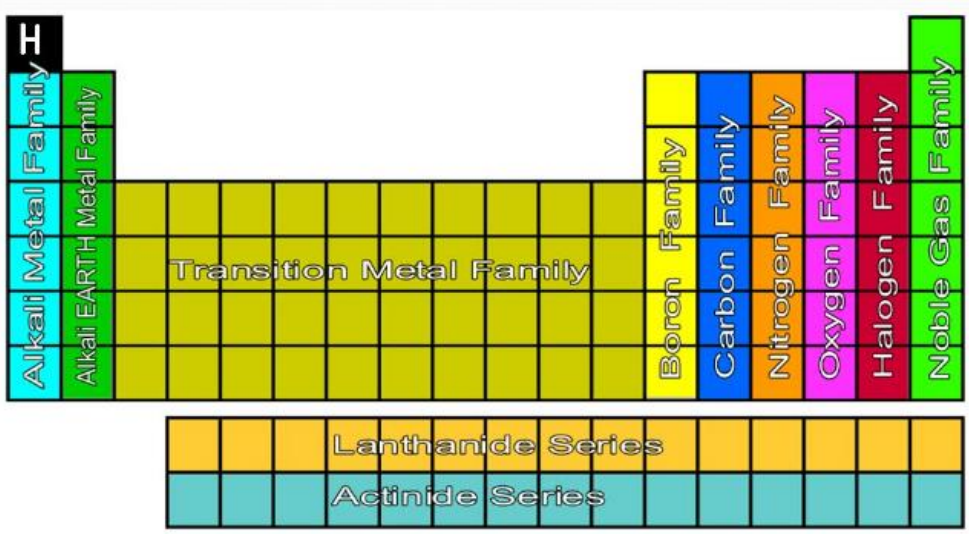


Figure V.6 : principal families of the periodic table

6.2 Metals and non-metals

Sanderson's rule: An element is metallic if the number of electrons in its valence shell is less than or equal to the number of its period. (Except H and Ge)

Examples:

Mg: 10 (Ne) $3s^2$. 2 electrons on n=3 and belongs to period 3. $2 < 3 \Rightarrow$ Mg is a metal

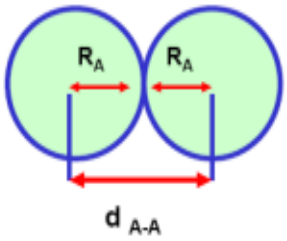
Ga: 18(Ar)$3d^{10}4s^24p^1$. 3 electrons on n= 4 and belongs to period

4. $3 < 4 \Rightarrow$ Ga is a metal

6.3 Calculation of the radius (r_a)

The atomic radius can be defined as half the distance between the centers of two atoms connected by a simple bond.

- In a period: as Z increases, r_a decreases
- In a column: as Z increases, r_a increases



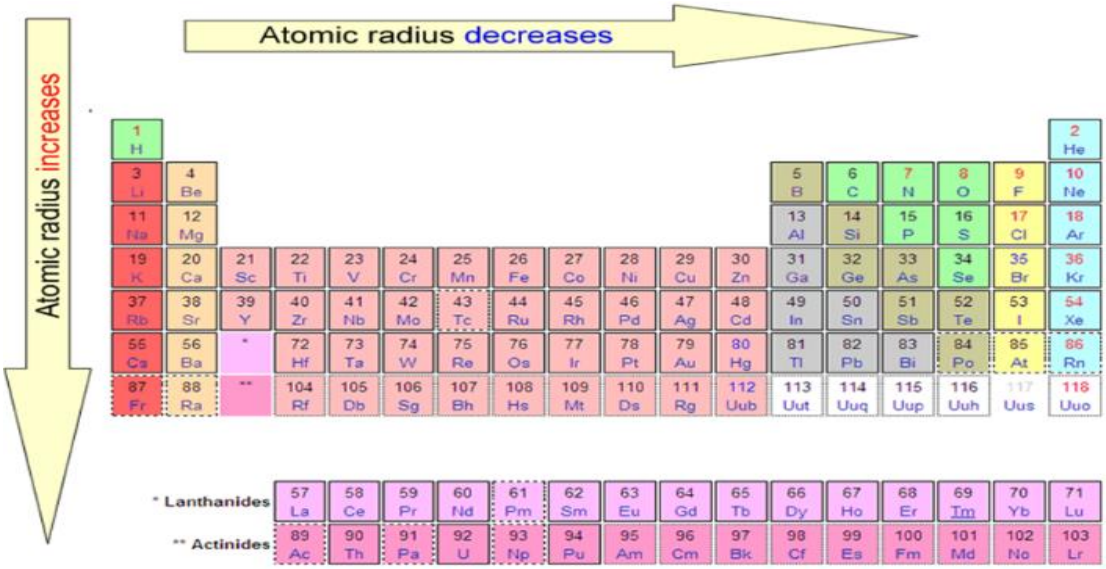


Figure V.6: The evolution of atomic radius in the periodic table

6.4 Successive ionization energies (IE)

This is the energy required to remove an electron from an atom (or ion) in its ground state and in the gaseous state.

The first ionization: E_{i1} (the energy required to remove the electron least strongly bound to the nucleus).

$E_{i1} = E(A^+) - E(A)$.

$K(g) \rightarrow K^+(g) + 1\ e^- + E_{i1}$ With $E_{i1} = 4{,}31$ eV. $E_{i1} = E(K^+) - E(K)$.

2^{nd} ionization: E_{i2} energy required to remove the 2^{nd} electron.

$E_{i2} = E(A^{++}) - E(A^+)$.

$K^+(g) \rightarrow K^{+2}(g) + 1\ e^- + E_{i2}$ with $E_{i2} = 31, 7$ eV.

$E_{i2} = E(K^{++}) - E(K^+)$.

n^{th} ionization: Thus $E_{i1} < \ldots\ldots < E_{in}$: if the electron is far from the nucleus, it is easy to extract. Internal electrons have a higher ionization energy than valence electrons.

$E_{in} = E(A^{+n}) - E(A^{+(n-1)})$

Ionization energy varies inversely with atomic radius:

• Within the same period: if Z increases, then $\mathbf{E_i}$ increases.

• Within the same group: if Z increases, then $\mathbf{E_i}$ decreases.

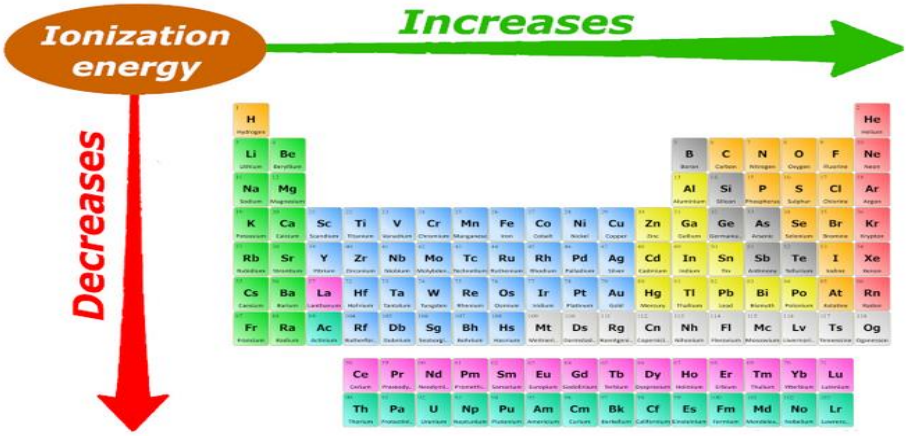


Figure V.7: The evolution of ionization energy in the periodic table

6.5 Electronegativity or electron affinity

This is the ability of an element to attract an electron. An element that easily loses one or more electrons is said to be electropositive. Electronegativity varies in the same way as ionization energy in the opposite direction to atomic radius.

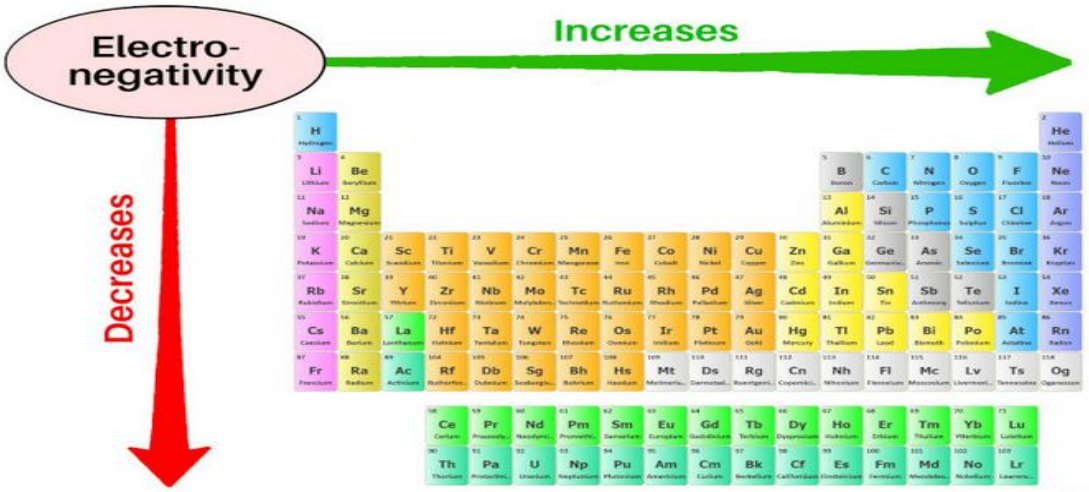


Figure V.8: The evolution of electronegativity in the periodic table

6.6 Electron affinity

This is the energy released by an atom when it receives an electron: $X + e^- \rightarrow X^- + AE$.

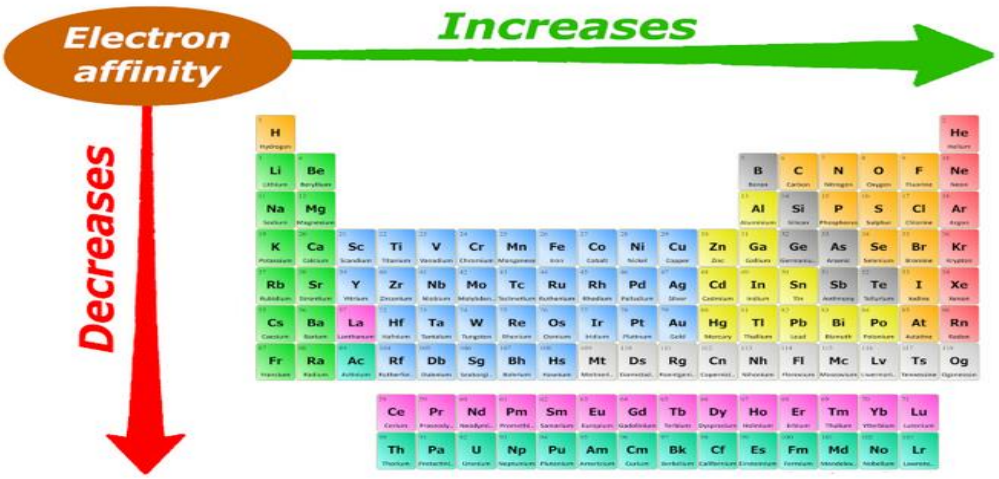


Figure V.9: The evolution of electron affinity in the periodic table

7. Calculation of electronegativity

MILLIKAN scale

Electronegativity is defined as the product of the average ionization energy and electron affinity values of an atom with a coefficient K of 0.317 eV

-The higher the electronegativity of an atom, the more that atom tends to attract electrons toward itself when it forms a chemical bond with other atoms. According to the **MILLIKAN scale**, electronegativity is calculated using the following formula:

$$\chi_M = K\left(\frac{AE+EI}{2}\right) \qquad \textbf{(V.1)} \qquad \textbf{K = 0,317 ; (AE and } \textit{EI} \textbf{) in eV}$$

PAULING scale

Pauling established an empirical relationship for calculating the difference in electronegativity between two atoms A and B forming an A-B bond.

The formula is as follows:

$$|\chi_A - \chi_B| = 1.102\sqrt{E_d(AB) - \sqrt{E_d(AA)E_d(BB)}} \qquad \textbf{(V.2)}$$

Where

$E_d(AB)$, E_d *(AA)* and E_d *(BB)* are the dissociation energies of A-B, A-A, and B-B bonds, expressed in kJ/mol.

ALLRED-ROCHOW scale

This scale is based on the effective attraction exerted on the peripheral electrons of the atom. It uses the effective charges Z_{eff} of the outer layer. Electronegativity according to the ALLRED-ROCHOW scale is calculated using the following formula:

$$\chi = \frac{(Z_{eff})}{r_{cov}^2} . e^2 \qquad \textbf{(V.3)}$$

$\mathbf{Z_{eff}}$ is the effective charge of the nucleus.

$\mathbf{r_{cov}}$ is the covalent radius of the atom expressed in Angstroms (A°).

(e) the elementary charge.

8. Calculation of polyelectronic energies using Slater's rule

Calculation of Z_{eff} $\mathbf{Z_{eff} = Z - \delta}$ **(V.4)**

To calculate **δ** :

- Group the electrons according to the following sequence:

(1S) (2S2P) (3S3P) (3d) (4S4P) (4d) 4f (5S5P) 5d……..

- Select the electron for which you are determining the effective charge $\delta = \sum \delta_i$. All other electrons will make a partial contribution δ_i to the total screen constant . This contribution depends on:

- The type of orbital **(s, p), (d), or (f)** of the electron and the electronic shell n of the electron.

- The value of δ_i is summarized in the following table

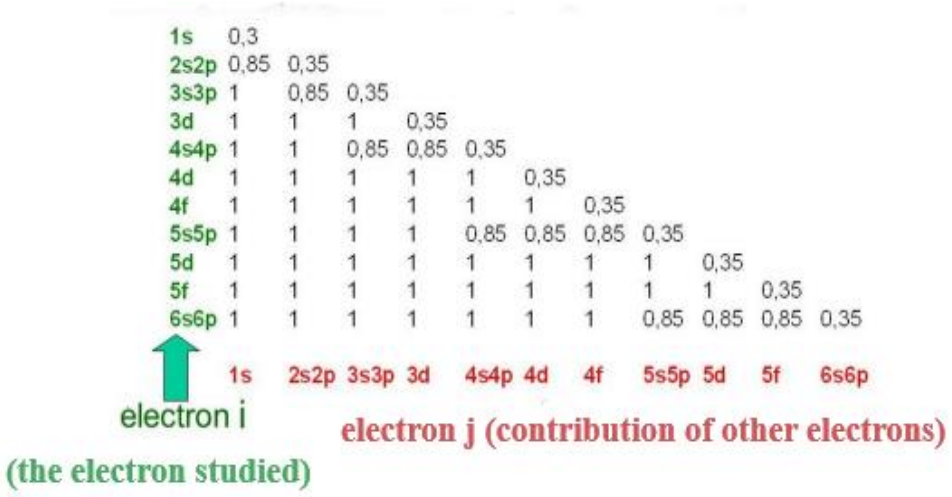
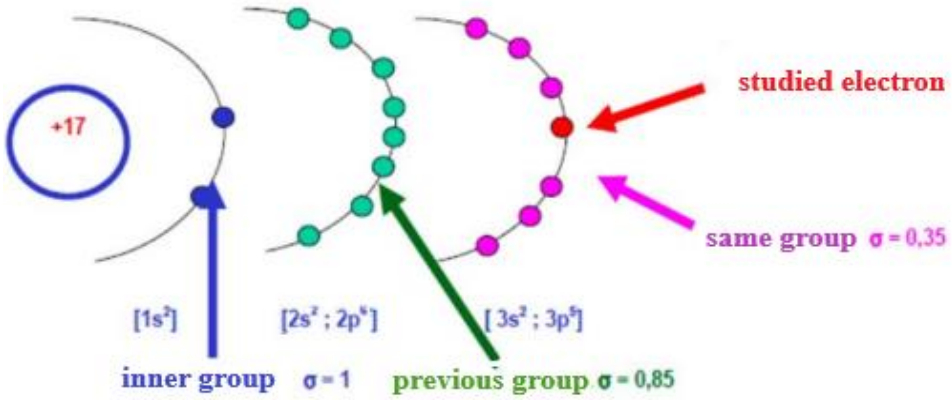


Figure V.10: SLATER's rule

Examples of effective charge calculations

$_{17}Cl$: $[1s^2]$; $[2s^2 ; 2p^6]$; $[3s^2 ; 3p^5]$:



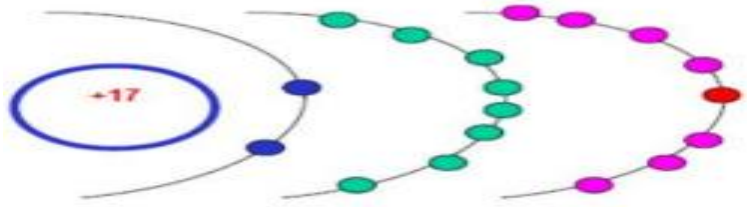
$$Z_{eff} = 17 - ((7 - 1) \times 0.35) - (8 \times 0.85) - (2 \times 1)$$

Studied electron

$$Z_{eff} = 17 - (6 \times 0.35) - (8 \times 0.85) - (2 \times 1) = 6.1$$

Example 2

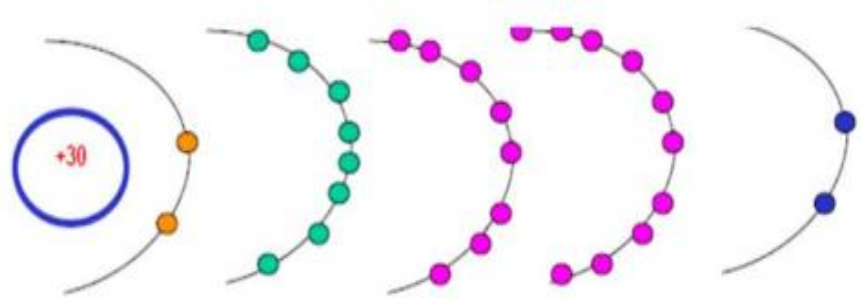
Calculation of Z_{eff} for ions: Cl^-



$Z_{eff} = 17- (7 \times 0.35) – (8 \times 0.85) – (2 \times 1) = 5.75$

Example 3

Zn : Z = 30 : $[1s^2]$; $[2s^2 ; 2p^6]$;$[3s^2 ; 3p^6]$; $[3d^{10}]$; $[4s^2]$



Z_{eff} (4s) = 30- (1 × 0.35) – (18×0.85) – (8×1) – (2 ×1) = 4.35

Z_{eff} (3d) = 30- (9 × 0.35) – (8×1) – (8×1) – (2 ×1) = 8.85

Z_{eff} (3s 3p) = 30- (7 × 0.35) – (8×0.85) – (2 ×1) = 18.75

Example 4

$_7N$: $1S^2$ /$2S^2$ $2P^3$

0.85 / 0.35

Calculate the Z_{eff} of an electron in the outer shell 2S2P

$\delta = (5-1) \times 0,35 + 2 \times 0,85 = 3,10$

$Z_{eff} = Z – \delta = 7 – 3,1 = 3,9$

Calculate the energy of a level by using Slater's rule:

$$E_n = \frac{13.6}{n^2}.Z_{eff}^2$$

$_7N : 1S^2 /2S^2\ 2P^3$

The energy of level 1S is: $E_{1S\ (n)} = \left(-\frac{13,6}{1^2} \times Z^2_{eff\,1S}\right) \times 2$

The energy of level 2S2p is: $E_{2S2P(n)} = \left(-\frac{13,6}{2^2} \times Z^2_{eff\,2S2P}\right) \times 5$

Calculate the energy of an atom

This is the energy of all the electrons in an atom.

$_7N : 1S^2\ 2S^2\ 2P^3$

$$E_N = E_{2S2P} \times 5 + E_{1S} \times 2$$

$$E_N = \left(-\frac{13,6}{1^2} \times Z^2_{eff\,1S}\right) \times 2 + \left(-\frac{13,6}{2^2} \times Z^2_{eff\,2S2P}\right) \times 5$$

Calculate the ionization energy

$X \rightarrow X^+ + 1e^-$

$Ei = E_{x+} - E_x$

$Na \rightarrow Na^+ + 1e-$

$Ei = E_{Na+} - E_{Na}$

$_{11}Na: 1S^2 /2S^2\ 2P^6 /3S^1$

1 0.85 0.35

$_{11}Na^+ : 1S^2 /2S^2\ 2P^6$

$E(I) = 2E_{1S} + 8E_{2S2P} - 2E_{1S} - 8E_{2S2P} - 1E_{3S}$

$E(I) = 2E_{1S} + 8E_{2S2P} - 2E_{1S} - 8E_{2S2P} - 1E_{3S}$

$E(I) = -1E_{3S} = 13.6(2.2)^2/(3)^2 = 7.31$

Ex+, Ex the energies of atoms X, X+ respectively

$E_{Na} = 2E_{1S} + 8E_{2S2P} + 1E_{3S}$

$E_{Na+} = 2E_{1S} + 8E_{2S2P}$

$$E_{3S} = -\frac{13,6}{3^2} \times Z^2_{eff3S}$$

$Z_{eff}(3S) = 11 - (8\times0,85) + (2\times1) = 2.2$

Calculate electron affinity

$X + 1e^- \rightarrow X^- + AE$

$AE = E_{x-} - E_x$

Example:

$Na + e^- \rightarrow Na^-$

$_{11}Na$-: $1s^2/2s^22p^6/3s^2$

$Z_{eff} = Z-\delta$

$\delta = (2-1)x0.35+8x(0.85) + 2x(1) = 9.15$

$Z_{eff-} = 11-9.15 = 1.85.$

Na: $1S^2\ 2s^22p^63s^1$

$\delta = (1-1)\ x\ 0.35 +8x(0.85) +2x(1) = 8.8$

$Z_{eff} = 11-8.8 = 2.2$

$E_{Na-} = 2E\ (1s^2\ ) + 8(E2s^22p^6\ )+2(E3s^2\ )$

$E_{Na} = 2E(1s^2\ )+ 8(E2s^22p^6\ )+ E(3s^1\ )$

$AE = E_{Na-} - E_{Na}$

$= 2E(1s^2\ )+ 8E(2s^22p^6\ )+2E(3s^2\ )-$
$2E(1s^2\ )- 8E(2s^22p^6\ )- E(3s^1\ )$

$= 2E(3s^2\ )-E(3s^1)$

$E(3S^2\ )= -13.6\ \ (1.85)^{\ 2}\ /(3)^2 =$ **-5.17**

$E(3S^1)= -13.6\ (2.2)^2\ /(3)^2$ **= -7.31**

$AE = -5.17+7.31 =$ **2.14 ev**

So, We can calculate Millikan's electronegativity

$\chi = 0.317\ (EA + EI)/2$

$\chi = 0.317x(2.14+7.31)/2 =$ **1.5 ev**

Conclusion

This chapter has highlighted the fundamental principles underlying the periodic classification of elements and its relationship with electronic structure. The organization of elements into periods, groups, and blocks explains the periodic recurrence of their physical and chemical properties. Variations in atomic radius, ionization energy, electron affinity, and electronegativity were analyzed to understand the behavior and reactivity of elements. Furthermore, the application of Slater's rules and effective nuclear charge calculations provides valuable tools for interpreting periodic trends and predicting atomic properties. These concepts form the basis for understanding chemical bonding and the behavior of elements in chemical reactions.

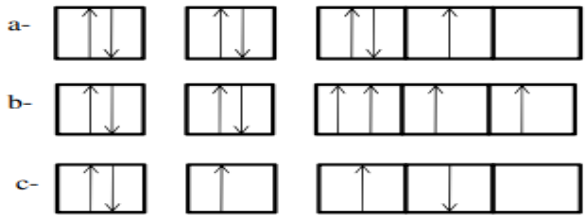
Exercises

Exercise 01

1) Which of the following sets (n, l, m, s) can describe an electron in an atom? Determine the orbital in which this electron is located.

a) (2; 2; 1; +1/2), b) (2; 2; -1; +1/2), c) (4; 0; -1; +1/2), d) (3; 1; 0; -1/2).

2) Here are some electronic structures written using quantum boxes. Correct those that are wrong.



Solution

1) a- n = 2, l = 2, m = 1, s = +1/2 impossible $0 \leq l \leq (n-1)$

b- n = 2, l = 2, m = -1 impossible $0 \leq l \leq (n-1)$

c- n = 4, l = 0, m = -1 impossible $(-l \leq m \leq l)$

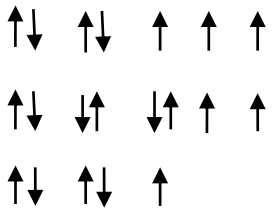
d- n = 3, l = 1, m = 0, s = -1/2 possible $[n > 0, 0 \leq l \leq (n-1), -l \leq m \leq l$ *and* $s = \pm 1/2]$.

l = 1, so it is the p subshell, m is 0, s = -1/2, so it is the last electron $3p^5$.

a- Is incorrect; Hund's rule is not respected.

b- Is incorrect; Pauli's rule is not respected.

c- Is incorrect; Hund's rule is not respected.



Exercise 02

Consider the following atoms: $_{9}F$, $_{13}Al$, $_{21}Sc$, $_{24}Cr$, $_{26}Fe$, $_{29}Cu$, $_{34}Se$, $_{47}Ag$, $_{79}Au$.

1. For each of these elements:

a. Give the electron configuration in the ground state and position them in the periodic table (period, family, block).

b. Give the number of valence electrons and present them in each case.

c. Specify the four quantum numbers of the valence electrons of $_{21}Sc$.

2. Molybdenum (Mo) belongs to the chromium $_{24}Cr$ family and to the fifth period. Give its electron configuration and atomic number.

Solution

Element	**Electronic configuration**	**Period**	**Number of valence electrons**	**Group**	**Block**	**Number of unpaired electrons**
$_{9}F$	$1s^2$ **$2s^2$ $2p^5$** Or $_{2}$[He] **$2s^2$ $2p^5$**	2	7	VII_A	p	1
$_{13}Al$	$1s^2$ $2s^2$ $2p^6$ **$3s^2 3p^1$** Or $_{10}$[Ne] **$3s^2 3p^1$**	3	3	III_A	p	1
$_{21}Sc$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ **$4s^2$ $3d^1$** Or $_{18}$[Ar] **$4s^2$ $3d^1$**	4	3	III_B	d	1
$_{24}Cr$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ **$4s^1$ $3d^5$** Or 18[Ar] **$4s^1$ $3d^5$**	4	6	VI_B	d	6
$_{29}Cu$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ **$4s^1$ $3d^{10}$** Or $_{18}$[Ar] **$4s^1$ $3d^{10}$**	4	11	I_B	d	1
$_{34}Se$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ **$4s^2$**$3d^{10}$ **$4p^4$** Or $_{18}$[Ar] **$4s^2$ $3d^{10}4p^4$**	4	6	VI_A	p	2
$_{47}Ag$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ **$5s^1$ $4d^{10}$** Or $_{36}$[Kr] **$5s^1$ $4d^{10}$**	5	11	I_B	d	1
$_{79}Au$	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^2$ $3d^{10}$ $4p^6$ $5s^2$ $4d^{10}$ $5p^6$ **$6s^1$ $4f^{14}5d^{10}$** Or $_{54}$[Xe] **$6s^1$ $4f^{14}5d^{10}$**	6	11	I_B	d	1

d) The four quantum numbers of the valence electrons of $_{21}Sc$.

$_{21}Sc$: $_{18}$[Ar] $4s^2$ $3d^1$ ↑↓ ↑

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

3. The electronic structure of chromium $_{24}Cr$: [$_{18}Ar$] $4s^1 3d^5$. It belongs to the transition metal family, with an electronic structure of valence shell type (n-1) d^5 ns^1.

Molybdenum (Mo) belongs to the same family as chromium and to the 5th period, so the structure of its valence shell is of the (n-1)d^5 ns^1 type with n=5:

Mo: $_{36}$[Kr] $4d^5$ $5s^1$ => Z = 42 => $_{42}Mo$

Exercise 03:

Consider the following elements:

Na (Z = 11), Mg (Z = 12), Si (Z = 14), Cl (Z = 17), Br (Z = 35)

1) Write the electron configuration for each element.

2) Locate these atoms in the periodic table.

3) Classify these elements in descending order of:

a- Electronegativity;

b- Atomic radius;

c- Ionization energy.

Solution

1) The electronic structure of the elements:

11Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

12Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

14Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

17Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

35Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

2) The position of the elements:

elements	Na	Mg	Si	Cl	Br
period	3	3	3	3	4
group	I_A	II_A	VII_A	IV_A	$VIII_A$

3)

a) Decreasing electronegativity:

Br, Cl, Si, Mg, Na

b) Decreasing atomic radius:

Na, Mg, Si, Cl, Br

c) Decreasing ionization energy:

Br, Cl, Si, Mg, Na

Exercise 04:

1) Write the electron configuration of 35X and state its position in the periodic table.
2) Give the atomic numbers of elements Y and Z, knowing that:

Y belongs to period 4 and group IIA

Z is located directly below Y

3) Classify these elements (X, Y, and Z) in ascending order of electronegativity.
4) Calculate the ionization energy of 5B using Slater's rule.

Given: $E_n = -13{,}6\frac{Z_{eff}}{n^2}(ev)\ \ avec\ \ Z_{eff} = Z - \sigma$

Solution

1) $_{35}X : 1s^2 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Period = 4, group $VIII_A$

2) Y ϵ (n= 4, II_A), So y : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Z= 20, So $_{20}Y$

Z ϵ (n= 5, II_A), so Z : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$

Z= 38, so $_{38}Z$

3)

Same period :

$\mathcal{X}(_{20}Y) < X(_{35}X)$

Same group :

$$\mathcal{X}(_{38}Z) < X(_{20}Y)$$

So : $\mathcal{X}(_{38}Z) < X(_{20}Y) < X(_{35}X)$

4) $_5B : 1s^2\ 2s^2\ 2p^1$

σ= [(2+1)-1]. 0,35 +2. 0,85 = 2,4 ; Z_{eff} = Z - σ = 5 - 2,4 = 2,6

$_5B^+$: $1s^2\ 2s^2$

$^+\sigma$ = (2-1). 0,35 + 2. 0,85 = 2,05 ; Z_{eff} = Z - $^+\sigma$ = 2,95

$E_i = [2\ E_{1s}{}^2 + 2E_{2s}{}^2] - [2E_{1s}{}^2 + 3E_{2s}{}^2{}_{2p}{}^1]$

$E_i = 2\ E_{2s}{}^2 - 3E_{2s}{}^2{}_{2p}{}^1$

$$E_i = 2\left[-\frac{13{,}6}{n^2}\ {}^+Z_{eff}^2\right] - 3\left[-\frac{13{,}6}{n^2}\ \ Z_{eff}^2\right]$$

$$E_i = 2\left[\frac{-13{,}6}{2^2}(2{,}95)^2\right] - 3[\frac{-13{,}6}{2^2}(2{,}6)^2]$$

E_i = 9,38 ev

Exercise 05

Find the electronic configuration of the following elements and give the stable ions they can form:

a. An alkali metal from the third period.

b. An alkaline earth metal from the fourth period.

c. A halogen from the fifth period.

d. A noble gas from the same period as $_{34}$Se.

e. An element that belongs to the same period as $_{20}$Ca and the same group as $_{43}$Tc.

f. An element that belongs to the same period as $_{23}$V and the same group as $_{16}$S.

Solution

Electronic configuration		**Z**	**The most stable ion**
a: $1s^2 2s^2 2p^6$ /**$3s^1$**	(Na)	11	Na^+
b: $1s^2 2s^2 2p^6 3s^2 3p^6$ /**$4s^2$**	(Ca)	20	Ca^{+2}
c: $1s^2 2s^2 2p^6 3s^2 3p^6$ /$4s^2 3d^{10} 4p^6$ /**$5s^2 4d^{10} 5p^5$**	(I)	53	I^-
d: $1s^2 2s^2 2p^6 3s^2 3p^6$/**$4s^2 3d^{10} 4p^6$**	(Kr)	36	/
e : $1s^2 2s^2 2p^6 3s^2 3p^6$ /**$4s^2 3d^5$**	(Mn)	25	Mn^{+2}
f : $1s^2 2s^2 2p^6 3s^2 3p^6$ /**$4s^2 3d^{10} 4p^4$**	(Se)	34	Se^{-2}

Exercise 06

1) Find the electron configuration of the following elements: $_{28}$Ni, $_{18}$Ar, $_{14}$Si, $_{16}$S, $_{12}$Mg, $_{46}$Pd.

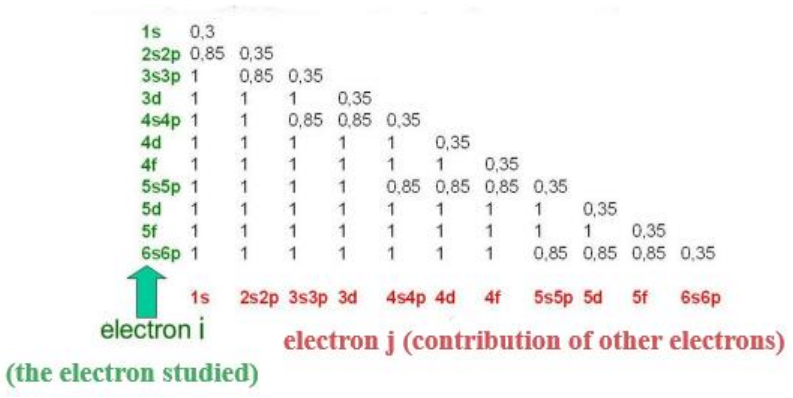
3) Calculate the effective Z ($Z_{effectif}$) for each element.

3) Calculate the radius of the electron orbit in the outer shell for each element.

4) Calculate the energy of the electron in the outer shell for each element in electron volts (ev) and then in joules.

5) Calculate the first ionization energy of magnesium.

Slater's screen constants:



Solution

1) $_{28}Ni$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$.

$_{18}Ar$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

$_{14}Si$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$.

$_{16}S$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$.

$_{12}Mg$: $1s^2\ 2s^2\ 2p^6\ 3s^2$

$_{46}Pd$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^8$.

2) $_{28}Ni$: $Z_{eff} = 28 - (1 \times 0{,}35 + 8 \times 0{,}85 + 8 \times 0{,}85 + 8 \times 1 + 2 \times 1)$. $Z_{eff} = 4{,}05$.

$_{18}Ar$: $Z_{eff} = 18 - (7 \times 0{,}35 + 8 \times 0{,}85 + 2 \times 1)$. $Z_{eff} = 6{,}75$.

$_{14}Si$: $Z_{eff} = 14 - (3 \times 0{,}35 + 8 \times 0{,}85 + 2 \times 1)$. $Z_{eff} = 4{,}15$.

$_{16}S$: $Z_{eff} = 16 - (5 \times 0{,}35 + 8 \times 0{,}85 + 2 \times 1)$. $Z_{eff} = 5{,}45$.

$_{12}Mg$: $Z_{eff} = 12 - (1x\ 0.35 + 8x\ 0.85 + 2x\ 1)$. $Z_{eff} = 2.85$

$_{46}Pd$: $Z_{eff} = 46 - (1 \times 0{,}35 + 8 \times 0{,}85 + 8 \times 0{,}85 + 28 \times 1)$. $Z_{eff} = 4{,}05$.

2) $r_n = 0{,}53 \times (n^2 / Z_{eff})$ (Å).

$_{28}Ni$: n = 4 ; $Z_{eff} = 4{,}05$; $r_n = 2{,}09$ Å.

$_{18}Ar$: n=3 ; $Z_{eff} = 6{,}75$; $r_n = 0{,}706$ A°.

$_{14}Si$: n = 3 ; $Z_{eff} = 4{,}15$; $r_n = 1{,}15$ Å.

$_{16}S$: n = 3 ; $Z_{eff} = 5{,}45$; $r_n = 0{,}875$ Å.

$_{12}Mg$: n=3 ; $Z_{eff} = 2{,}85$; $r_n = 1{,}674$ Å.

$_{46}Pd$: n=5 ; $Z_{eff} = 4{,}05$; $r_n = 3{,}27$ Å.

3) $E_n = -13{,}6x\ (Z^2_{\ eff} / n^2)$ [ev] and 1 ev= $1{,}6 \times 10^{-19}$ Joules.

$_{28}Ni$: n = 4 ; $Z_{eff} = 4{,}05$; $E_n = -13{,}94$ ev = $-22{,}3 \times 10^{-19}$ Joules.

$_{18}Ar$: n=3 ; $Z_{eff} = 6{,}75$; $E_n = -68{,}85$ ev = $-110{,}16 \times 10^{-19}$ Joules.

$_{14}Si$: n=3 ; $Z_{eff} = 4{,}15$; $E_n = -26{,}02$ev = $-41{,}64 \times 10^{-19}$ Joules.

$_{16}S$: n=3 ; $Z_{eff} = 5{,}45$; $E_n = -44{,}88$ev = $-71{,}8 \times 10^{-19}$ Joules

$_{12}Mg$: n=3 ; $Z_{eff} = 2{,}85$; $E_n = -12{,}274$ ev = $-19{,}638x\ 10^{-19}$ Joules

$_{46}Pd$: n=5 ; $Z_{eff} = 4.05$; $E_n = 8{,}92$ ev = $-14{,}27 \times 10^{-19}$ Joules

4) The first ionization energy of Magnesium ($_{12}Mg$).

$Mg \rightarrow Mg^{+} + 1e^{-}$

$EI = E_{Mg^+} - E_{Mg}$

$_{12}Mg$: $1s^2\ 2s^2\ 2p^6\ 3s^2$

$Z_{eff} = 12 - (1x\ 0.35 + 8x\ 0.85 + 2x\ 1)$. $Z_{eff} = 2.85$.

$_{12}Mg^{+}$: $1s^2\ 2s^2\ 2p^6\ 3s^1$

$Z_{eff}^{+} = 12 - (8x\ (0.85) + 2x(1))$. $Z_{eff}^{+} = 3.2.$

$E_{Mg} = 2E(1s^2) + 8E(2s^2 2p^6) + 2E(3s^2)$

$E_{Mg^+} = 2E(1s^2) + 8E(2s^2 2p^6) + E(3s^1)$

$EI = 2E(1s^2) + 8E(2s^2 2p^6) + E(3s^1) - 2E(1s^2) - 8E(2s^2 2p^6) - 2E(3s^2)$

$EI = E(3S^1) - 2E(3S^2)$.

$E(3S^2) = -13.6x\ (Z_{eff})^2/n^2 = -13.6x(2.85)^2/(3)^2 = -12.274$ ev

$E(3S^1) = -13.6x(Z_{eff}^{+})^2/n^2 = -13.6x(3.2)^2/(3)^2 = -15.474$ ev

$EI = -15.474-(2x-12.274) = 18.674$ ev.

CHAPTER VI

CHEMICAL BONDS

1. Introduction

Understanding chemical bonding is fundamental to explaining the formation, stability, and properties of molecules. Atoms interact with one another primarily through their valence electrons, leading to different types of chemical bonds such as covalent, ionic, and coordinate (dative) bonds.

This chapter first presents Lewis theory, which makes it possible to represent valence electrons and understand the formation of single, double, and triple bonds. It then introduces the concepts of bond polarity and dipole moment, which are essential for explaining the physical properties of molecules.

Finally, molecular geometry is examined through the VSEPR (Gillespie) model, which allows the prediction of molecular shapes, as well as through the quantum model of chemical bonding based on orbital hybridization and molecular orbital theory (LCAO, Linear Combination of Atomic Orbitals).

2. Covalent bonding in Lewis theory

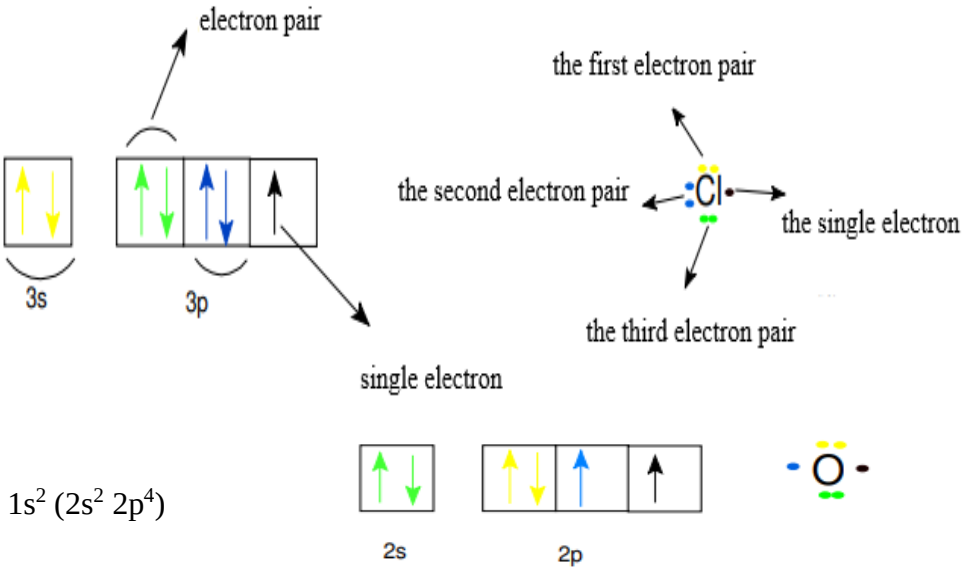
a- Valence shell In the ground state

The electrons in the shell with the highest principal quantum number n play the principal role in reactions; it is these electrons in particular that participate in the formation of bonds between atoms. This shell is called the valence shell, outer shell, or peripheral shell.The existence in this shell of doublets of electrons, single electrons, or empty atomic orbitals (empty boxes) determines the chemical properties of an atom.

Example

$_{6}C : 1s^2 (2s^2\ 2p^2)$

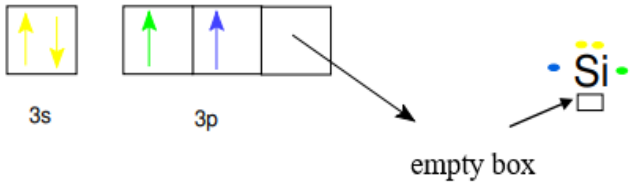
$_{17}Cl : 1s^2\ 2s^2\ 2p^6 (3s^2\ 3p^5)$



$_8O : 1s^2 (2s^2\ 2p^4)$

The valence shell of oxygen has two doublets and two unpaired electrons.

$_{14}Si : 1s^2\ 2s^2\ 2p^6\ (3s^2\ 3p^2)$



The valence shell of silicon has a doublet, two unpaired electrons, and one empty box.

Lewis structures can generally be used. They consist of representing the electrons in the valence shell (outer electrons) as dots arranged around the symbol of the element, and the empty box as a rectangle.

b- The different types of bonds

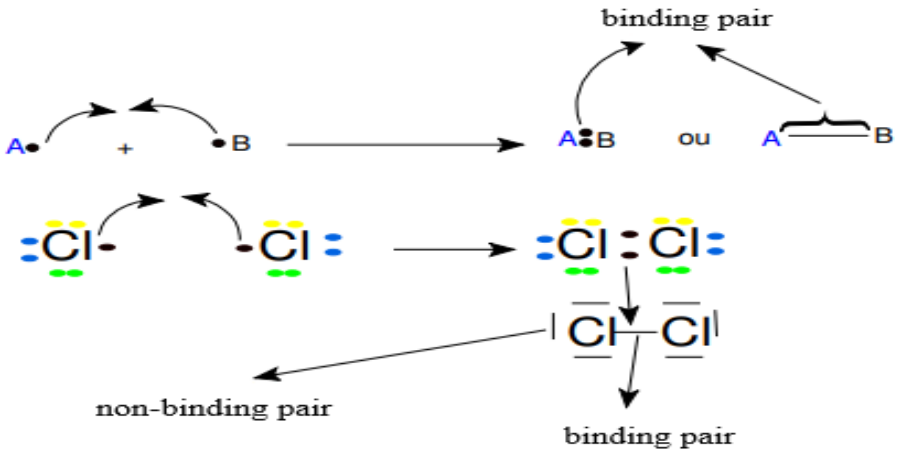
Covalent bonds, dative bonds, ionic bonds, and polar bonds.

- **Covalent bonding**

When two atoms come into contact, they can share their valence electrons and form a bond. Each of the two atoms provides one of its unpaired electrons from the valence shell, which occupies a single quantum state . These two electrons combine to form a bond between atom A and atom B.

The covalent bond is a strong σ bond.

✓ **Simple covalent bonds**



✓ **Multiple covalent bonds**

This involves the sharing of several electrons between two atoms (i.e., each atom contributes more than one electron (two or three) to form a double or triple bond.

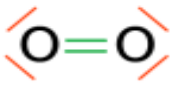
Example

Oxygen molecule (O_2)

The first oxygen atom contributes two electrons and the second oxygen atom contributes two electrons to form a double bond.

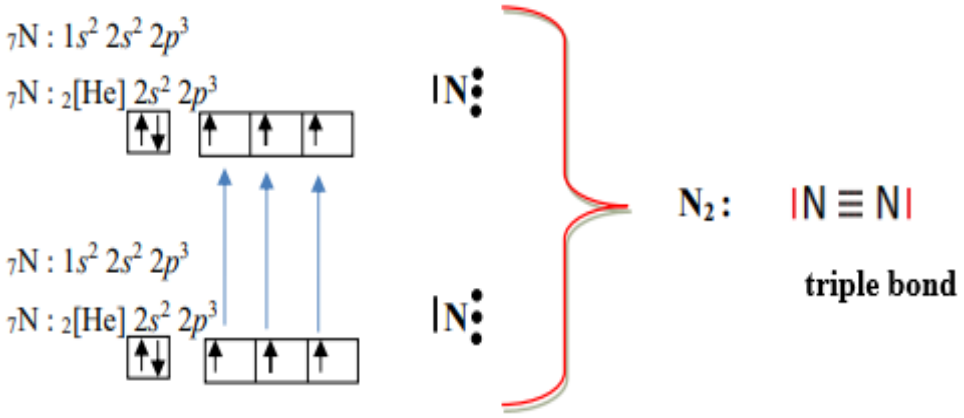


O_2



The nitrogen molecule (N_2)

Each nitrogen atom provides 3 unpaired electrons forming a triple bond.

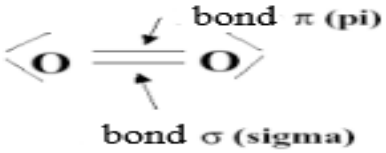


- A simple covalent bond is a σ bond.

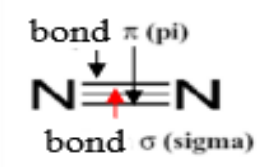
Example: H-H (the bond between H and H is a σ (sigma) bond.



❖ A double bond consists of a σ bond and a π bond.



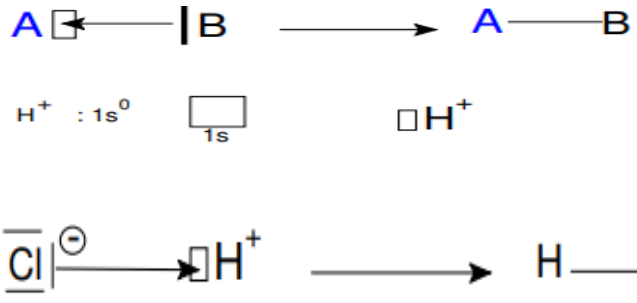
❖ A triple bond consists of one σ bond and two π bonds



❖ The σ bond is stronger than the π bond.

The dative bond (coordination)

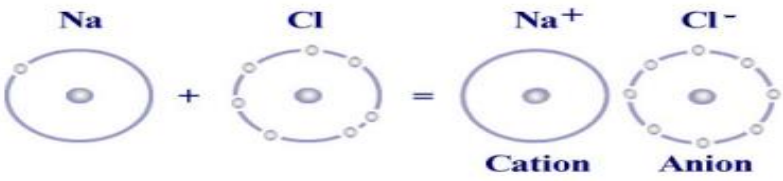
It forms between two atoms, one of which (atom B) (the donor) provides a pair from its outer shell, while the other atom (atom A) (the acceptor), which has an electronic vacuum (empty box) in its valence shell, receives this pair.



Ionic bonding

If the two atoms A and B in molecule A-B have a significant difference in electronegativity, the more electronegative element catches (takes) an electron from the other less electronegative element. The molecule consists of two ions, A^+ and B^- .There is an electron transfer from one atom to another. This is the ionic bond.

Example $NaCl \rightarrow Na^+ + Cl^-$



$_{11}Na : 1s^2\ 2s^2\ 2p^6\ 3s^1 \longrightarrow {}_{11}Na^+ : {}_{10}[Ne]\ 3s^0 = {}_{10}[Ne]$

$_{11}Na : {}_{10}[Ne]\ 3s^1$

Na•

$_{17}Cl : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5 \longrightarrow {}_{17}Cl^- : {}_{10}[Ne]\ 3s^2\ 3p^6 = {}_{18}[Ar]$

$_{17}Cl : {}_{10}[Ne]\ 3s^2\ 3p^5$

Cl•

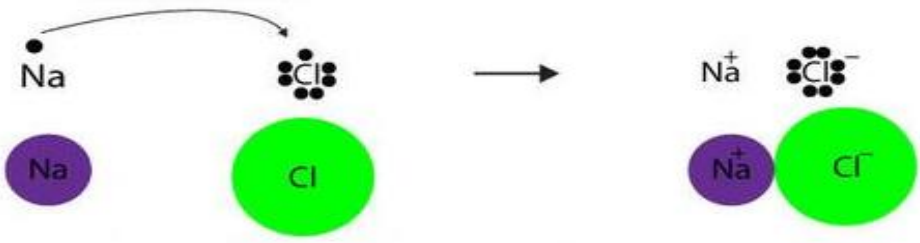


Figure VI.1: Ionic bond in sodium chloride (NaCl)

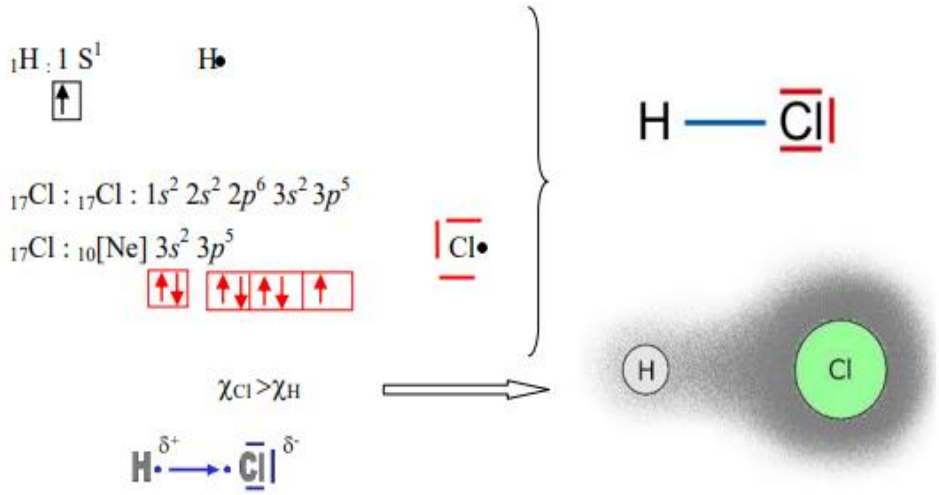
Polarization of bonds

When two atoms bonded by covalence are identical (H2, Cl2, N2, etc.), the pair of electrons they share is divided equally between the two, and the electron cloud is symmetrical with respect to the plane perpendicular to the axis of the A-B bond. However, if the two atoms are not identical (HCl, CO, etc.), one is more electronegative than the other and attracts the electrons towards itself. The electron cloud is not symmetrical along the entire bond; it is displaced towards the more electronegative element. The covalent bond is polarized. The more electronegative element has an excess of negative charge δ-, while the other has a charge deficit δ+.

Example

HCl





Note

The bond is purely covalent: $\delta=0$.

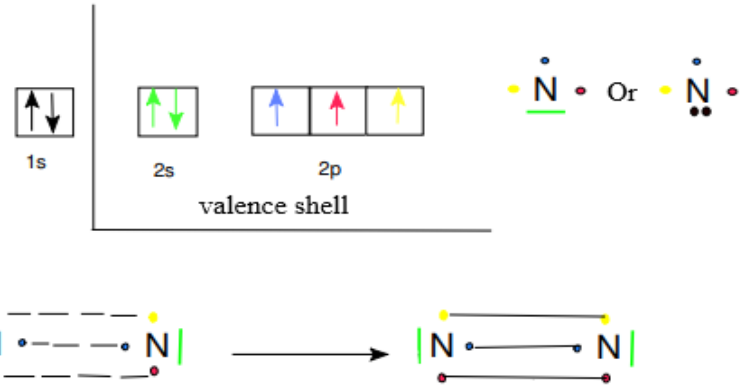
The covalent bond is polarized: $0 \leq \delta \leq 1$.

The covalent bond is ionic: $\delta=1$.

3. Lewis diagrams of molecules and molecular ions

In 1919, Lewis proposed a model in which he defined covalent bonding as the result of electron sharing between two atoms. Lewis diagrams can be used to represent bonds by visualizing the distribution of valence electrons within neutral molecules and ions. Single electrons are represented by dots, electron pairs are represented by dashes, and we can distinguish between bonding pairs and non-bonding pairs.

$_7N : 1s^2 (2s^2\ 2p^3)$



❖ **Octet rule**

The word octet means 8. Atoms with an atomic number $Z \geq 6$ tend to combine in such a way that they have 8 electrons in their valence shell to resemble a noble gas and thus acquire great stability.

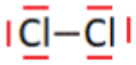
Example: Cl_2

Cl : $1s^2\ 2s^2\ 2p^5$



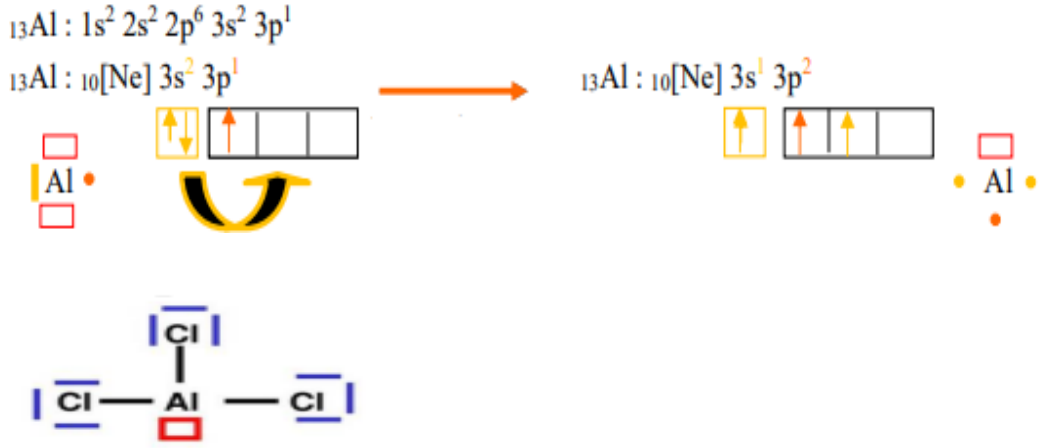
Cl : [He] $2s^2\ 2p^5$



Each Cl a  ded by 8 1 bonding pair, 6 non-bonding pairs } The octet rule is respected

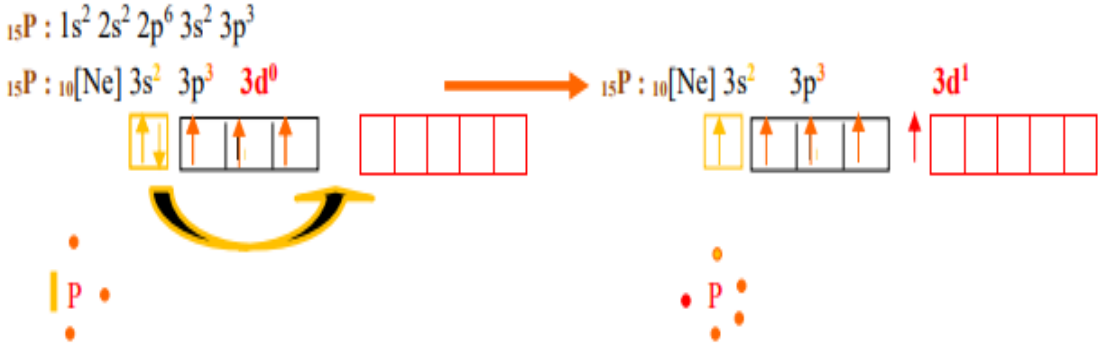
❖ **Exceptions to the octet r**

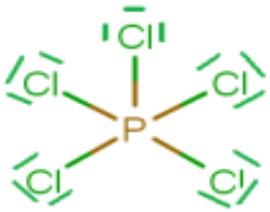
In some molecules, there may be an atom that does not follow the octet rule, such as phosphorus (P), aluminum (Al), and sulfur (S).



Al is surrounded by 6 electrons.

Example: PCl_5





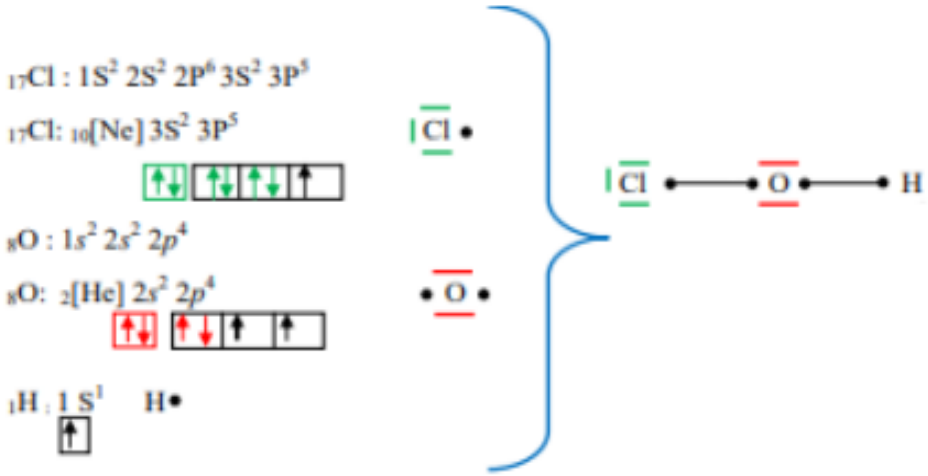
P is surrounded by 10 electrons.

Example

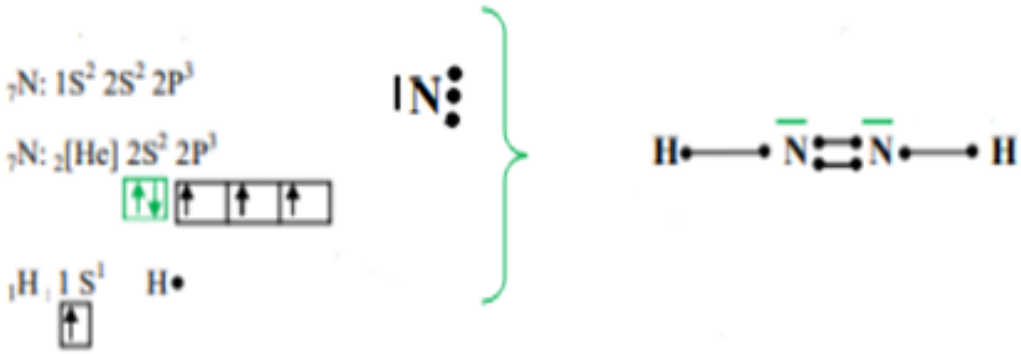
1. For each of the following species, give the Lewis structure (the central atom is indicated in bold): Cl**O**H, **N**$_2$H$_2$.

2. Give the types of bonds for each species.

ClOH



N$_2$H$_2$



4. Dipole moment of a polarized covalent bond

The dipole moment associated with a polarized covalent bond A-B is a vector quantity denoted by μ and oriented from the positive partial charge (δ^+) to the negative partial charge (δ^-). Its value is expressed in Debye (symbol D) and is proportional to the value of the partial charges and the distance between them.

$$\mu = q \cdot d_{A-B} = \delta \text{ .e. } d_{A-B}$$

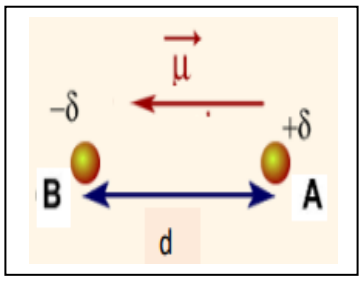


Figure VI.2: Dipole moment

μ: electric dipole moment. It is expressed in C.m (Coulomb. meter) and often in Debye (D)

With 1D = 3.33 x 10^{-30} C.m.

q: the partial charge carried by the atom (unit: Coulomb). 0 < q < e

e: the charge of the electron e = 1.6 × 10^{-19} C.

d_{A-B}: the length of the bond in meters (1 Å = 10^{-10} m).

δ: the partial charge (0 < δ < 1).

Note: The total dipole moment $\overrightarrow{\mu_{total}}$ of a polyatomic molecule is the vector sum of the dipole moments of the bonds that make up the molecule.

Example

The experimental dipole moment of the sulfur dioxide molecule SO_2 is

5.39 × 10^{-30} C·m.

The bond length is 1.431 Å, and the bond angle α is 119°.

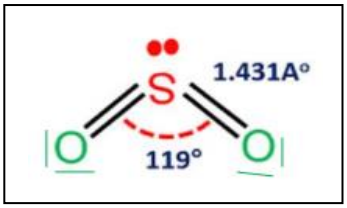
1- Give Lewis's representation of this molecule.

2- Calculate the dipole moment of the bond.

3- What is the nature of the S-O bond?

Solution

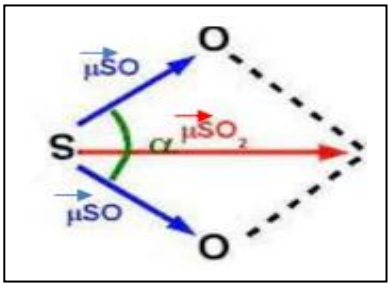
1- Lewis's representation

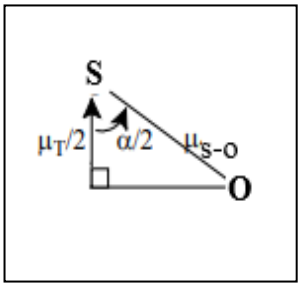


2- The dipole moment of the bond

$$\cos\frac{\alpha}{2} = \frac{\mu_{SO_2}}{2\mu_{SO}}$$

$$\mu_{SO} = \frac{\mu SO2}{2\,Cos\frac{\alpha}{2}} = 5{,}3.10^{-30}\text{C.m}$$





3- The nature of the S-O bond:

$\mu_{SO} = \delta.e.d \Longrightarrow \delta = \mu_{so}/e.d = 5.3x10^{-30} / 1.6x10^{-19}\times 1.431.10^{-10}$.

$\delta = 0.23 \Longrightarrow 0 < \delta < 1$

The bond is covalent in nature polarized.

5. Character of bonds (Molecular geometry: Gillespie or VSEPR theory)

The VSEPR model (Valence Shell Electron Pair Repulsion), initiated by Sidgwick and Powell and then developed by Gillespie in 1957) can predict very simply the geometric shape of molecules from their molecular Lewis diagram.

- According to this theory, the geometric shape of an AX_mE_n molecule around the (central) atom A can be predicted based on the number of bonding pairs X_m and free pairs (doublets) E_n carried by this atom.

According to Gillespie, a polyatomic molecule is symbolized by:

AX_mE_n

A: is a central atom.

X: is an atom bonded to A.

E: is a free electron pair (or doublet) of the central atom.

m: number of bonds.

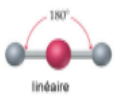
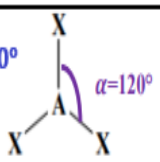
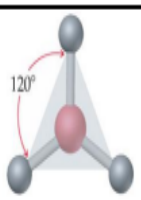
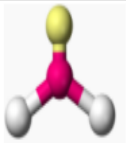
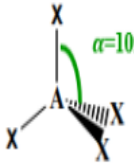
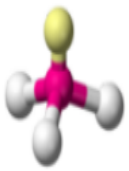
n: the number of non-bonding (free) doublets of the central atom

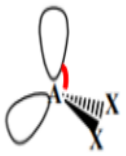
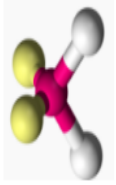
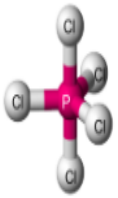
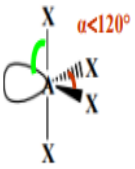
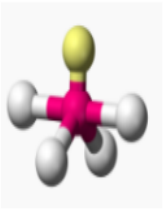
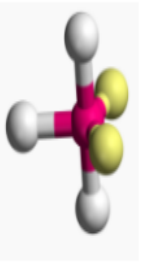
The arrangement of atoms in an AX_mE_n molecule is determined by the sum $\Sigma\sigma + \Sigma NL$.

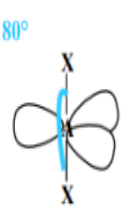
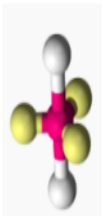
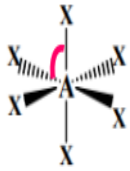
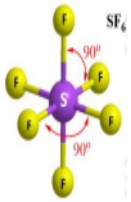
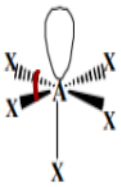
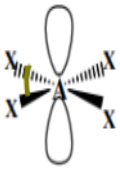
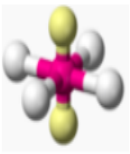
$\Sigma\sigma$: the sum of the σ bonds that the central atom can form with the other atoms in the molecule.

ΣNL: the sum of the non-bonding doublets of the central atom

Table VI.1: Structure of molecules and ions according to the VSEPR method

Structure of molecules and ions according to the VSEPR (AX_mE_n) method.							
m+n	m	n	Type	Σσ+ΣNL	Hybridation	Geometry (shape and representation)	Example
2	2	0	AX_2	2	sp	Linear α=180°  	CO_2, HCN, $BeCl_2$, NO^{+2}, BeF_2
3	3	0	AX_3	3	sp^2	Triangular α=120°  	BF_3, BCl_3, COF_2 NO^{-3}, COCl2, CO_3^{-2}
	2	1	AX_2E_1	3	sp^2	Bent α<120° (V-shaped  	SO_2, O_3, $SnCl_2$, NOCl
4	4	0	AX_4	4	sp^3	α=109°28' Tetrahedral 	CH_4, $CHCl_3$, NH^{+4}, SO_4^{-2} 
	3	1	AX_3E_1	4	sp^3	Trigonal pyramidal α< 109° 28'  	H_3O^+, PCl_3, NH_3, SO_3^{-2}

	2	2	AX_2E_2	4	sp^3	Bent $\alpha \approx 104^v$  	H_2O, ClO^{-2}, SCl_2, NH_2^-
5	5	0	AX_5	5	sp^3d	Bi-Trigonal pyramidal β=90° α=120° 	PCl_5, PF_3Cl_2, SOF_4 
	4	1	AX_4E_1	5	sp^3d	Tetrahedral distorted β< 90° α<120°  	$SeCl_4$, IOF_3,
	3	2	AX_3E_2	5	sp^3d	T-shaped β< 90°  	ICl_3, $BrF3$,

	2	3	AX_2E_3	5	sp^3d	Linear $\alpha=180°$  	I_3^-, XeF_2
6	6	0	AX_6	6	sp^3d^2	$\alpha=90°$ Octahedral 	SF_6 
	5	1	AX_5E_1	6	sp^3d^2	square pyramidal $\alpha< 90°$  	IF_5, BrF_5, TeF_5^-
	4	2	AX_4E_2	6	sp^3d^2	Square plane $\alpha=90°$  	XeF_4, BrF_4^-

6. Chemical bonds in the quantum model

This is the combination of the atomic orbitals of an atom in the same electron shell to form other identical atomic orbitals to describe the bond between atoms and determine the geometry of the molecule.

a. Sp^3 hybridization

This is the combination of one s orbital and three p orbitals (px, py, and pz) to form four identical Sp^3 hybrid orbitals.

Example: The CH_4 (methane) molecule.

The central atom of the CH_4 molecule is carbon.

$_{12}C : 1s^2$ **$2s^2\ 2p^2$**

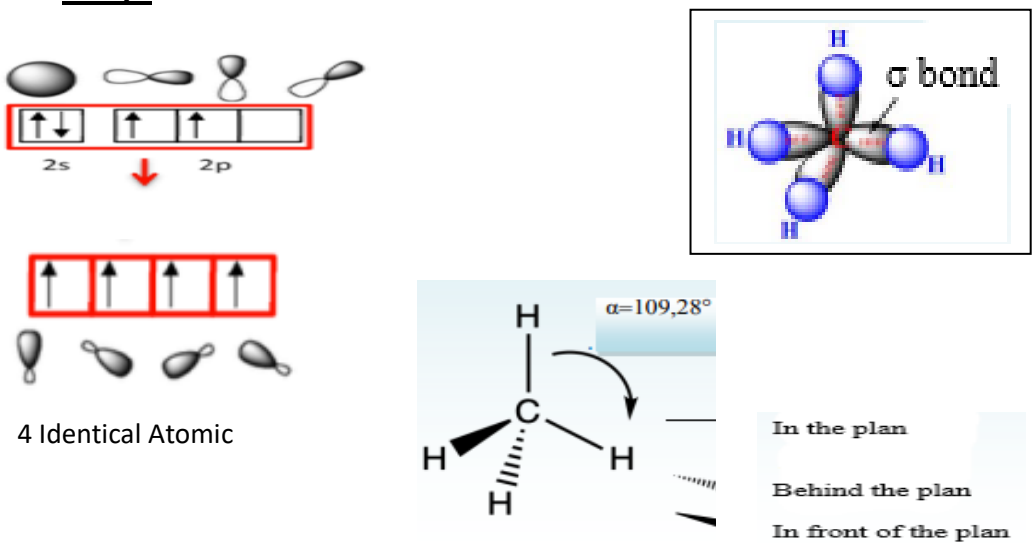


Figure VI.3: Sp^3 hybridization

The CH_4 molecule consists of four identical σ bonds (1S- Sp^3)

• The carbon atom in CH_4 is Sp^3 hybridized.

• The geometry of the molecule is tetrahedral with an angle α=109.28°

b. Sp^2 hybridization

This is the formation of three hybridized orbitals: Sp^2 from one s orbital and two p orbitals (px and py, for example). The pz orbital remains unchanged (forms the π bond between C1 and C2).

Example: The C_2H_4 molecule (ethylene)



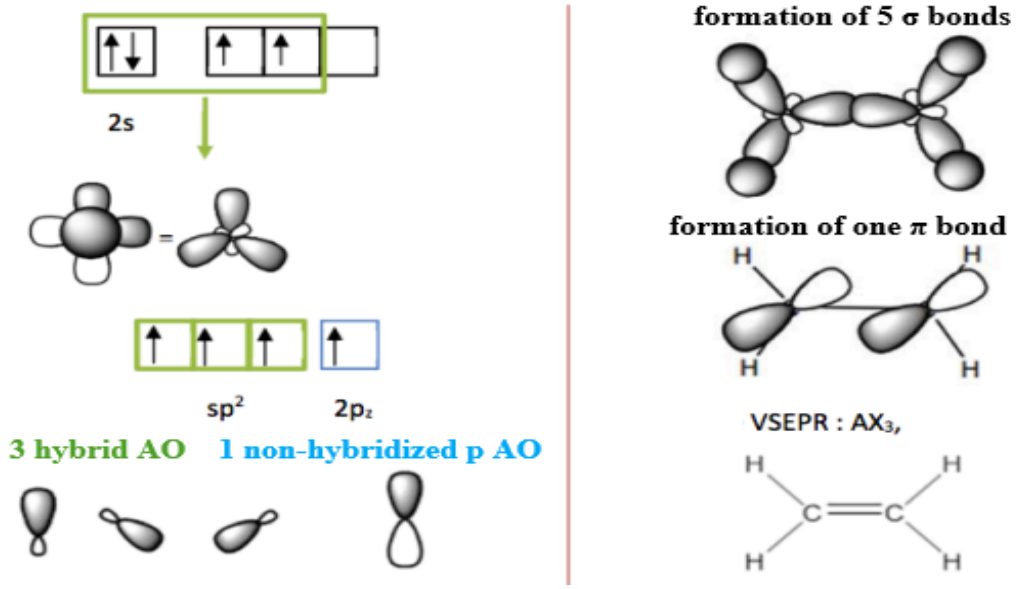


Figure VI.4: Sp^2 hybridization

The σ bonds of the molecule will be:

- sp^2 combination of C with 1s of H

- sp^2 combination of C with 1s of H

- sp^2 combination of C with sp^2 of the other carbon

• The $2p_z$ orbital of each carbon did not participate in hybridization.

• These two orbitals will combine to form the π bond.

The geometry of the trigonal or triangular plane molecule α= 120°

c. Hybridization sp

Two p orbitals form two π bonds, one atomic p orbital that merges with one atomic s orbital to give two sp hybrid orbitals.

-The two sp hybrid orbitals that adopt a linear geometry (along a straight line) form 180° between them.

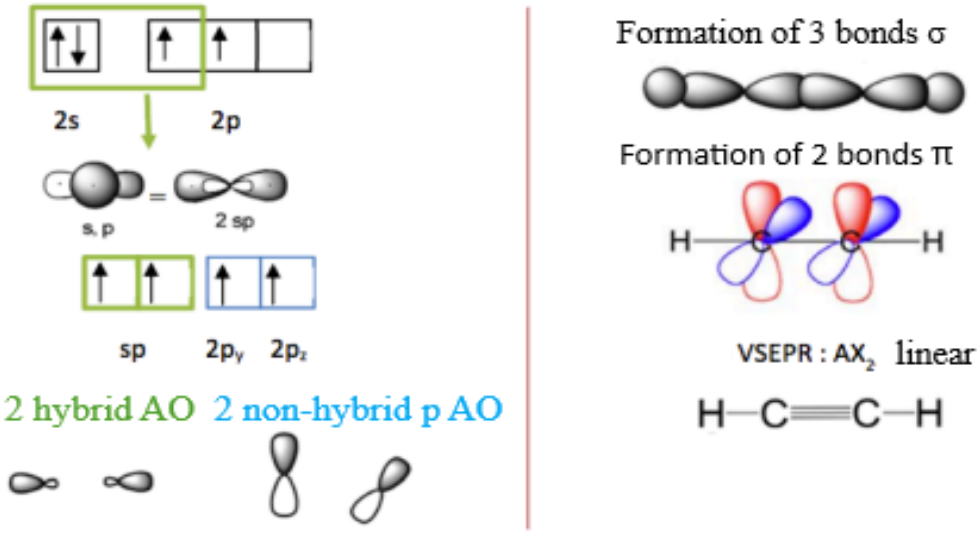
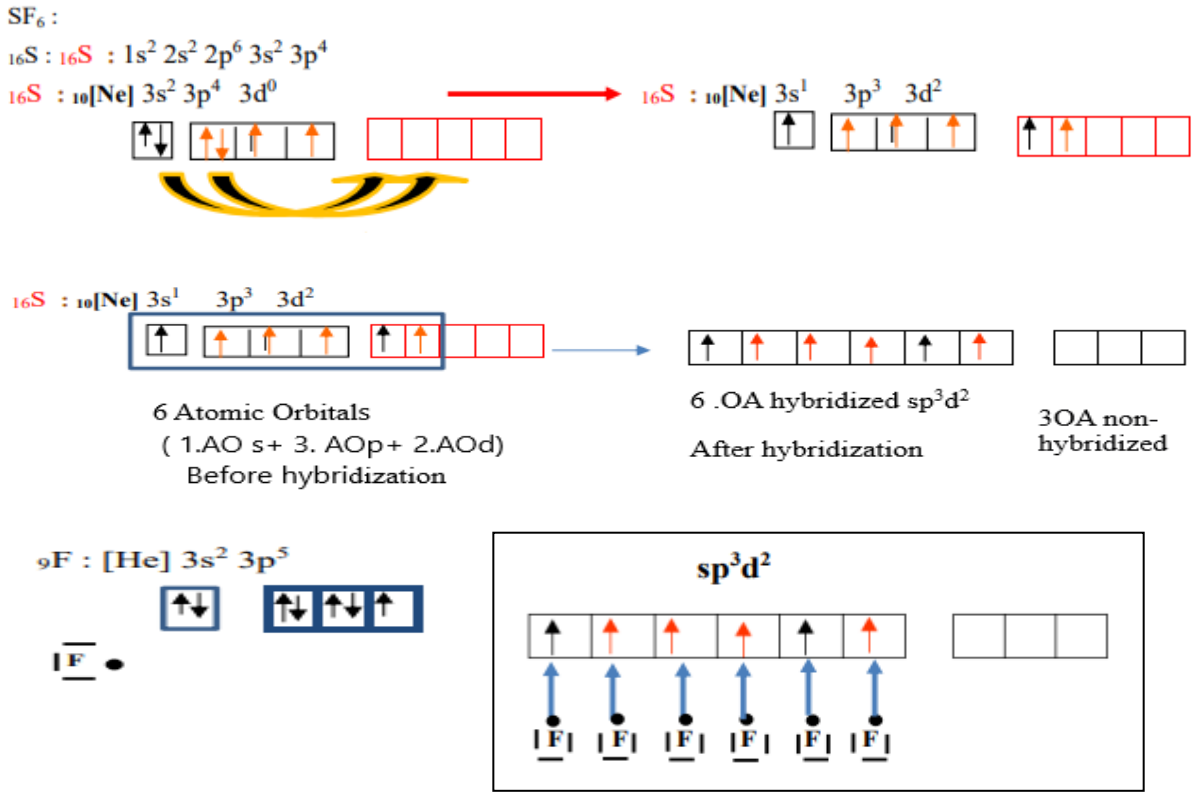


Figure VI.5: Sp hybridization

d. sp^3d^2 hybridization

This is the formation of equivalent hybridized orbitals by linear combination of one s orbital, three p orbitals, and two d orbitals from the same electron shell of the same atom.



This type of hybridization occurs in molecules of the AX_6, AX_5E, and AX_4E_2 type, whose repulsion figure is octahedral or square-planar, square-pyramidal.



Figure VI.6: sp^3d^2 hybridization (SF_6)

e. sp^3d hybridization

This is the formation of equivalent hybrid orbitals by linear combination of ones orbital, three p orbitals, and one d orbital from the same electron shell of the same atom.

Example: PCl_5

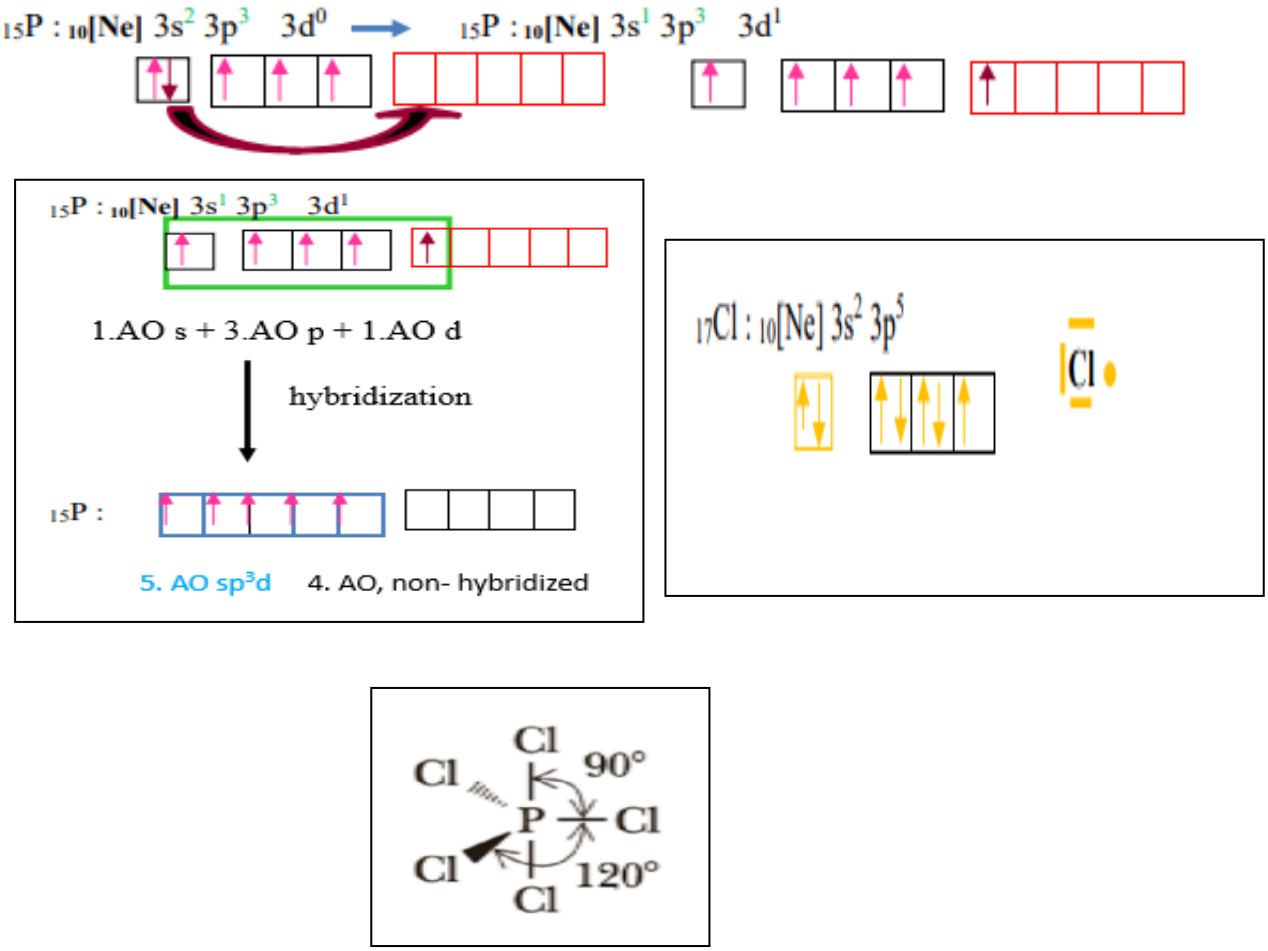
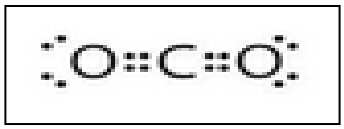


Figure VI.7: sp^3d hybridization (PCl_5)

Examples

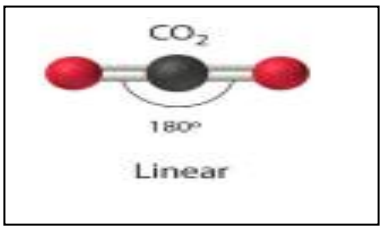
AX_2: CO_2



The Lewis electron structure is

The molecular geometry of CO_2 is linear

The hybridization of the C atom is *sp*.



AX_3: BCl_3

There are three electron groups around the central atom

All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

the molecular geometry of BCl_3 is *trigonal planar*

the hybridization on the B atom is sp^2 and the shape of the orbitals is triangonal planar.

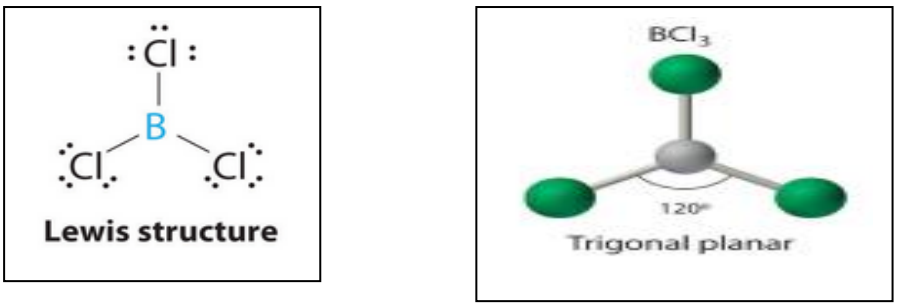


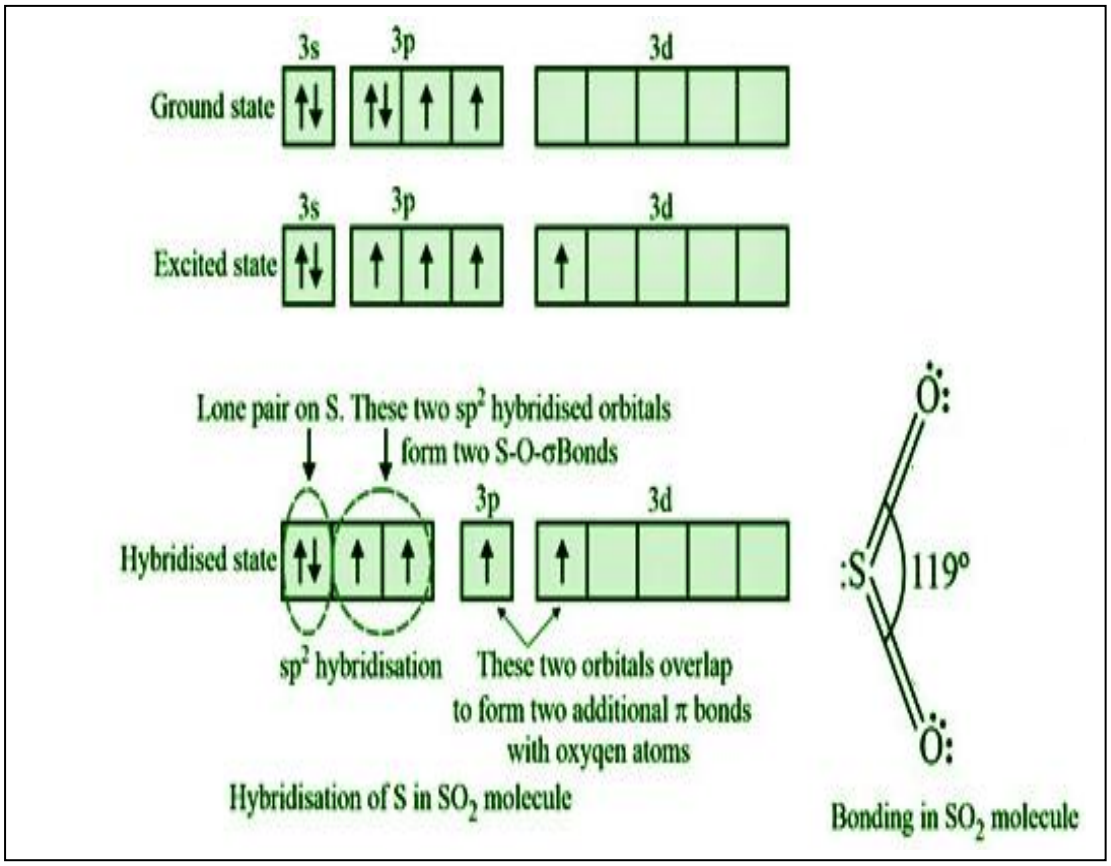
Figure VI.8: Molecular geometry of BCl_3

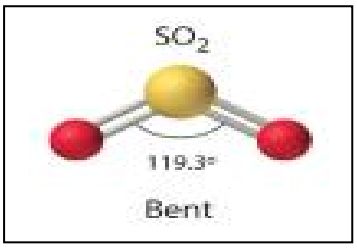
AX_2E: SO_2

There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs

with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement

The hybridization of the S atom orbitals is sp^2.





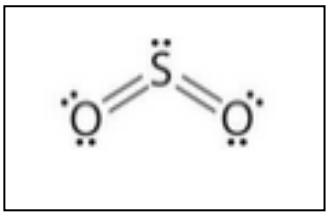


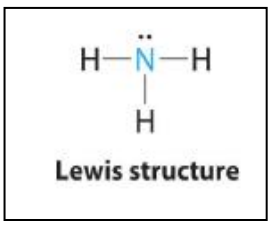
Figure VI.9: Molecular geometry of SO_2

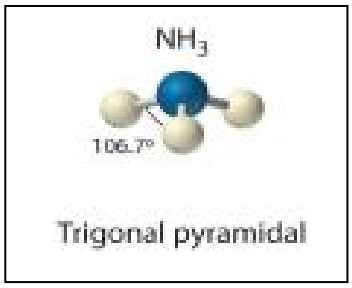
AX_3E: NH_3

With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E.

The molecular geometry is trigonal pyramidal

The hybridization of the N atom orbitals is sp^3.





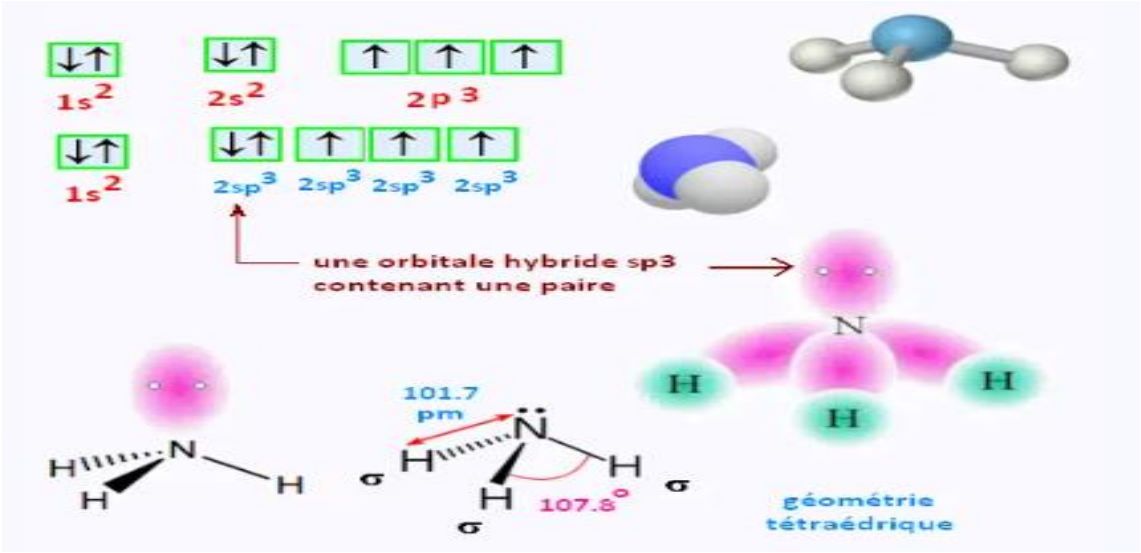
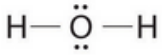


Figure VI.10: Molecular geometry of NH_3

AX_2E_2: H_2O

The Lewis electron structure is



With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs.

The molecular shape is *bent*, or *V shaped*,

The hybridization of the O atom orbitals is sp^3.

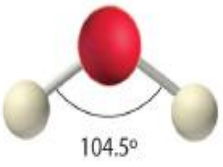
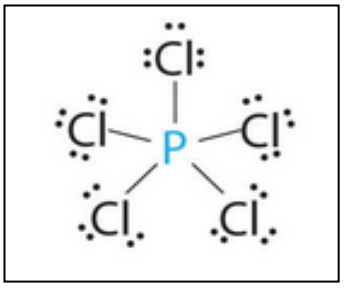


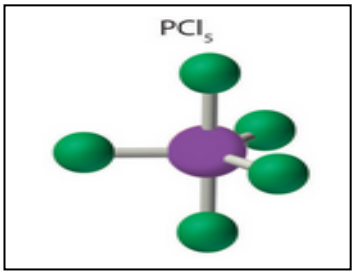
Figure VI.11: Molecular geometry of H_2O

AX_5: PCl_5

The Lewis electron structure is:



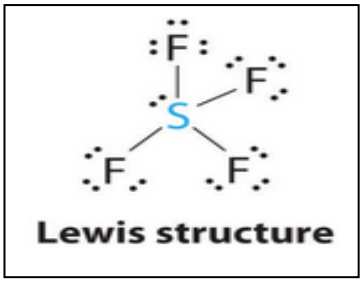
The molecular geometry of PCl_5 is ***trigonal bipyramidal***.



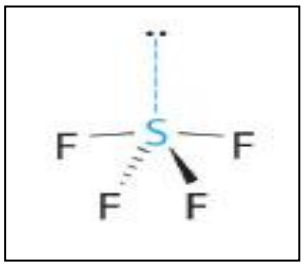
The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane.

AX_4E: SF_4

The Lewis electron structure is



We designate SF_4 as AX_4E; it has a total of five electron pairs



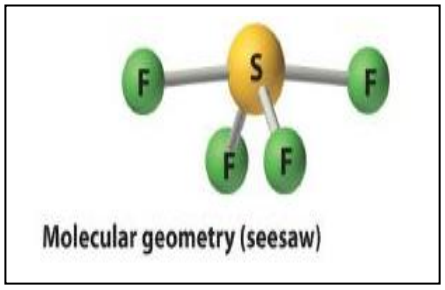


Figure VI.12: Molecular geometry of SF_4

7. LCAO method Linear combination of atomic orbitals

7.1Formation and nature of bonds

Several types of atomic orbital overlaps are possible

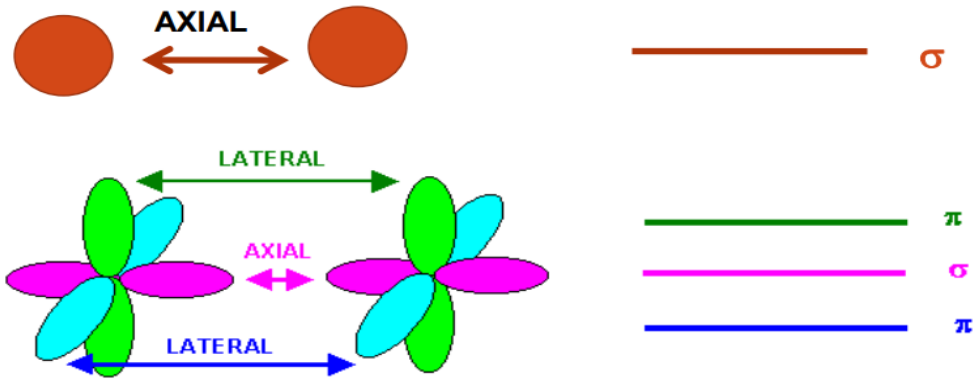


Figure VI.13: Nature of bonds

- ✓ **Axial overlap: σ bond**

This is an overlap of two s orbitals, or one s orbital and one p orbital, or two coaxial p orbitals. The molecular orbitals thus formed are called *σ* orbitals. Axial overlap gives two sigma (σ, σ*) molecular orbitals. There is free rotation around the σ bond.

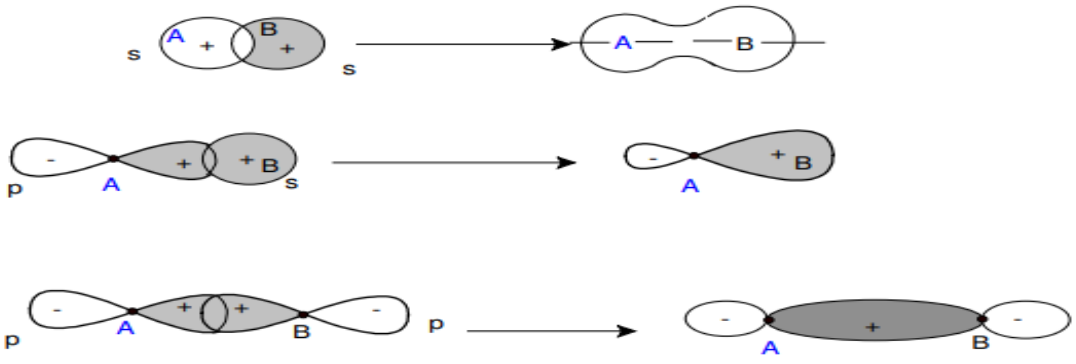


Figure VI.14: Axial overlapping σ bond formation

- ✓ **Lateral overlapping: π bond**

This concerns p orbitals whose axes are parallel. This overlapping leads to aπ orbital. The corresponding bonds are weaker than σ bonds.

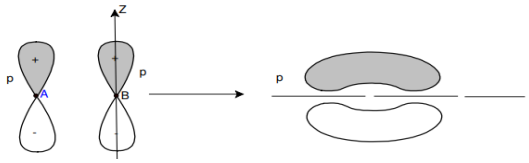


Figure VI.15: Lateral overlapping formation of the π bond

7.2 Different types of molecular orbitals

Table VI.2: Different types of molecular orbitals

Type d'orbitale moléculaire	Symbole	Orbitales atomiques	Schéma d'orbitale moléculaire
Sigma liante	σ	ns+ns	
		ns+np_z	
		np_z+np_z	
Sigma antiliante	σ*	ns+ns	
		ns-np_z	
		np_z-np_z	
Pi liante	π_x	np_x + np_x	
	π_y	np_y + np_y	
Pi antiliante	π^*_x	np_x - np_x	
	π^*_y	np_y - np_y	
Non-liante	NL	ns+$np_{x,y}$	

7.3 Energy diagram of molecular orbitals

From two atomic orbitals of the same energy, two molecular orbitals are constructed: a bonding MO and an antibonding MO. The Pauli principle, the stability principle, and Hund's rule are applicable to molecular orbitals.

Priority for filling the lowest energy levels (Filling by increasing energy).

At the same filling level, several large numbers are possible with parallel spins (Hund's rule)

The overlap of two atomic orbitals with the same energy produces two molecular orbitals with different energies, one stabilized bonding orbital and one destabilized antibonding orbital.

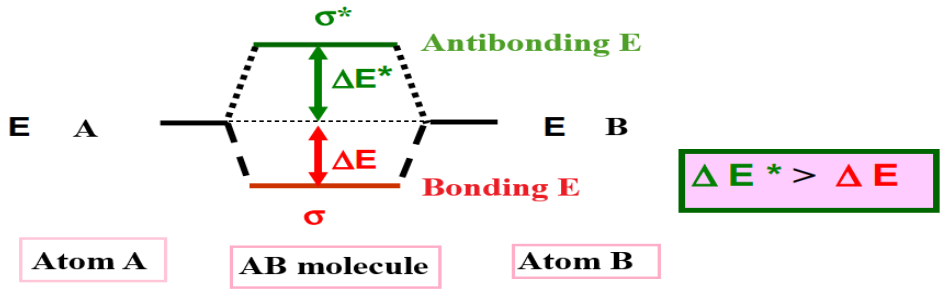


Figure VI.16: Energy diagram of molecular orbitals

Orbitals are designated by the letter σ or π, andan asterisk * is placed as a superscript for antibonding orbitals.

The diagram is represented by two parallel arrows that represent the energy levels of the AOs and MOs, between the two arrows.

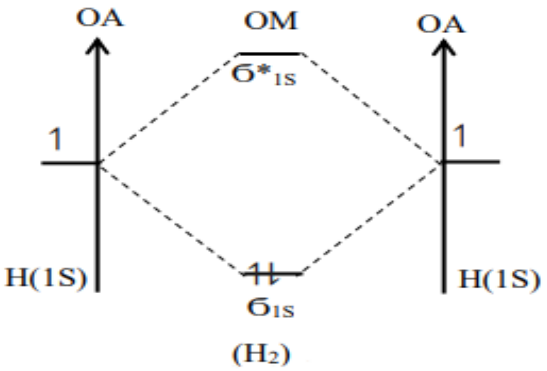


Figure VI.17: Energy diagram of the H_2 molecule

Electronic configuration: H_2: σ_{1S}^2

- **Bond index I**

The bond index gives the number of bonds

I =**1**/**2**(number of bonding electrons – number of antibonding electrons).

I = 2 (two σ + π bonds).

I = 3 (three σ +2 π bonds).

I = 0 (no bonds)

- **Paramagnetic molecules**

Are molecules that have unpaired electrons.

- **Diamagnetic molecules**

Are molecules that do not have unpaired electrons.

I_{H2} = 1/2 (2 –1) = 1 bond

Example 1:

The molecule $(He)_2$

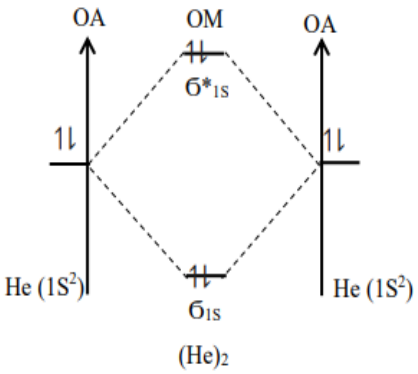


Figure VI.18: Energy diagram of the $(He)_2$

Electronic configuration: Z ≤ 7: $(He)_2$: $\sigma_{1S}^2\ \sigma_{1S}^{*2}$

$I(He)_2$ =1/2(2 –2) = 0 No bond

7.3.1 Homonuclear molecules

Are atoms of the same type.

Example: H_2 and O_2

Note:

For homo-nuclear diatomic molecules A_2, the order of energy levels is as follows:

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < \pi_{2py} = \pi_{2pz} < \pi^*_{2py} = \pi^*_{2pz} < \sigma^*_{2px}$

If Z > 7: the position of σ first

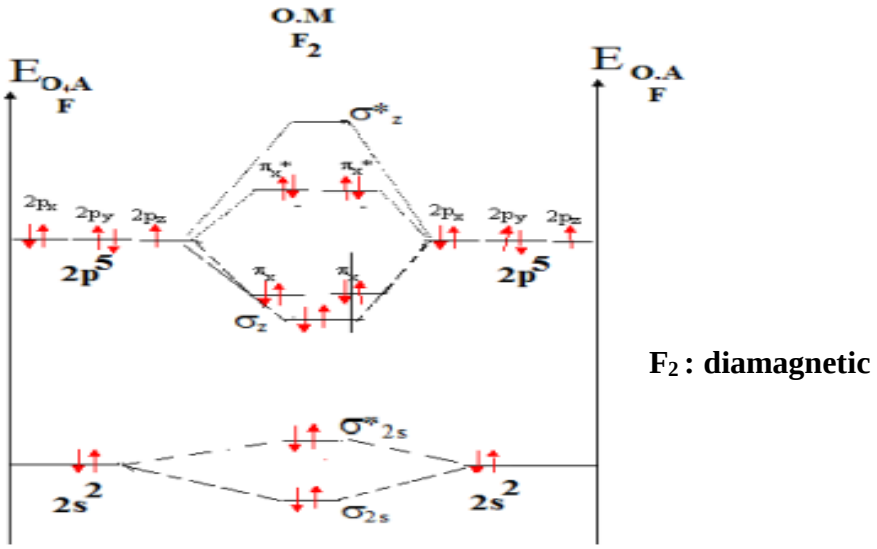
If Z ≤ 7: the position of π first.

If Z ≤ 7, the energy difference between S and P decreases, resulting in an inversion between σ and π (π first)

Example 2:

- Molecule F_2

$_9F$: $1S^2 2S^2 2P^5$



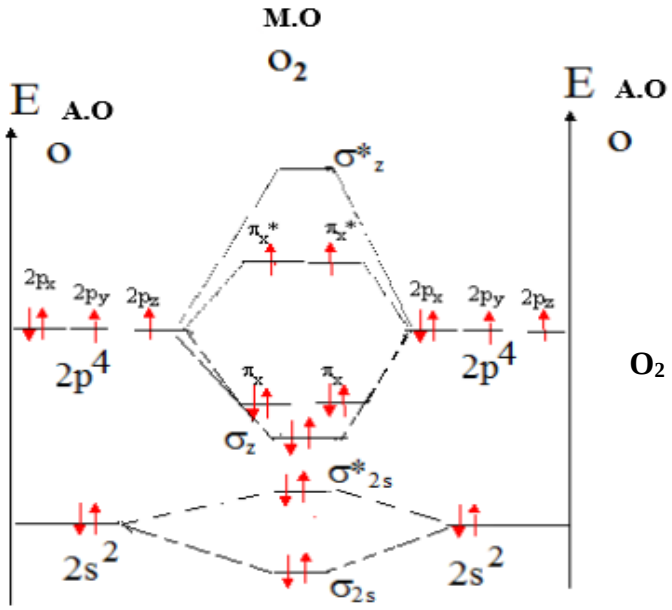
F_2 : diamagnetic

Figure VI.19: Energy diagram of molecule F_2

$I(F)_2 = 1/2(8 - 6) = 1$

Electronic configuration: **(σ_{1s}^2) $(\sigma^*_{1s}^2)$ (σ_{2s}^2) $(\sigma^*_{2s}^2)$ (π_{2px}^2) (π_{2py}^2) (σ_{2pz}^2) $(\pi^*_{2px}^2)$ $(\pi^*_{2py}^2)$.**

O_2 (Z = 8) :$1S^2$ $2S^2$ $2P^4$ Z > 7



O_2 : Paramagnetic

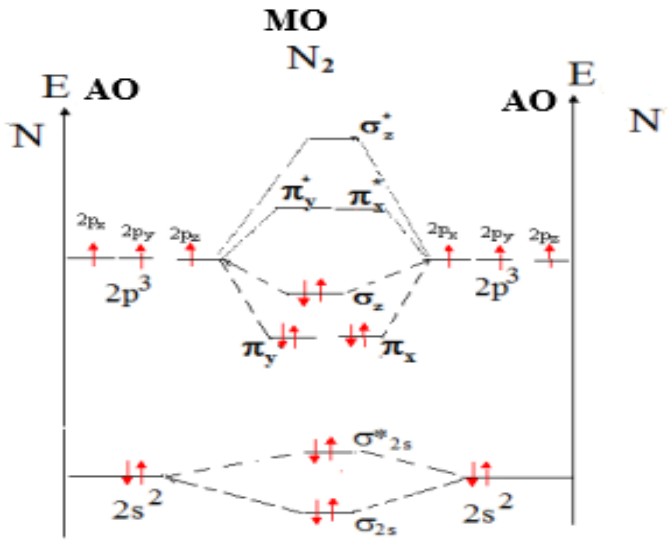
Figure VI.20: Energy diagram of molecule O_2

I = 1/ 2 (8 – 4) = 2 bond for O_2 (1σ +1 π)

O_2 : σ_{1S}^2 σ_{1S}^{*2} σ_{2S}^2 σ_{2S}^{*2} σ_{2Z}^2 π_x^2 π_y^2 π_x^{*1} π_y^{*1}

Z(N) ≤ 7 there is an inversion of the molecular orbitals σ_z and π_x, π_y

N_2 (Z = 7) :$1S^2$ $2S^2$ $2P^3$



N_2 : diamagnetic

Figure VI.21: Energy diagram of molecule N_2

I = (8–2)/2 = 3 ⇒ 3 bonds.

Electronic configuration: $\sigma_{1S}^2\ \sigma_{1S}^{*2}\ \sigma_{2S}^2\ \sigma_{2S}^{*2}\ \pi_x^2\ \pi_y^2\ \sigma_Z^2$

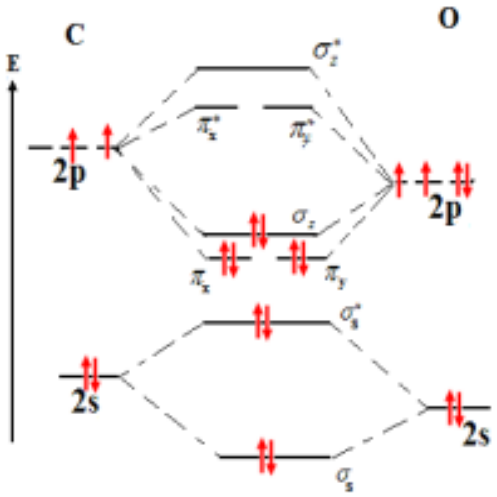
7.3.2 Heteronuclear molecules

Are atoms of different natures.

Example: NO and CO

For heteronuclear atoms (the position of π always comes first).

CO



CO : diamagnetic

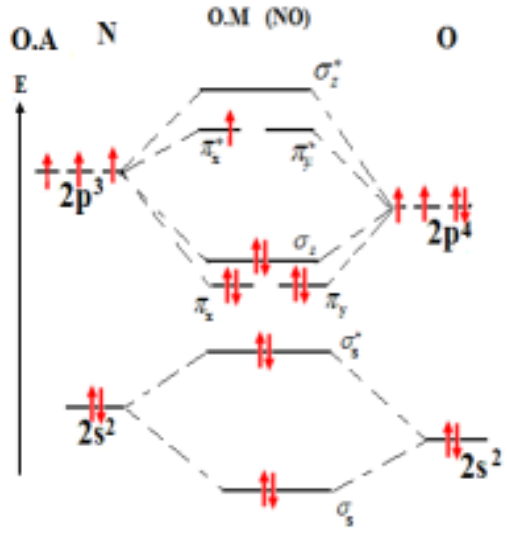
Figure VI.22: Energy diagram of molecule CO

- **Bond order of CO.**

I = (8 – 2)/2 = 3.

Electronic configuration: $(\sigma_{1s}^2)\ (\sigma^*_{1s}{}^2)\ (\sigma_{2s}^2)\ (\sigma^*_{2s}{}^2)\ (\pi_{2px}^2)\ (\pi_{2py}^2)\ (\sigma_{2pz}^2)$.

NO



NO: Paramagnetic

Figure VI.23: Energy diagram of molecule NO

- **Bond order of NO.**

I= (8 – 3)/2 = 5/2 = 2.5.

Electronic configuration: **(σ_{1s}^2) $(\sigma^*_{1s}{}^2)$ (σ_{2s}^2) $(\sigma^*_{2s}{}^2)$ (π_{2px}^2) (π_{2py}^2) (σ_{2pz}^2) $(\pi^*_{2px}{}^1)$.**

Conclusion

Chemical bonds form the foundation of the structure of matter and explain the formation of molecules and their properties. Lewis models provide a simple initial understanding of electronic interactions, while VSEPR theory effectively predicts molecular geometry.

However, a more in-depth description is provided by quantum mechanics through orbital hybridization and molecular orbital theory, which explain the true nature of chemical bonds and their stability.

Thus, the study of chemical bonding bridges classical and quantum models and constitutes an essential tool for understanding the structure, reactivity, and properties of chemical compounds.

Exercises

Exercise 01

Write the Lewis structures 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

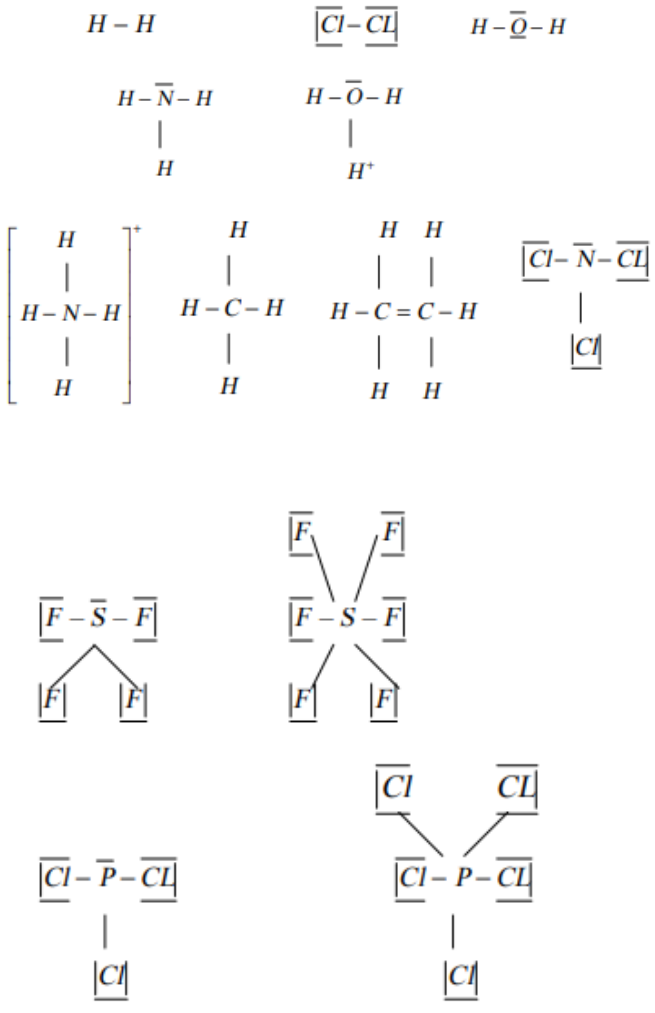
2. Which of these compounds do not follow the octet rule?

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

4. List the different possible valences of phosphorus. Both PCl_3 and PCl_5 exist. Explain why only the NCl_3 compound is known, while the NCl_5 compound does not exist.

Solution

Lewis structure of the following molecules and ions:



1) The compounds that do not follow the octet rule are: SF_4; SF_6; PCl_5

Exercise 02

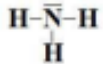
2. Determine the Lewis structures, VSEPR types, and geometries of the following molecules and ions. Draw a diagram to justify the geometries and discuss the values of the bond angles.

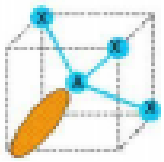
a- NH_3. b- CH_4. c- SiO_2. d- BF_3. e- H_3O^+. f- PCl_5. g- SF_6. h- ICl_3. i- NH_4^+.

Solution

2. Lewis structures and geometries:

a. AX_3E_1 type,

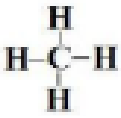




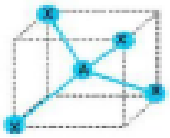
Pyramidal geometry

The bond angles are less than 109°28'.

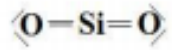
b. AX_4 type,



Tetrahedral geometry. Angles of 109°28'.

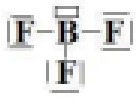


c. AX_2 type,

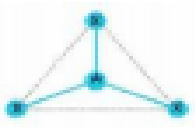


Linear molecule. Angles of 180°.

d. AX_3 type,



Planar trigonal geometry: Angles of 120°.

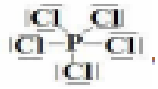


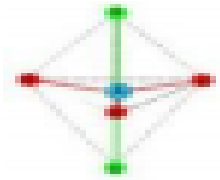
e. AX_3E_1 type,



Pyramidal geometry. 

The angles between the bonds are less than 109°28’.

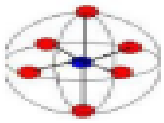
f. AX_5 type, 

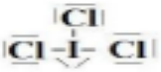
Trigonal bipyramidal geometry. 

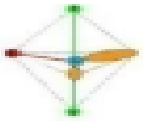
The angles between bonds in the same plane (in red) are 120°, and the angles between green and red bonds are 90°.

g- AX_6 type, 

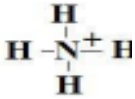
Octahedral geometry.

The angles are 90°. 

h- AX_3E_2 type, 

“T”-shaped geometry. 

The angles are 90°.

i- AX_4 type, Tetrahedral geometry. 

Angles of 109°28’. 

Exercise 03:

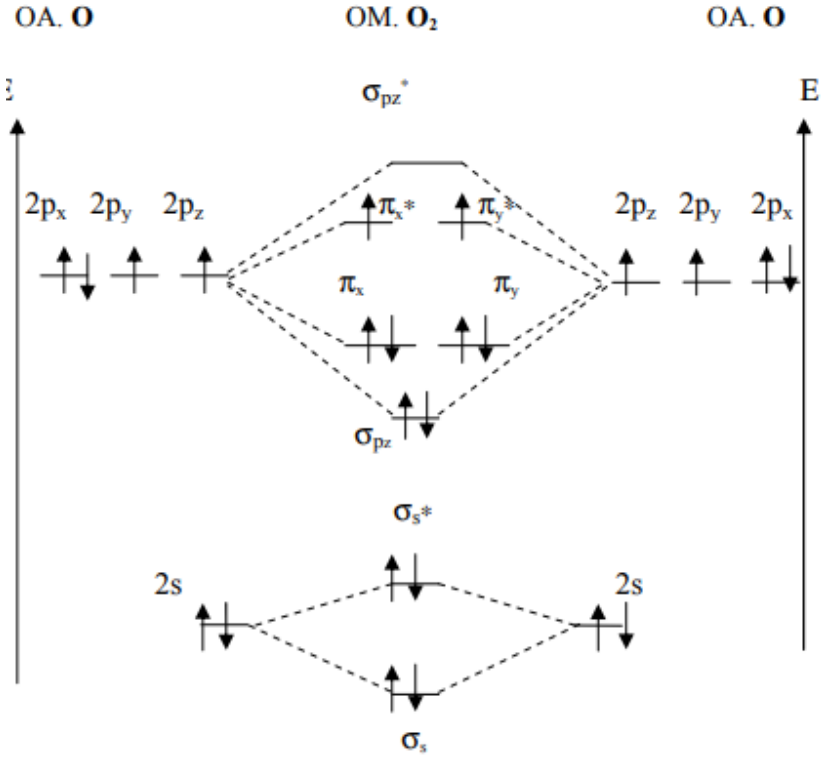
Draw the energy diagram of the molecular orbitals (MO) for the homonuclear O_2 molecule.

2. Use this to determine the electronic structure of the following molecular ions: O_2^-; O_2^+; and O_2^{2+}

Solution

O_2 :

O (Z = 8): $1s^2\ 2s^2\ 2p^4$



The electronic structure of O_2 is: $\sigma s^2\ \sigma s^{*2}\ \sigma pz^2\ (\pi x^2 = \pi y^2)\ (\pi x^{*1} = \pi y^{*1})$

The bonding index is: $I(O_2) = ½(n\text{-}n^*) = ½(8 - 4) = 2$

2. Electronic structure of the following molecular ions: O_2^-; O_2^+; and O_2^{2-}

- The electronic structure of O_2^- is: $\sigma s^2\ \sigma s^{*2}\ \sigma pz^2\ (\pi x^2 = \pi y^2)\ (\pi x^{*2} = \pi y^{*1})$

- The electronic structure of O_2^{2-} is: $\sigma s^2\ \sigma s^{*2}\ \sigma pz^2\ (\pi x^2 = \pi y^2)\ (\pi x^{*2} = \pi y^{*2})$

- The electronic structure of O_2^+ is: $\sigma s^2\ \sigma s^{*2}\ \sigma pz^2\ (\pi x^2 = \pi y^2)\ \pi x^{*1}$

Exercise 04

Draw the energy diagrams of the molecular orbitals (MO) for the N_2 and CN molecules.

2. Use these diagrams to determine the magnetic properties of N_2 and CN.

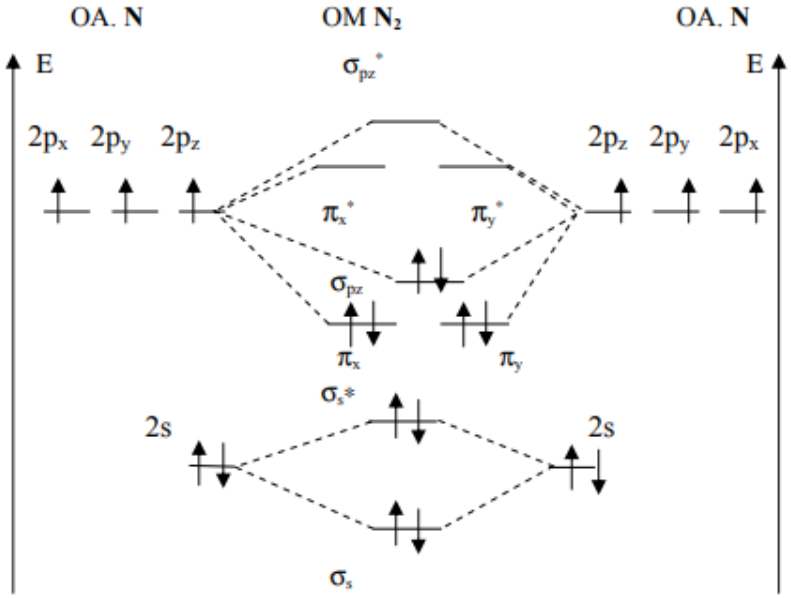
3. Compare the stability of the following chemical species, justifying your answers: N_2 and N_2^+; CN and CN^-.

Solution

1.

<u>N_2</u>

N (Z = 7) : $1s^2\ 2s^2\ 2p^3$

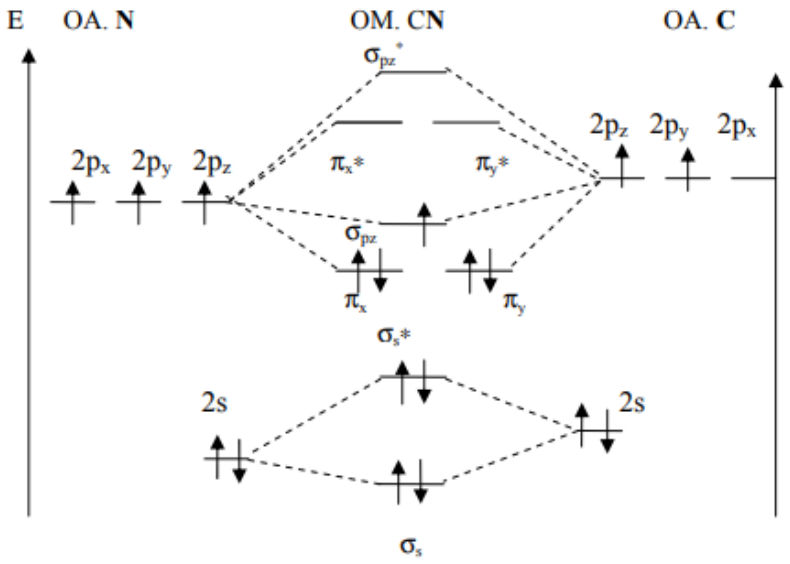


N_2 : $\sigma_s^2\ \sigma_s{}^{*2}\ (\pi_x^2 = \pi_y^2)\ \sigma_{pz}^2$

<u>CN</u>

N(Z = 7) : $1s^2\ 2s^2\ 2p^3$

C(Z = 6) : $1s^2\ 2s^2\ 2p^2$



CN: $\sigma_s^2\ \sigma_s{}^{*2}\ (\pi_x^2 = \pi_y^2)\ \sigma_{pz}^1$

1. The magnetic properties of N_2 and CN.

   N_2: Diamagnetic.

   CN: Paramagnetic

3. Comparison of the stability of the chemical species: N_2 and N_2^+; CN and CN^-

$I(N_2) = ½(8-2) = 3$;

$I(N_2^+) = ½(7-2) = 2,5$;

$I(CN) = ½(7-2) = 2,5$;

$I(CN^-) = ½(8-2) = 3$.

As the bond index decreases, the bond length increases, the interaction weakens, the bond strength decreases, and the dissociation energy ΔH_d decreases:

$I(N_2^+) < I(N_2) \rightarrow \Delta H_d(N_2^+) < \Delta H_d(N_2)$

N_2^+ is less stable than N_2

$I(CN) < I(CN^-) \rightarrow \Delta H_d(CN) < \Delta H_d(CN^-)$

CN is less stable than CN^-

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